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BIOMASS AND OIL SHALE CO-PYROLYSIS

BIOMASSI JA PÕLEVKIVI KOOSPÜROLÜÜS

MASTER THESIS

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Tallinn, 2019

AUTHOR'S DECLARATION

Hereby I declare, that I have written this thesis independently.

No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

Tallinn, 5th June 2019

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Thesis is in accordance with terms and requirements

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THESIS TASK

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  1. Study Estonian biomass and oil shale co-pyrolysis

  2. Preparing necessary set up for the experiments

  3. Study the mass losses obtained from the experiments

  4. Make a characterization of the non-condensable gases obtained in the pyrolysis process

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1.	Literature overview	01/03/19
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PREFACE

In this project it is carry out the pyrolysis of oil shale, the pyrolysis of biomass and the co-pyrolysis of oil shale and biomass using the batch reactor. It is used nitrogen as an inert gas in order to ensure pyrolysis at different temperatures so as to perform the experimental part. Temperatures chosen in this project are 550ºC, 750ºC and 900ºC. The first one is the temperature at which the highest yield of shale oil is achieved in the co-pyrolysis process, whereas the other two are used in order to make a comparison with the first one.

The first objective for the thesis is to observe the effect of the mass losses in order to compare them with other experiments that have already been carried out in this field. The second objective set is to characterize the product gases at different temperatures using the FTIR. Moreover, the concentration per mass of organic matter is calculated and the measured and calculated concentrations in co-pyrolysis are compared. In addition, the composition of the gas mixture is analyzed, using the GC-TCD and compared with calculated results. Finally, the evolution of the char obtained in each experiment for the different temperatures used is also observed.

LIST OF ABBREVIATIONS AND SYMBOLS

CFB	Circulating Fluidized Bed
OS	Oil Shale
BM	Biomass
CSTR	Continuous Stirred Tank Reactor
ppm	Parts per million
FTIR	Fourier Transform Infrared spectroscopy
FID	Flame Ionization Detector
GC-TCD	Gas Chromatography – Thermal Conductivity Detector
OMOS	Organic Mass of Oil Shale
OMBM	Organic Mass of Biomass
VOC	Volatile Organic Compound
S_i	Initial sample mass
S_f	Final simple mass

INTRODUCTION

The current rate of fossil fuel consumption is known to be increasing both our planet pollution and the global climate change. Furthermore, resources to produce the necessary energy for consumers are not inexhaustible, that is why it is needed to find new alternative ways to produce this energy. One of the most interesting chances is to produce synthetic petroleum using co-pyrolysis of Kukersite oil shale and biomass. This method is considerably interesting as far as the efficient conversion between biomass with oil shale to obtain fuel or other valuable products is concerned. Also, it has demonstrated higher efficiency than processing these resources individually. Moreover, including oil shale in co-pyrolysis increases the capacity for producing quantities of fuels and chemical feedstock. [1]

Additionally, this technique to obtain synthetic petroleum has lots of advantages. One of which is the availability of resources. Also, the capacity of oil shale all over the world is 2 and a half time bigger than that of coal and 30 times than that of petroleum [2]. As for Estonia, Kukersite oil shale is the most important energy source and it is the basis of its economy because it is used as a source of energy to produce electricity, heat, liquid fuels and lots of chemicals following combustion and liquefaction methods. [3]

In the case of biomass is known to be practically an inexhaustible renewable resource of feedstock for energy and chemical needs so there is high availability of this kind of source.

Another important matter about this energy is its environmental benefits because it might reduce the level of polluting emissions to the atmosphere much better than using fossil fuels. Moreover, this technique is eco-friendly because it is considered as a promising recycling method. A good example is the conversion of waste plastics into liquid hydrocarbons. Thus, with this technique it can be reused and recycled plastics to produce energy. [1]

The goal of this thesis is to study biomass and oil shale co-pyrolysis to determine and analyze the mass losses, the composition of the gas mixture and the char that is obtained under different pyrolysis/co-pyrolysis conditions.

1 LITERATURE

1.1 Pyrolysis

Pyrolysis is a thermochemical decomposition of organic matter caused by heat in absence of oxygen or other reactive. During the pyrolysis process, large complex hydrocarbon molecules are transformed into different smaller molecules of gas, liquid and char. Therefore, the goal of this process is to obtain non-condensable gases, solid char and liquid product heating the feedstock in absence of oxygen at maximum temperature to product these molecules at maximum yield value.

This process consists of different steps. First of all, feedstock is introduced into the reactor where the feedstock is heated until pyrolysis temperature (maximum temperature) which its decomposition begins. After that, both the condensable and non-condensable steams liberated from the feedstock leave the chamber. The produced solid char remains into the chamber but also partly into the gas. So, the next step consists of separating the gas from the char and cooled downstream of the reactor. Finally, the condensable steam condenses as pyrolysis oil, the non-condensable gases leave the reactor as a product gas and the solid char is collected as a commercial product or used as a combustible to produce the necessary heat for pyrolysis. [4]
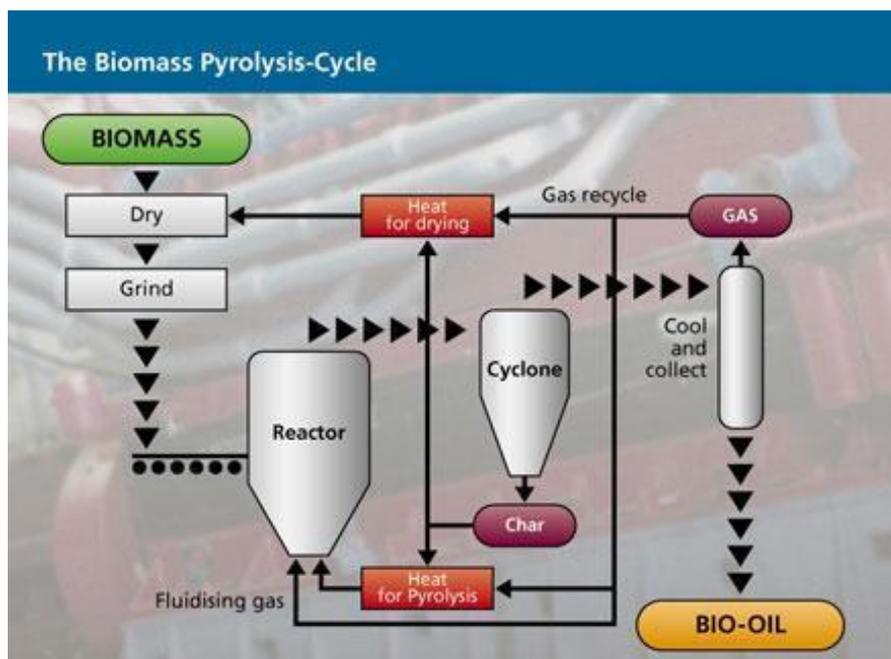
Figure 1. Pyrolysis Cycle [5]

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1.2 Pyrolysis products

The most important product to be obtained through pyrolysis method is the liquid product because it can be an important substitute for fossil fuels, whose nature depends on different parameters. These factors are the type of feedstock used in the process, the temperature also depending on the characteristics of feedstock, heating rate, reaction time and the particle size of feed. [1]

As it has been mentioned before, three types of products are obtained through pyrolysis process; gases, solid char and liquid product as shown in Figure 2.
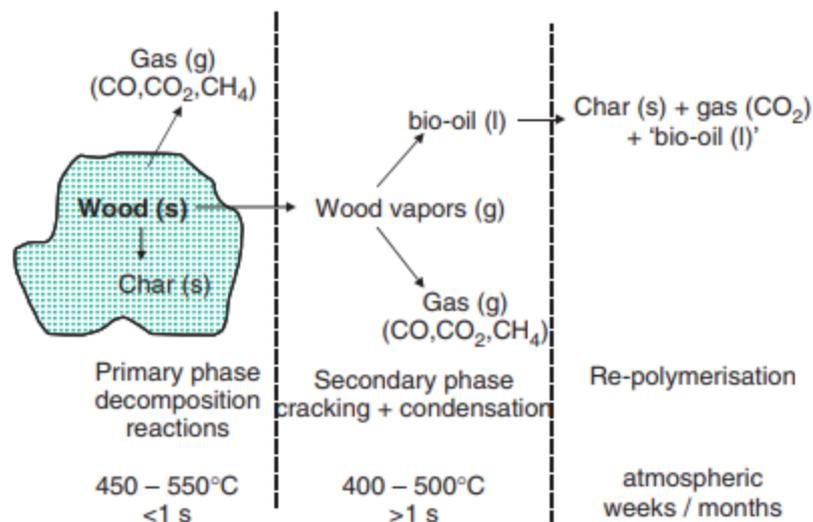
Figure 2. Products obtained in pyrolysis of biomass [6]

1.2.1 Gas

Gas is obtained from non-condensable gases when the gas exits from the chamber. The composition of the non-condensable gases obtained after pyrolysis are the volatile organic compounds (VOCs), water and small quantities of light hydrocarbons. These organic compounds depend basically on the feedstock used during the process. The most typical volatile organic compounds are carbon monoxide (CO), carbon dioxide (CO_2), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), benzene (C_6H_6) and methane (CH_4). [7]

1.2.2 Liquid

Liquid is obtained from condensable gases which are directed from reactor to condenser. On the one hand, using biomass as a feedstock the product of pyrolysis is a blend of tar (also called bio-oil or biocrude), heavier hydrocarbons and water. This liquid is a black tarry fluid that contains as much as 20% of water and is usually formed by molecular fragments of cellulose, hemicellulose and lignin polymers. On the other hand, in case that the feedstock of

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the pyrolysis is oil shale, the product that can be obtained is shale oil. This liquid is yellow and contains a complex mixture of hydrocarbons and its composition depends on the oil shale origin and composition. This composition is formed by large quantities of olefinic and aromatic hydrocarbons and some quantities of heteroatoms such as oxygen, nitrogen and sulphurs. [4]

1.2.3 Solid

After the pyrolysis process, the produced solid component remains into the chamber in the form of char or carbon. This solid char or carbon can be used as a commercial product or also as a combustible to produce heat. For example, this solid product can be used to get the necessary heat for the pyrolysis process. [8]

1.3 Types of pyrolysis

Pyrolysis process can be classified into two types: slow pyrolysis and fast pyrolysis. These kinds of pyrolysis depend on two parameters; the time to heat the fuel to the pyrolysis temperature (t_{heat}) and the characteristic pyrolysis reaction time ($t_{reaction}$). If the t_{heat} is much bigger than $t_{reaction}$, it is slow pyrolysis and if the t_{heat} is smaller than $t_{reaction}$, is is fast pyrolysis. [9]

Table 1. Types of pyrolysis [10]

Mode	Heating rate	T (ºC)	Residence Time	Material Size (Diameter)	Main Products
Slow Pyrolysis	Slow 1-20ºC/m	400-650	Minutes to days	1 – 200 mm	Oil gas, char ~ 1/3 each
Fast Pyrolysis	Very fast > 300ºC/s	700	Second	<1 mm	Bio-oil, 75% Char, 10-20%
Gasification	2-100ºC/m	> 800	5-30 min	5-20 mm	Gas, 80% Char, 10-20%

1.3.1 Slow pyrolysis

In slow pyrolysis, steam residence time in the pyrolysis zone is in minutes or even days. On the contrary to conventional pyrolysis where the goal is the production of liquid, slow pyrolysis method is used to produce char. It can be divided into two types of slow pyrolysis:

- Carbonization: the main goal of this process is to obtain charcoal or char and it has been the oldest method of pyrolysis. In this technique, feedstock is heated slowly in absence of oxygen with a low temperature, around 400°C, and using lots of time to maximize the char formation. [11]

- Torrefaction: the aim of this thermal process is to convert biomass to obtain coal which has better fuel characteristics than the original feedstock. In this method, feedstock is heated slowly in absence of oxygen to a temperature between 200 and 400°C. [12]

1.3.2 Fast pyrolysis

In fast pyrolysis, steam residence time in the pyrolysis zone is on the order of seconds or milliseconds and this technique is used to produce bio-oil and gas. The aim of the fast pyrolysis is to maximize production of liquid or bio-oil. It can be divided into two types: flash and very quick pyrolysis:

- Flash Pyrolysis: in this process biomass is heated quickly in absence of oxygen to a temperature between 450 and 600°C. The product that can be obtained with this kind of pyrolysis is the liquid fuel called bio-oil and its yield is about 70-75% of the total pyrolysis product. [13]
- Ultra rapid Pyrolysis: in this method biomass is heated extremely fast in absence of oxygen to a temperature around 1000°C for gas and around 650°C for liquid. These temperatures maximize the product yield of the gas. [4]

1.4 Parameters that affect the pyrolysis process

In this point, the parameters that affect the pyrolysis process are explained. As it had been said before, these parameters are the type of feedstock that is used in the process, temperature that also depends on the characteristics of feedstock, heating rate, reaction time and the particle size of feed. These factors can affect directly the yields of the solid, liquid and gaseous products that can be obtained by the pyrolysis. [1]

1.4.1 Type of the feedstock

The type of feedstock that is used in pyrolysis is important because each component of the biomass presented different temperatures of thermal decomposition. That means that they contribute to the results of the method in a different way. The hydrogen-to-carbon (H/C) atomic ratio of biomass is quite influential with the pyrolysis yield. Thus, depending on the type of feedstock that it is chosen, the obtained products could be different. [14]

1.4.2 Temperature

Temperature is quite influential as far as the final results of the pyrolysis products are concerned. For example, during the pyrolysis of biomass the escape of different product gases changes with different temperatures and also the amount of char produced depends on this parameter. It has been studied that for higher temperatures the process provides big quantities of non-condensable gases like syngas or synthetic gas ($CO + H_2$). Instead, if the process is done with lower temperatures it provides the production of solid products like charcoal, bio-coal or torrefied fuels. [14]

1.4.3 Heating rate

The heating rate is important because it has a big influence on the yield and composition of the product that can be obtained after the pyrolysis process. For example, if the process is done with rapid heating using moderate temperatures, more liquids will be obtained and if the process is done with a slower heating, it will produce more char. [14]

1.4.4 Reaction time

Reaction time influences the degree of thermal conversion of the solid product and the residence time of the steam. This residence time of the vapour affects the composition of steams, which means that influences if they are in a condensable or non-condensable phase. [14]

1.4.5 Particle size of feed

The particle size of feed is an important parameter because it affects the speed in which material is submissive to the pyrolysis process. Normally, lower particle size materials are faster influenced by the thermal decomposition and because of this reason they can achieve more quantities of pyrolysis oil than in case of bigger particle size. [14]

Some examples of particle sizes of samples can be found in the literature. For example, in the study [2] that talks about co-pyrolysis of oil shale and plastics, samples of oil shale were ground and sieved to give particle size of 0.1 mm. Another example is in the study [15], which talks about the co-pyrolysis of oil shale and wheat straw where all samples were first air-dried, crushed, and sieved to a grain size of ≤3 mm. Finally, another example is with the study on co-liquefaction of Estonian kukersite oil shale with peat and pine bark [3], where all samples were air-dried and finely powdered with a size less than 0.1 mm.

1.5 Materials

The materials to be used during the co-pyrolysis process are biomass and Kukersite oil shale, so right now some characteristics of these two materials are introduced.

1.5.1 Biomass

Biomass is organic matter of plant or animal origin, which includes materials that come from natural or artificial transformation and can be used as a source of energy, either as fuel or for other processes. This material is a valuable feedstock because it allows to obtain energy from a renewable source and it can be one interesting alternative for the production of energy. [16]

1.5.1.1 Biomass resource

Biomass is known to be practically an inexhaustible resource of feedstock for energy and chemical needs. For this reason, there is high availability of this kind of source and now and there are several types of biomass that can be found in the world.

European Committee for Standardization have defined biomass classification: virgin biomass and waste biomass. Virgin biomass includes terrestrial and aquatic biomass. Terrestrial biomass is product that can be obtained from forest or energy crops and an example of aquatic biomass is the algae or water plants. Waste biomass includes: municipal waste, agricultural solid waste, forestry residues and industrial waste.

If biomass is studied as for its origin, it can be defined by four categories: woody biomass, herbaceous biomass, fruit biomass and blend and mixtures. Woody biomass includes trees, bushes and shrubs and fruit biomass is composed by fruits or seeds. Herbaceous biomasses are the plants that die when the growing season ends such as grains or cereals. Finally, blend and mixtures are composed by different types of biomass.

As it can be seen, there are lots of different types of biomass, although in this project is focused in Scots pine (woody biomass) in order to achieve the fixed goals. [17]

Figure 3. Sample of woody biomass used in the experiments

1.5.1.2 Biomass composition

As it has been said before, biomass is a mixture of different organic materials. The main components of woody biomass are: extractives, cell wall components (cellulose, hemicellulose and lignin) and ash.

At first, extractives are formed by different substances that are present in animal or vegetable tissue. These substances can be separated with solvents and through evaporation of the solution can be obtained again.

The cell wall component provides the structural strength to the plant. This component is formed basically by cellulose or hemicellulose fibres (carbohydrates) and lignin:

- Cellulose: is the most common organic compound in the world. It is a homopolysaccharide formed by hundreds or thousands of β-glucose monomers. It has a fibrous structure, formed by chains of glucose that are linked by hydrogen bonds of hydroxyl groups, giving rise to waterproof fibres that make up the cell wall of plant cells. It is the dominant component of wood and it represents about 40-44% by dry weight.

- Hemicellulose: is a heteropolysaccharide formed by different types of monomers. This polymer forms part of the walls of plant cells, coating the surface of the cellulose fibres and allowing the binding of pectin. It represents about 20-30% of the dry weight of most wood.

- Lignin: is one of the most abundant organic polymers in the world. Thus, it is the most complex natural polymer as far as its structure and heterogeneity is concerned. This molecule has a high molecular weight because of the union of different phenylpropyl alcohols and acids. The random coupling of these radicals origin one three-dimensional structure that is being as an amorphous polymer. This element provides rigidity to the cell wall and resistance of lignified tissues to protect them from the microorganisms, preventing the penetration of destructive enzymes in the cell wall. It represents about 18-35% of dry weight of most wood.

Finally, ashes are considered as the inorganic component of biomass. [18]

1.5.1.3 Biomass applications and products

The way of transforming biomass into energy depends on different factors but the most important are the type of biomass and the energy type that is need to be obtained. The different processes and systems of transformation of biomass can produce thermal energy, electrical energy and mechanical energy.

Thermal energy is the most common application of biomass energy, which is used basically for heating. From this energy hot water can be generated, hot air and steam. Residually, it is possible to take advantage of the steam that is emitted for the production of electrical energy or other industrial processes.

To generate electrical energy there are different technologies. The first one is steam cycle, which is based on the combustion of biomass in order to generate steam. Thus, moving a turbine that with the help of one alternator, electricity can be produced. The second technology is the gas turbine which is based on the gasification of biomass in order to generate steam and in this way to move a turbine. The difference from the first technology is that if the generated gases from the turbine are used in a steam cycle, then it is a combined cycle. Another important technology is the cogeneration that produces electrical energy and takes advantage of the heat surplus to produce thermal energy.

Finally, the last application that it can be found is mechanical energy. Through biomass transformation, for example pyrolysis, it is possible to obtain bio-fuels and bio-alcohols that are capable of feeding explosion motors. [19]

1.5.1.4 Environmental considerations

Right now, the discussion will be focused on some environmental aspects that showed why this energy can be considered as a renewable one. First of all, woody biomass is a sustainable product that generates a renewable energy obtained from the management of forests and can help improve the forest masses, which mean to reduce excessive density. It also contributes to the compatibility with the operations of prevention of incentives and reduction of the risk of fire and to reduce the risk of forest pests. Another important point to be treated is that there are neither sulphur emissions (SO_2) nor nitrogen oxides (NO_x), which are components of acid rain, so there is quite an improvement of air quality.

The most important disadvantage is that there might be some risk of overexploitation and incorrect combustion of biomass. The risk of overexploitation happens only in case of exceeding the production capacity of the system and incorrect forest management. In addition, the incorrect combustion conditions of biomass may produce the liberation of contaminating gases which are harmful for the planet. [20]

1.5.2 Oil Shale

Oil shale is a sedimentary rock that contains an organic-rich material called kerogen. This material is used as a feedstock in order to obtain a liquid fuel used in the pyrolysis method. In addition, this material could be one of the substitutes of the conventional crude oil because of its large reserves. [15]

Figure 4. Sample of oil shale used in the experiments

1.5.2.1 Oil shale resource

The oil shale deposits can be found all over the world, but most of them cannot be exploited economically due to their depth. That is why the reserves of oil shale all over the world can be exploited economically in more than 30 countries. The most important reserves of oil shale are in the United States, in the Green River, which represents the 72% of the world's reserves. Also reserves can be found in countries such as: China, Russia, Brazil, Morocco and Jordan. Estonia has become the eighth country as for this kind of resources, with 16.3 billion barrels, as it can be seen in the Figure 5. [21]
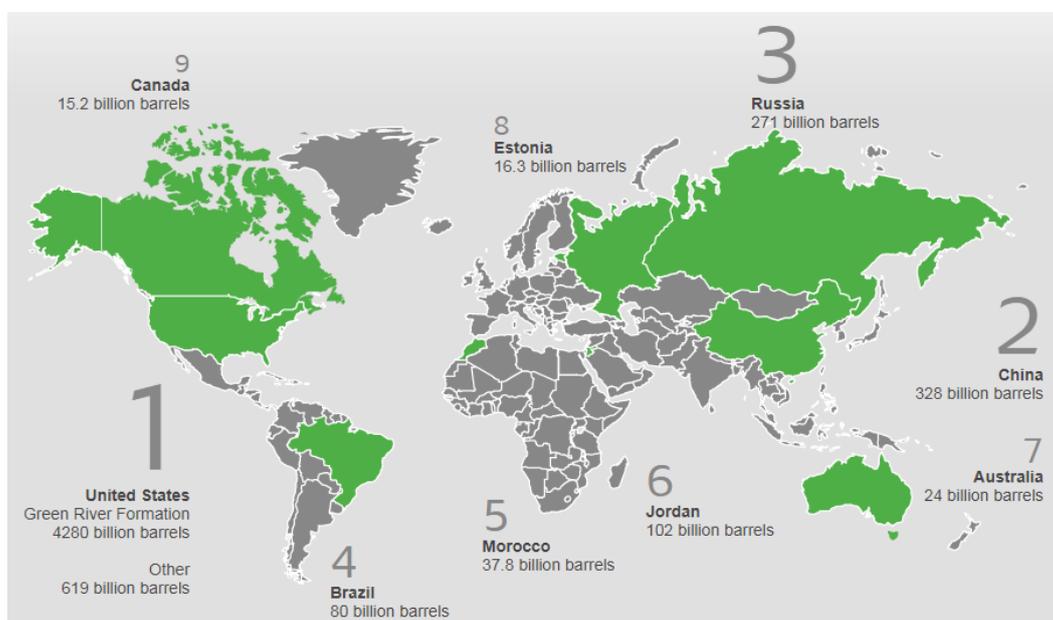
Figure 5. Most important countries that have reserves of Oil Shale [21]

1.5.2.2 Oil shale extraction and processing

The extraction of oil shale implies mining. Once extracted the oil shale it can be burned directly and used as a power generation or used for further processing. The most common processes of extraction are open pit mining and strip mining. The useful components of extraction of this material usually take place above the ground but nowadays are appearing some new technologies to do it underground. [22]

After extraction, the process which kerogen is decomposed or pyrolysed in different components in absence of oxygen is called retorting. During this process, kerogen in oil shale is heated at temperatures about 300-350°C and is converted into organic intermediates like bitumen. In this moment, also some molecular substances as carbon dioxide, interlayer water and moisture are liberated. After that, the temperature continues rising into temperatures between 400 and 550°C and the organic intermediate is decomposed generating gases, shale oil and residual carbon as it can be seen in the Figure 6. [15]
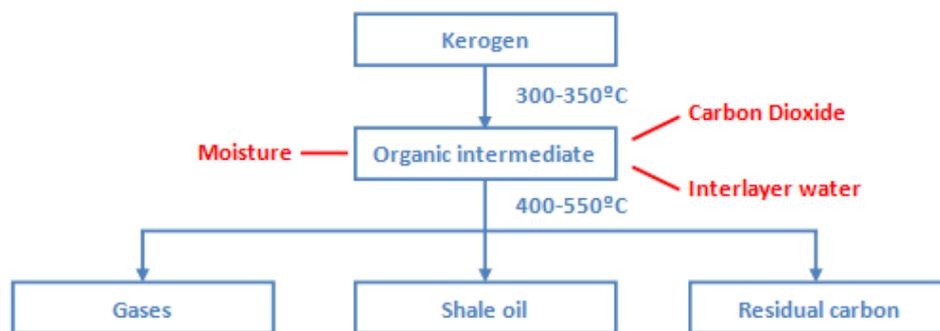
Figure 6. Scheme of the retorting process [15]

1.5.2.3 Oil shale applications and products

Oil shale is mainly used as a fuel for thermal-power plants, where it is burnt to run the steam turbines. As a result, electrical energy is produced that can be supplied as the domestic energy applications or the industrial plants.

Another application to use the oil shale as a fuel is the production of residential heat. In addition, it can be used to produce some chemical products such as carbon fibers, adsorbent carbons, phenols, resins, glues, tanning agents or fertilizers. Also, this product can be founded in the construction field used to produce cement or used for construction and decorative blocks. [23]

In Estonia, the oil shale is mostly used as a source of energy for the production of electricity becoming one of the most energy independent states in Europe. In this country, the production of electricity using the oil shale as a source of energy is above 84% [24].

Additionally, oil shale is also used as a liquid fuel, for residential heat or for chemical industry.

1.5.2.4   Environmental considerations

In this point, some environmental aspects that have to be considered are explained. The first one is that the extraction of oil shale has a big environmental impact. That is why with this technique some metals such as mercury have been introduced into the surface/groundwater water, erosion increases, sulphur gas emissions rise too, and during processing and transport some particulates increase air pollution.

Another disadvantage that should be considered is that for the extraction of oil shale is required enormous quantities of water that after this process will be polluted.

Another aspect to keep in mind is that when oil shale is heated, it emits carbon dioxide to the atmosphere. That affects directly to the atmosphere contributing to the greenhouse effect which this greenhouse gas absorbs and retains heat in the Earth's atmosphere. That last point is very important because it contributes in a sharp way to accelerating the climate change. [22]

1.6 Techniques and process used for pyrolysis

Just now the discussion is about the different techniques and process to carry out the pyrolysis or co-pyrolysis. Therefore, the discussion will be focused on the types of pyrolyzers most commonly used at present when it comes to performing this process. Modern reactors can be classified as fixed bed, fluidized bed and entrained bed and then they can be according to the design characteristics. So, the most commonly pyrolyzers now are the fixed or moving bed, the bubbling fluidized bed, the circulating fluidized bed (CFB), the rotating cone, the ablative reactor and the vacuum reactor.

1.6.1 Type of reactor

1.6.1.1   Fixed or moving bed reactor

This reactor is the first pyrolyzer that appears, which operates in batch mode. In this kind of reactors, the heat for the thermal decomposition of the feedstock could be provided by an external source or internal one, as for example a resistant into the reactor. When the pyrolysis process is carried out, the gas flows out of the reactor because of volume expansion and the char product abides into the reactor. One important point to consider in this kind of reactors is that after pyrolysis an inert sweep gas is used in order to remove the remaining product gas

into the reactor. This gas could be, for example, nitrogen and has to be oxygen free. In the Figure 7 the scheme of this type of reactor is shown. [25]
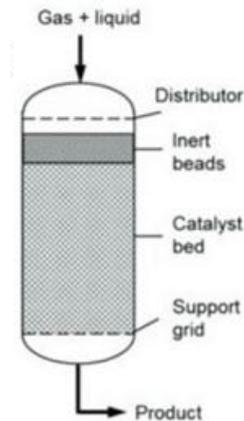
Figure 7. Fixed or moving bed reactor [26]

1.6.1.2 Bubbling fluidized bed reactor

This kind of reactor is easy to build, thus it is easy to scale up. Its mode of operation consists of introducing feedstock into a bubbling bed of hot sand or other solids. Once this has been realised, this bed is fluidized using one inert gas, such as nitrogen, which allows having a good control of temperature and a high heat transfer to the solids.

In order to make the pyrolysis process, the necessary heat can be supplied by burning part of the gas product included into the bed or by burning the solid char in a different chamber and transferring the heat that is produced in this chamber to the remaining solids into the bed. The char that is contained in the bed is used as a vapour-cracking catalyst and the char particles that are mixed with the gas product must be separated. So as to separate these particles, the technique that is usually used is single or multistage cyclones. In Figure 8, the operation mode of this kind of reactor using biomass as a feedstock is shown. [27]
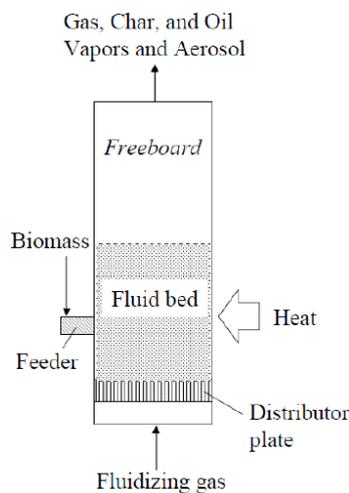
Figure 8. Bubbling fluidized-bed reactor [27]

1.6.1.3   Circulating fluidized bed reactor (CFB)

This reactor presents similar characteristics to the bubbling fluidized-bed reactors. The most important difference is that the circulating fluidized bed reactor has shorter residence time for chars and vapours, which implies that the gas has higher speed and there is more char in the bio-oil. One important point to emphasize is that this kind of reactor is used for high performances, although it implies more complex hydrodynamics. This special hydrodynamics is known as a fast bed and this kind of reactor allows good control of temperature. Another advantage of this kind of reactor is that the char that is pulled out from the reactor can be separated and burnt easily in an external reactor. After that, combustion heat is transferred to inert bed solids that are recycled to the reactor.

Currently, there are two types of this kind of reactors: single circulating fluidized bed reactor and double circulating fluidized bed reactor. [28]

1.6.1.4   Rotating cone reactor

In these types of reactors, the pyrolysis process occurs due to a mechanical blend of feedstock and hot sand, instead of using inert gas because it is the most effective way to transfer heat. The process consists of feeding into the bottom this mixture of feedstock and hot sand to the base of the rotating cone. After that, the solids are moved up to the lip of the cone using the centrifuge force that pushes the particles. Once this has been realised, char and sand are sent to a combustor where sand is heated again. Finally, this sand is introduced into the base of the cone with fresh raw material. In Figure 9 the operation mode of a rotation cone reactor using biomass as a feedstock is shown. [29]
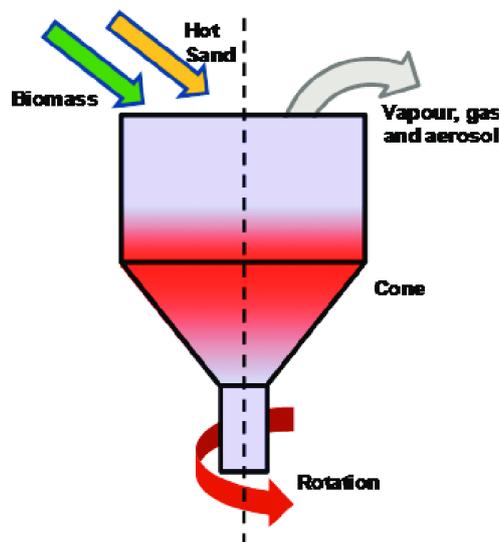
Figure 9. Rotating cone reactor [30]

1.6.1.5 Ablative reactor

The most common ablative reactors currently used are the ablative vortex reactor and the ablative rotating disk reactor. In this type of reactors the operation mode consists of transferring heat to a melt layer at the hot reactor surface with the absence of inert gas. In order to pressure the feedstock against a heated wall of the reactor is used the mechanical pressure. After that, the material in contact with the wall is melted and as it is moved away the residual oil evaporates as pyrolysis vapours.

On the one hand, the most important advantage offered by this type of reactor is that the size used as a feedstock introduced into the reactor is much larger than other types of reactors. On the other hand, due to mechanical nature of the system, these types of reactors have a more complex configuration. [31]

1.6.1.6 Vacuum reactor

This type of reactor is formed by several stacked heated circular plates. The pyrolysis process in this reactor consists of introducing feedstock to the top plate, which is at a temperature about 200°C, and is falling towards the lower plates successively using means of scrapers. Feedstock goes through drying and pyrolysis while is moving over the plates until it reaches the last plate, which is approximately at 400°C. When the feedstock reaches the lowest plate, the char is left and during the process the use of the carried gas is not necessary. The design of the vacuum reactor is complex due to embedding of the vacuum pump. [32]

2 EXPERIMENTAL

In this section, the experimental part is performed. In order to do this, first, the main characteristics of the materials that are used when performing the experiments are exposed. Next, it is explained the equipment and procedures to be able to perform the experiments. Below are some preliminary considerations where the system's repeatability is checked and a signal correction is made due to the condenser affects it. Finally, the test plan that has been followed of the different experiments is shown.

2.1 Materials

In this point, it is stated about the main characteristics of the materials that are used when performing the experiments. Firstly, the chemical composition of oil shale and biomass gets defined. Next, it is explained how samples have been prepared to perform the different experiments and finally, the conditions that have been used during the experiments are presented.

2.1.1 Oil Shale

As it has been mentioned earlier, oil shale deposits can be found throughout the world, but most of it cannot be exploited economically due to their great depth. However, in Estonia this element is easy to exploit and is used as the country's main power source because it represents roughly the 84% of the energy production [24]. In this project, the approach is applied to the Kukersite oil shale, which is the most common in Estonia. Table 2 shows its chemical composition.

Table 2. Chemical composition of Kukersite Oil Shale

Chemical composition of Kukersite Oil Shale							
Loss on ignition at 550°C	Ash content at 815°C (dry matter)	Carbonate CO_2	Elemental composition				
			C	H	N	S	O
41.21/41.56%	47.35%	17.6%	33.78%	3.71%	0.09%	1.73%	60.69%

Once the chemical composition of this material has been defined, the samples are prepared as it is shown below. There are two steps for preparation of the samples of Kukersite Oil Shale to carry out the experiments. In the first place, oil shale was crushed using a crushed jaw and then a sieve was used for 2 minutes in order to make the particle size between 0.25 and 0.5 mm.

The conditions used to carry out the experiments with this element are three temperatures (550°C, 750°C and 900°C) with a sample of 5 g in the pyrolysis of oil shale and 2.1 g in the co-pyrolysis of oil shale and biomass. This sample used in the co-pyrolysis is due to the fact that the higher heating value is meant to be 1:1 energetically speaking (OS: 9.72 MJ/kg and BM: 20.4 MJ/kg).

2.1.2 Biomass

As it is known, biomass is virtually an inexhaustible renewable source of energy and chemical needs. In this case, the project focuses on the Scots pine as it is one of the most common trees in Estonia (33% of the total area of stands) [33]. Therefore, this is why this project is used as there is a high availability of this type of biomass. Table 3 describes its chemical composition.

Table 3. Chemical composition of Scots pine

Chemical composition of Scots pine								
Type	Content (%)	Humidity (%)	Ash (%)	HV, analytical sample (MJ/g)	HHV (MJ/kg)	LHV (MJ/kg)	C (%)	H (%)	N (%)
Bark	10.66	4.78	3.05	20.38	21.4	20.08	52.79	6.08	1.19
Trunk/stem	89.34	4.82	0.33	-	-	-	50.12	6.59	0.19

Once the chemical composition of this element has been defined, the samples are prepared as it is explained below. There are four steps for preparation of the samples of Scots pine to carry out the experiments. First, the Scots pine logs have been cut into smaller pieces using an electric able saw and an axe. After that, the cut pieces have been shredded into wood chips. The next step has been to pulverise the wood chips into sawdust using a laboratory sample pulveriser. The last step has been fractioning the sawdust in order to get a consistent particle size suitable for the reactor and the sample holder.

In this case, conditions used to carry out the experiments with this element are three temperatures (550°C, 750°C and 900°C) with a sample of 1.7 g in the pyrolysis of biomass and 1 g in the co-pyrolysis of oil shale and biomass. For the same reason as the oil shale, this sample used in the co-pyrolysis is due to the fact that the higher heating value is meant to be 1:1 energetically speaking.

2.2 Equipment and procedure

First of all, in order to be able to do the experimental part of the setting up has to be explained. The most important elements that are necessary to make the co-pyrolysis process in order to obtain the results are the fixed bed reactor, the condenser, the gas chromatography-thermal conductivity detector, the rotameter, the carrier gas and the gas analyzers (FTIR and FID) as it is shown in Figure 10.
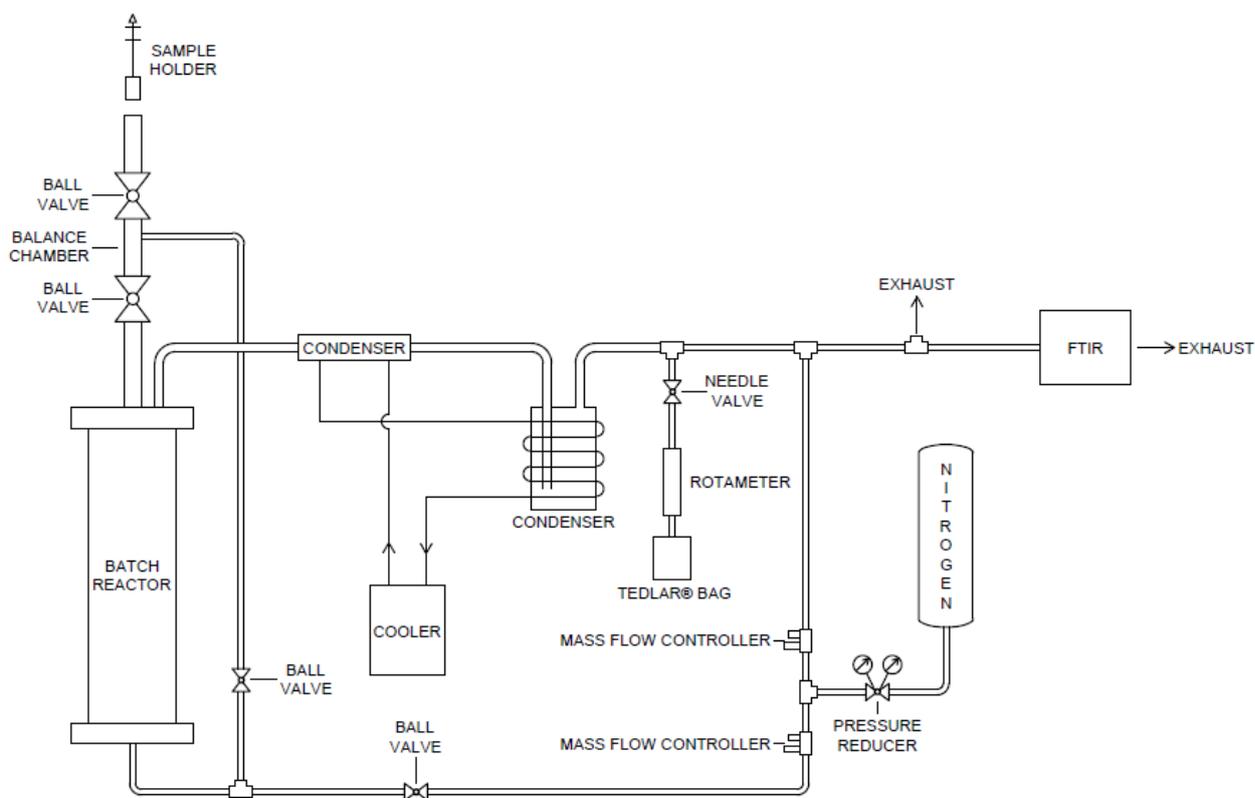
Figure 10. Gasification Batch reactor test set up

2.2.1 Fixed bed reactor

The reactor used in this project is the batch reactor in order to achieve the pyrolysis at the desired temperatures (Figure 11). The experimental system consists of one reactor-heater, the temperature-control system, the gas mixing-control system and the control system. On the one hand, in this type of reactor the heat for the thermal decomposition of the feedstock is provided by an internal source. In this case, heat is provided with electric heaters. On the other hand, the temperature-control system is provided using the thermocouple, the gas mixing-control system comprises masses flow controllers and the control system is carried out through the computer by the LabView program.

One important point to consider is that this reactor has been designed to achieve a working temperature up to 950°C, it is one of the reasons why the experiments are carried out with the temperatures of 550°C, 750°C and 900°C. [34]

The procedure of the experiments consists of the following tasks: firstly introduce nitrogen to the reactor in order to remove the remaining product gas and the oxygen inside the chamber; secondly introduce the sample holder into the balance chamber and then dropped into the reactor to begin the process of pyrolysis.

Figure 11. Batch reactor

2.2.2 Gas analyzer

The gas analyzer is an industrial device designed so as to measure the composition of gases produced in the co-pyrolysis process. In this project, the used analyzer is the Gasmet DX4000 which is usually configured to measure H_2O, CO_2, CO, NO, NO_2, N_2O, SO_2, NH_3, CH_4, HCl, HF and different volatile organic compounds (VOC's). It is possible to measure 50 gases at the same time. So as to measure all these gases simultaneously, this device uses the Fourier Transform Infrared spectroscopy (FTIR) technology. This technology identifies all the molecules with their characteristic absorption spectrum. That is why every molecule receives infrared radiation at its characteristic frequency. Besides, each molecule has its unique combination of atoms, which means that they produce one unique spectrum for each molecule when they are receiving infrared light. In spite of this, there are some molecules that have the same number of atoms but they can be distinguished because they are in different positions in exception of the diatomic elements and the noble gases. [35]

In this kind of technology the infrared radiation is plotted according to wavelength or wavenumber. In particular, this analyzer measures all the infrared radiation wavelengths at the same time and plots the full spectrum as it is shown in Figure 12.
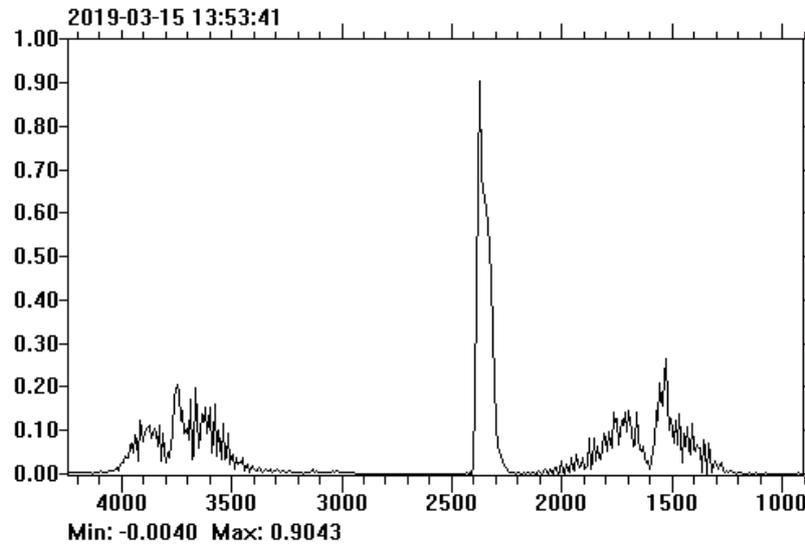
Figure 12. Spectrum obtained in the gas analyzer

In addition, this device heats its corrosion resistant sample cell to 180°C to ensure that the sample is always kept in a gas phase so as to obtain the measures correctly. Therefore, it is necessary to heat up to avoid condensation since if the liquid condenses, it can contain corrosive compounds that would destroy the gold-plated mirrors. Finally, this device is equipped with software that allows obtaining the results in the computer in order to be able to analyze them accurately. [36]

2.2.3 FID Analyzer

The flame ionization detector (FID) analyzer is an industrial apparatus designed to measure the total composition of the hydrocarbons produced in the co-pyrolysis process. In this project, the analyzer used is Fidamat 6 of the Siemens company.

The measurement of this device is not specific to a component, but to a class of materials. The result that shows the measures of the device is proportional to the number of the carbon atoms in the correspondent molecule.

This apparatus can have different uses such as trace measurement of hydrocarbons in pure gases. This is possible thanks to high resolution and the minimum difference in the response factors. Another use can be the total content measurement of hydrocarbons in presence of corrosive gases. For this last application, it is important to use a filer free of wear and resistant to corrosion. Also it is important to use a quartz capillary as the measuring gas

capillary. The high operating temperature can be adjusted for the internal gas path and the detector also allows to measure mixtures of high boiling point and measure hydrocarbons at vapour concentrations up to 100%.

In short, the use of this device has a number of advantages. The first one, as is has been said before, is that it has a wide range of applications. It also has very low sensibility to cross interference from disturbing gases, has low consumption combustion air and a low influence of oxygen in average value. Finally, this device has an alarm and fault system that is important for safety. [37]

2.2.4 Gas chromatography – Thermal Conductivity Detector (GC-TCD)

Gas chromatography is a technique that is used to identify and quantify volatile substances in the gas phase. In this technique, the constituents of the sample are dissolved in a solvent and vaporized to obtain the separation of the analytes by distributing the sample between two phases: a stationary phase and a mobile phase. The mobile phase is a carrier gas used to transport the particles of the analyte through the heated column.

Some of the most common application of this technique is the analysis of petroleum and derivatives and the analysis of volatile substances in different fields as it can be the perfumery.

There are two types of chromatography: the gas-solid chromatography (GSC) and the gas-liquid chromatography (GLC). Nowadays, the last one is used more widely and it can be called gas chromatography (GC). [38]

In this project, the apparatus used to analyze the composition of the sample is the Shimadzu gas chromatograph GC-2014. This device has the characteristic that uses the thermal conductivity detector. This detector works measuring the change produced in the carrier gas thermal conductivity when the presence of the sample which has another thermal conductivity appears.
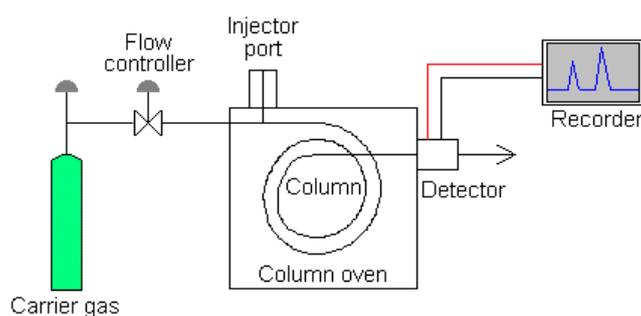
Figure 13. Schematic diagram of a gas chromatograph [39]

2.2.5 Condenser

The condenser used is the Cool-Care brand and this element of the system serves to separate condensable gases from non-condensable during the pyrolysis process. In addition, in order to improve condensation, this element is made up of two subsystems as well as ceramic and cotton pieces have been added to avoid shale oil leaks to the following elements of the system as it is shown in Figure 14.
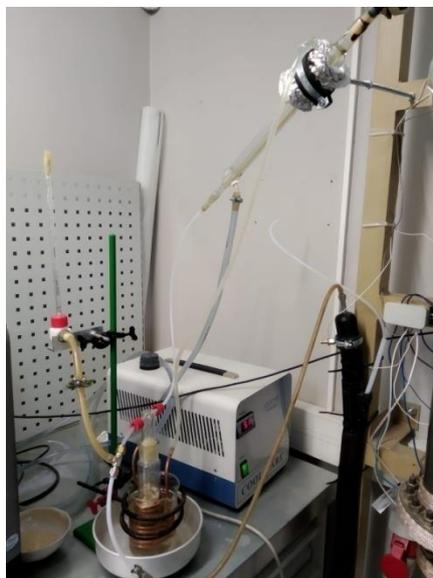
Figure 14. Condenser

2.2.6 Rotameter

The rotameter is a device used to measure the flow of fluid that circulates through a conduit. It is an indicator that fits through a graduated tube. In this case, the rotameter is used to regulate the flow of fluid that reaches the Tedlar® bag in order to be able to accurately measure the properties of the non-condensable gases.
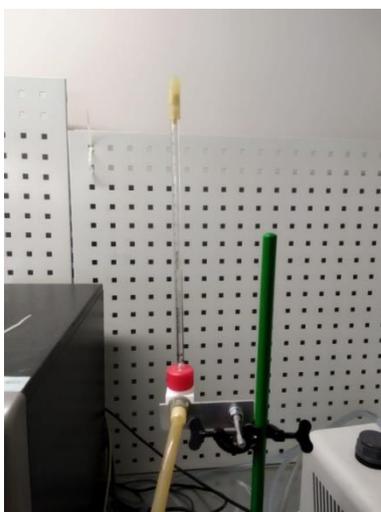
Figure 15. Rotameter

2.2.7 Gas Agents

The gas used in this project is nitrogen (>99.5 vol.%) since it is an inert gas. Its use is very important in order to ensure that pyrolysis is carried out properly. This is because the introduction of this agent eliminates the presence of oxygen as this is a reactive gas. The total nitrogen flow used in this study is 3.8 L/min. Of this flow, 0.3 L/min goes directly to the reactor and 3.5 L/min is used for the dilution.

Figure 16. Gas Agents

2.3 Previous considerations

At this point, previous considerations taken into account when carrying out of the study are getting exposed. First of all, the proper operation of the system has been checked while repeating the experiment several times and seeing similar obtained results. After that, concentration is known to be obtained before and after the condenser be different due to this element. Therefore, in this section the purpose is to find a model that allows the correction of this signal through a mathematical model to ensure the results be as accurate as possible.

2.3.1 Repeatability

As it has been mentioned before, in this section what it is intended is to demonstrate the proper operation of the system through the repetition of experiments. In order to achieve this proposal, it takes co-pyrolysis as an example, which has been made at 750°C using oil shale and biomass and then comparing the evolution of the concentrations of one of the gases during reaction.
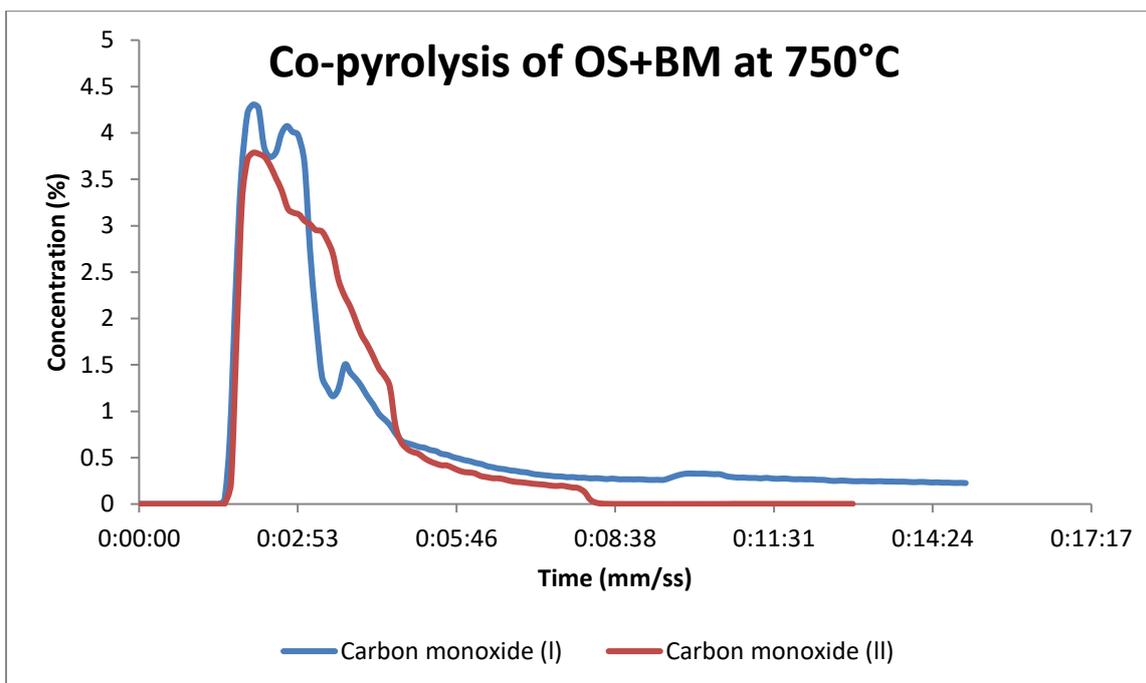
Figure 17. Repeatability of the system

As it can be seen in Figure 17, repeatability is met since in both cases the results have been quite similar. First, it is observed that the values of concentrations are very similar. This can be demonstrated by calculating the average concentration where in the case of the curve of the carbon monoxide (l) it takes a value of 14841 ppm and in the cases of the curve of the carbon monoxide (ll) it takes a value of 15801 ppm. However, there are small variations in the maximum values of concentrations. This is because the flow of the rotameter was adjusted during reaction and this causes the accentuated peaks that can be seen in the curve of the carbon monoxide (l). In addition, reaction times in both cases are very similar. Therefore, it can be concluded that the system works correctly since repeatability occurs.

2.3.2 Signal

As it is known, the obtained hydrocarbon concentration before and after the condenser has a small delay due to this device. Firstly, so as to demonstrate this phenomenon, what is done is to connect the FID analyzer just after the reactor and connect the gas analyzer (FTIR) just after the condenser to see the obtained signals. In Figure 18 the scheme that is followed to perform the experiment is shown.
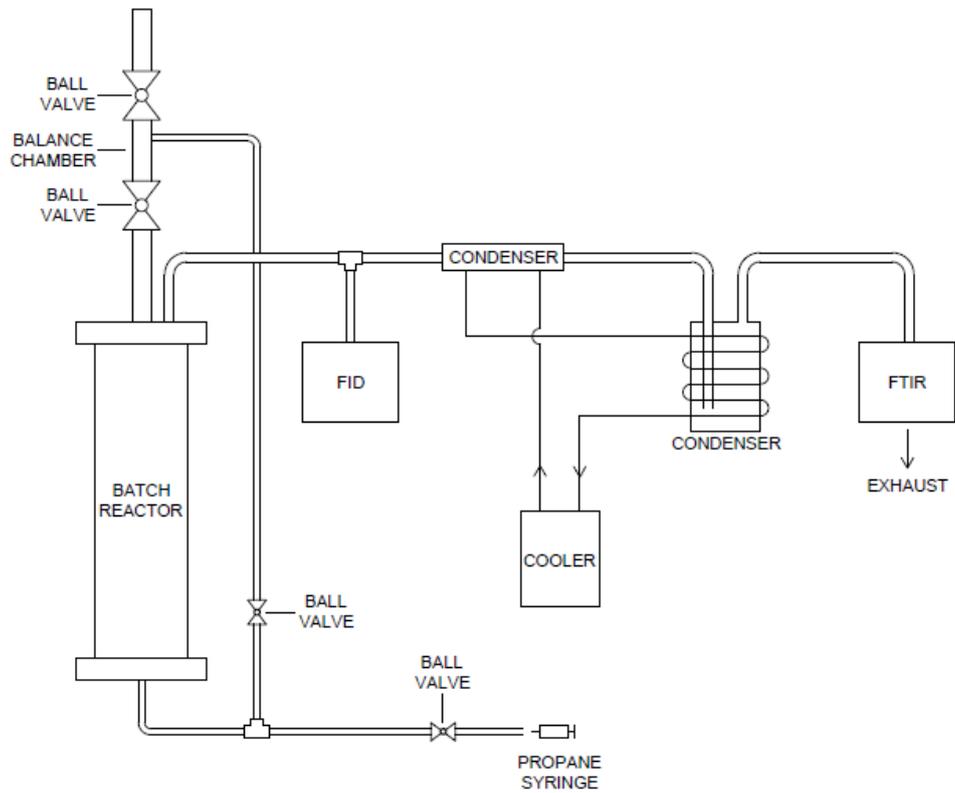
Figure 18. Set up to check the signal

Once everything has been connected correctly, what is done is to inject propane through a syringe at room temperature in order to see which the delay between both signals is. Once this has been done, the obtained signals are the ones that are shown below in Figure 19:
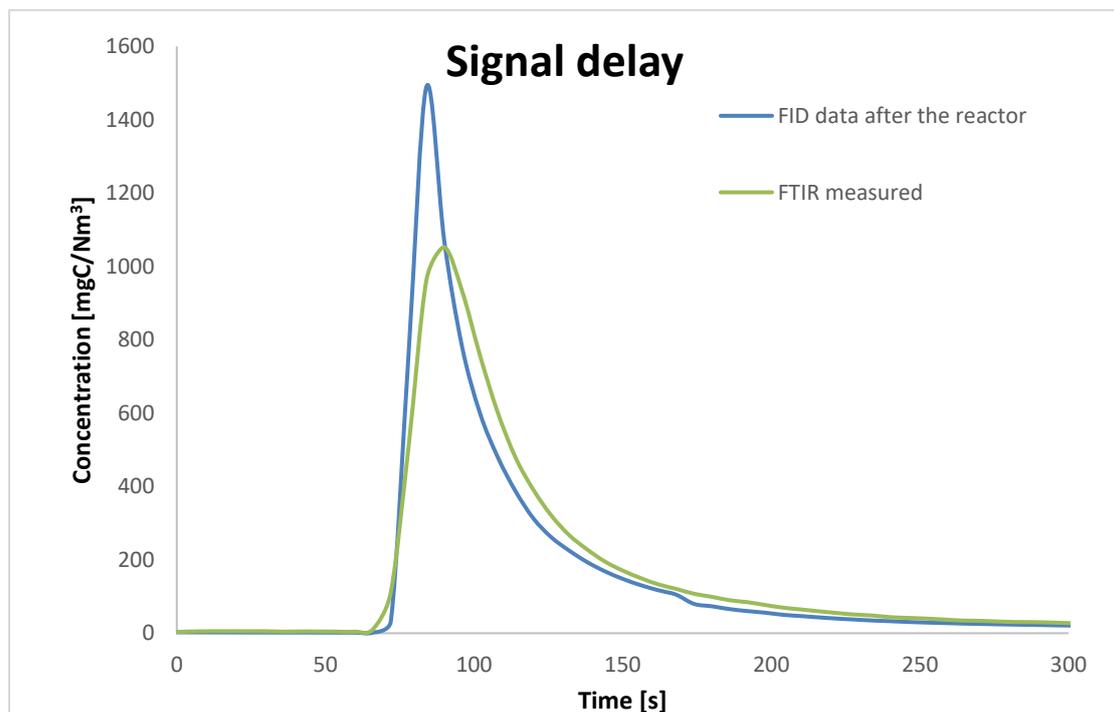
Figure 19. Signal delay

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As it can be seen, what is predicted is confirmed where the signals obtained before and after the condenser is different. It is for this reason that a correction of this FTIR signal is made using the mathematical model more adjusted to the reality considering that the condenser behaves like a continuous stirred tank reactor (CSTR). [40]

In this model, what is intended is to see how the concentration within the condenser changes during the reaction time. So, the goal of this model is to get one expression that links both signals. In order to get this, the following mathematical model is used:

$$\frac{V}{q} \cdot \frac{dC_A}{dt} = C_{A,in} - C_{A,out} \tag{1}$$

Where V is the Volume of the condenser (L), q is the volumetric flow rate (L/s), $C_{A,in}$ is concentration that enters to the condenser (ppm), $C_{A,out}$ concentration that goes out from the condenser (ppm) and t is the time (s). So, assuming perfect mixing in the condenser such that $C_{A,out} = C_A$ then the equation (1) gets integrated:

$$\int_{C_{A1}}^{C_{A2}} \frac{dC_A}{C_{A,out} - C_{A,in}} = -\frac{q}{V} \cdot \int_0^t dt \tag{2}$$

Solving the integral, the equation (3) is obtained:

$$\ln\frac{C_{A2} - C_{A,in}}{C_{A1} - C_{A,in}} = -\frac{q}{V} \cdot t \tag{3}$$

And:

$$C_{A2} - C_{A,in} = \left(C_{A1} - C_{A,in}\right) \cdot e^{-\frac{q}{V} \cdot t} = C_{A1} \cdot e^{-\frac{q}{V} t} - C_{A,in} \cdot e^{-\frac{q}{V} t} \tag{4}$$

$$C_{A2} = C_{A,in} + C_{A1} \cdot e^{-\frac{q}{V} t} - C_{A,in} \cdot e^{-\frac{q}{V} t} = C_{A1} \cdot e^{-\frac{q}{V} t} + C_{A,in} \cdot \left(1 - e^{-\frac{q}{V} t}\right) \tag{5}$$

Resting C_{A1} to both sides of the equation (5):

$$C_{A2} - C_{A1} = C_{A1} \cdot e^{-\frac{q}{V} t} + C_{A,in} \cdot \left(1 - e^{-\frac{q}{V} t}\right) - C_{A1} =$$

$$= C_{A,in} \cdot \left(1 - e^{-\frac{q}{V} t}\right) - C_{A1} \cdot \left(1 - e^{-\frac{q}{V} t}\right) = \left(C_{A,in} - C_{A1}\right) \cdot \left(1 - e^{-\frac{q}{V} t}\right) \tag{6}$$

So, the equation linking both signals is:

$$C_{A,in} = C_{A1} + \frac{C_{A2} - C_{A1}}{1 - e^{-\frac{q}{V} \cdot t}} \tag{7}$$

Where that C_{A1} is concentration that goes out from the condenser in the time before and C_{A2} is the concentration that goes out from the condenser the time after. So, in order to express equation (7) clearly:

$$C_{A,in} = C_{A,out}(t_1) + \frac{C_{A,out}(t_2) - C_{A,out}(t_1)}{1 - e^{-\frac{q}{V} \cdot t}} \tag{8}$$

Now, using equation (8), the corrected signal is obtained as it can be seen in Figure 20:
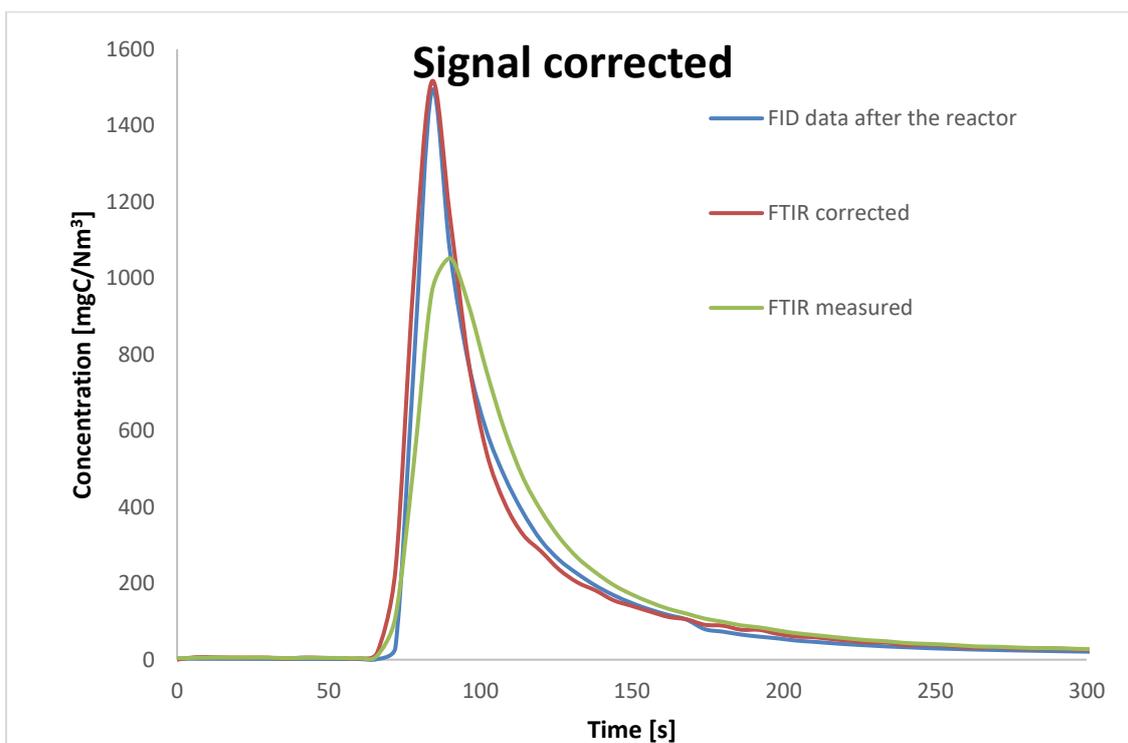
Figure 20. Signal corrected

However, in this project the signal correction will not be performed, but it has been considered convenient to mention.

2.4 Test plan

In Table 4 the test plan is shown, which will be done in order to achieve the goals that are fixed in the thesis. These temperatures should be said to have been chosen since it is known that the temperature of 550ºC is the one that gives maximum yield in co-pyrolysis [2] and the other two temperatures, those of 750ºC and 900ºC, in order to compare with the first temperature. As far as selected materials are concerned, apart from being two local materials, it has been considered interesting how these materials behave when they are mixed together. Finally, the gas agent chosen is the nitrogen because it is one of the most typical inert gas used for pyrolysis.

Table 4. Test plan

Test plan			
Sample	**Temperature (°C)**	**Gas agent**	**Date**
OS	550	N_2	17/04/2019
	750	N_2	29/04/2019
	900	N_2	22/04/2019
BM	550	N_2	24/04/2019
	750	N_2	24/04/2019
	900	N_2	24/04/2019
OS + BM	550	N_2	24/04/2019
	750	N_2	02/05/2019
	900	N_2	02/05/2019

3 RESULTS AND DISCUSSION

In this section the results and the discussion are exposed after the experimental part. First, it is analyzed the effect of the mass losses in order to compare them with other experiments that have already been carried out in this field. Next, is to characterize the gases making a comparison of the gases at different temperatures to see which the most important components during the evolution of the reactions are. Moreover, the concentration per mass of organic is calculated and the measured and calculated concentrations in co-pyrolysis are compared. In addition, the composition of the gases is analyzed, using the GC-TCD, and a comparison between the composition of the gas measured and calculated is performed. Finally, the evolution of the char obtained in each experiment for the different temperatures used is shown.

3.1 Mass losses

This section explains the mass losses obtained during the different experiments. Firstly, it is necessary to define how mass losses have been calculated. To do this, expressions (9) and (10) have been used:

$$Mass\ losses = S_i - S_f\ [g] \tag{9}$$

$$Mass\ losses = \frac{S_i - S_f}{S_i} \cdot 100\ [\%] \tag{10}$$

Where parameter "S_i" is the weight of the initial sample and parameter "S_f" is the weight of the sample after pyrolysis. So, the results obtained are presented in the Table 5.

Table 5. Mass losses

Sample	Temperature (°C)	S_i (g)	S_f (g)	Mass losses (g)	Mass losses (wt. %)
BM	550	1.6761	0.3251	1.3510	80.60
	750	1.7411	0.2533	1.4878	85.45
	900	1.6815	0.2082	1.4733	87.62
OS	550	4.9186	3.7116	1.2070	24.54
	750	4.9734	3.6536	1.3198	26.54
	900	5.0536	2.9191	2.1345	42.24
OS + BM	550	3.0975	1.8723	1.2252	39.56
	750	3.1240	1.6661	1.4579	46.67
	900	3.0959	1.2240	1.8719	60.46

It should be added that in some of the experiments they were repeated to check the validity of the mass losses. For example, in the experiment of the pyrolysis of oil shale at 550ºC it was repeated, obtaining losses of 25.21%.

As it can be seen in the previous table (Table 5), as the temperature increases, the massive losses are increased. In order to demonstrate this, in Figure 21 the evolution of the losses with the temperature is shown more clearly.
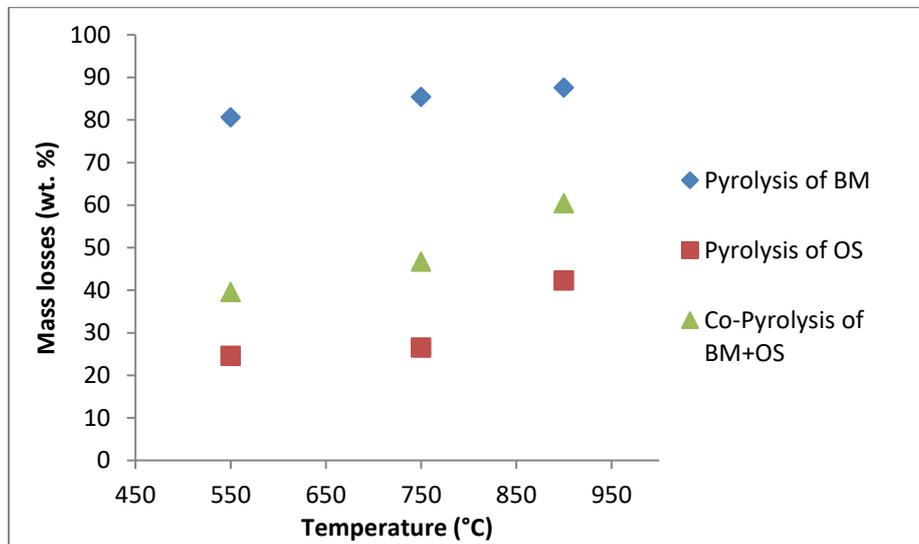
Figure 21. Evolution of the mass losses with the temperature

As it can be seen as for pyrolysis of biomass, the mass losses are between 80-88%. In order to compare the results of the mass losses in pyrolysis of biomass from the literature of the article [41] where it is explained the effect on the temperature on biochar yield, expressed in wt% of biomass feedstock. Figure 2 of this article [41] shows this evolution and is shown below (Figure 22).
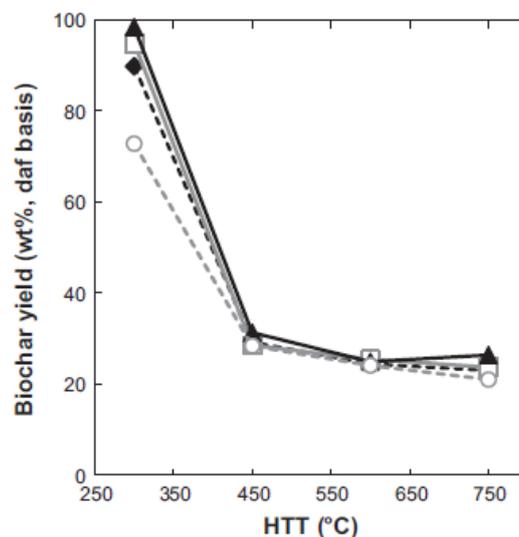
Figure 22. The effect of HTT on biochar yield, expressed in wt% of biomass feedstock, on dry and ash-free basis (Daf). Biochar samples prepared from wood (◊), straw (□), green waste (Δ) and algae (○) [41]

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As it can be seen in Figure 22, the biochar yield at temperatures of 550ºC and 750ºC using wood as a feedstock are 25% and 20% approximately. That means that the mass losses of this wood biomass are approximately 75% for a temperature of 550ºC and 80% for a temperature of 750ºC. According to the results obtained in experiments, mass losses were 80.60% for a temperature of 550ºC and 85.45% for a temperature of 750ºC. If the comparison is made between results, it can be observed that in both cases a similar trend is followed, although there are some small differences in percentages because the materials do not have exactly the same chemical composition. Therefore, results can be said to be valid because the trend of both experiments is very similar.

As for pyrolysis of oil shale, the mass losses are between 24-42%. In order to compare the results of the mass losses in the pyrolysis of oil shale from the literature of the study [42] where it is analyzed the mass change in function of the temperature for oil shale of different origins in Figure 7.
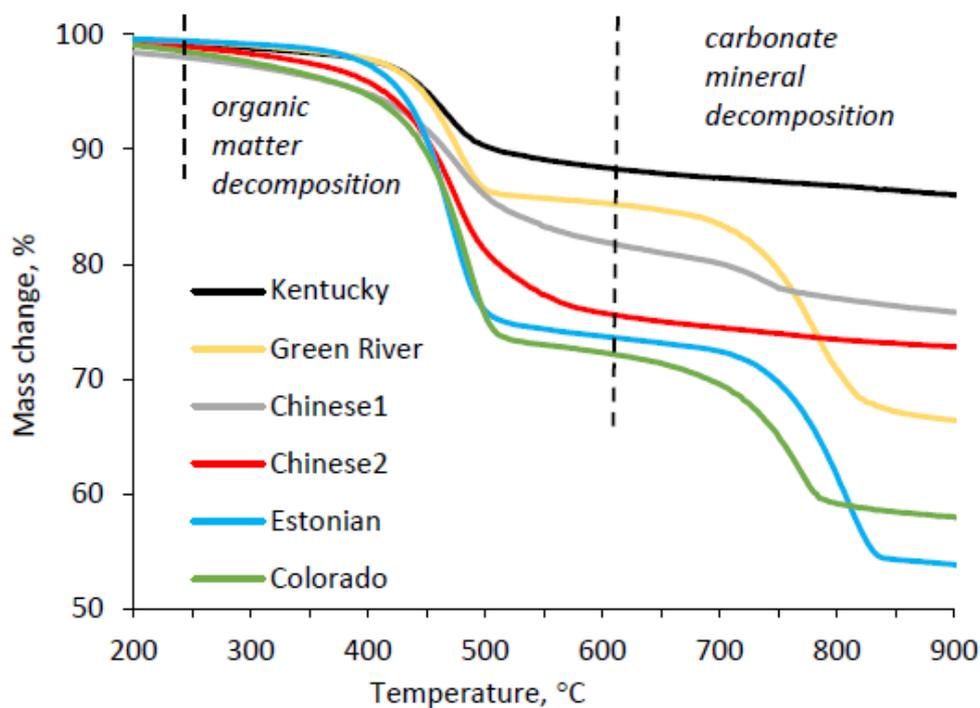
Figure 23. Thermographs of the analyzed oil shale samples [42]

As it can be seen in the Figure 23, the residual mass of the Estonian oil shale at the temperature of 550ºC is approximately 75%, at the temperature of 750ºC is 73% and at the temperature of 900ºC is 55%. That means that the mass losses of this oil shale are approximately 25% for a temperature of 550ºC, 27% for a temperature of 750ºC and 45% for a temperature of 900ºC. According to the results obtained in the current study, mass losses were 24.54% for a temperature of 550ºC, 26.54% for a temperature of 750ºC and 42.24% for

a temperature of 900ºC. If comparison is made between results, it can be observed that in both cases results are practically identical. So, results can be said to be valid because in both experiments these have been very similar.

Finally, in the case of co-pyrolysis between biomass and oil shale, these losses are between 40-60%. In this case, to compare the losses obtained, what is done is to calculate the theoretical value of losses of co-pyrolysis from the obtained losses in pyrolysis of biomass and oil shale and then compare this value with that has been obtained in the experiments of the losses in co-pyrolysis. In order to do this, the sample applied to co-pyrolysis (1 g of Scots pine and 2.1 g of oil shale) is multiplied by the percentage of mass losses in each pyrolysis for each temperature. Once this has been done, it has to be divided by the total sample mass (3.1 g of Scots pine and oil shale) as it is indicated in the equation (11).

$$\frac{Sample\ of\ BM\ (g) \cdot Mass\ loss\ (\%) + Sample\ of\ OS\ (g) \cdot Mass\ loss\ (\%)}{Total\ sample\ mass\ (g)}\ [\%] \qquad \textbf{(11)}$$

So, solving the equation (11) in each temperature, the theoretical mass losses that are obtained in the co-pyrolysis are 42.62% for a temperature of 550ºC, 45.54% for a temperature of 750ºC and 56.88% for a temperature of 900ºC. According to the results obtained in the experiments, mass losses were 39.56% for a temperature of 550ºC, 46.67% for a temperature of 750ºC and 60.46% for a temperature of 900ºC. If the comparison is made among the results, it can be observed that in both cases the results are very similar. So, results for the co-pyrolysis can be said to be valid.

3.2 Characterization of gases

In this section, results obtained during the experiments in the laboratory are analysed. Firstly, comparison of the different types of gases is made that have been obtained at different temperatures in the FTIR. In order to do this, one of the elements is analysed to be able to see in more detail the evolution of reaction for each temperature. After that, concentration of some of the gases per unit of organic mass is also calculated using the values obtained in the FTIR. In addition, the percentage composition of each type of gas obtained through the GC-TCD is analysed and compared with theoretical value.

3.2.1 Comparison of the gases at different temperatures

As it has been mentioned above, at this point the evolution of different pyrolysis gases at different temperatures will be compared. However, at first, the evolution of pyrolysis of

biomass (Figure 24 and Figure 25), pyrolysis of oil shale (Figure 26 and Figure 27) and co-pyrolysis of biomass and oil shale (Figure 28 and Figure 29) at a temperature of 750°C are shown in order to see what gases are obtained in these reactions and to compare if the results obtained are similar to those that the literature states.
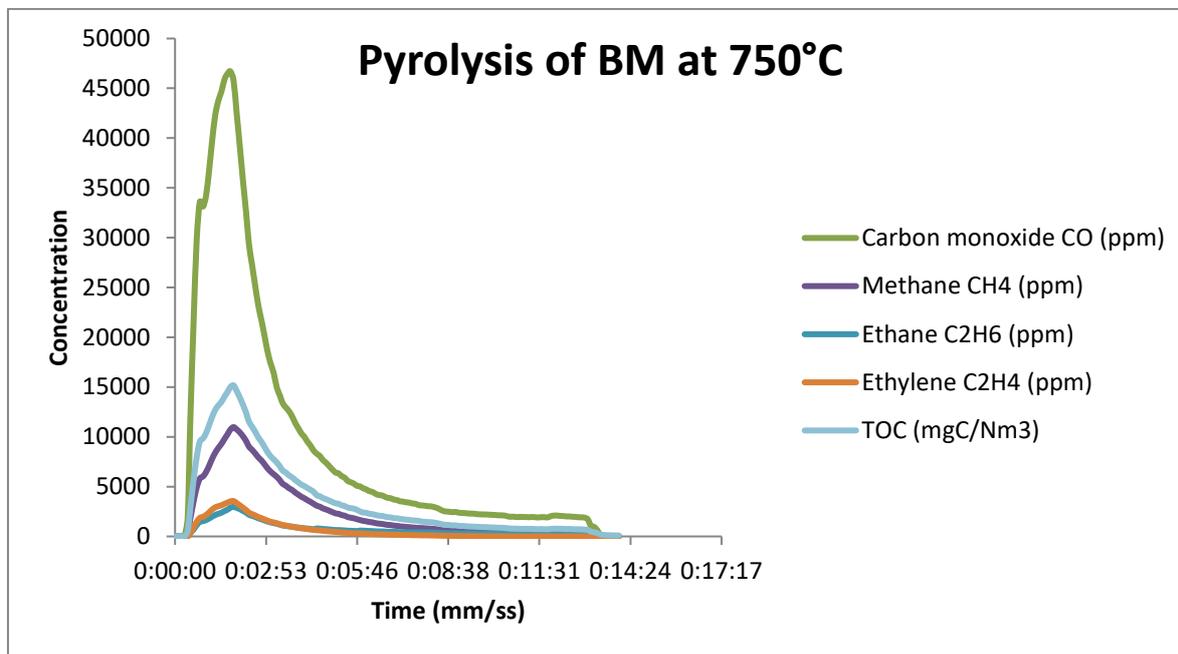
Figure 24. Pyrolysis evolved gas compounds of biomass at 750°C (1)
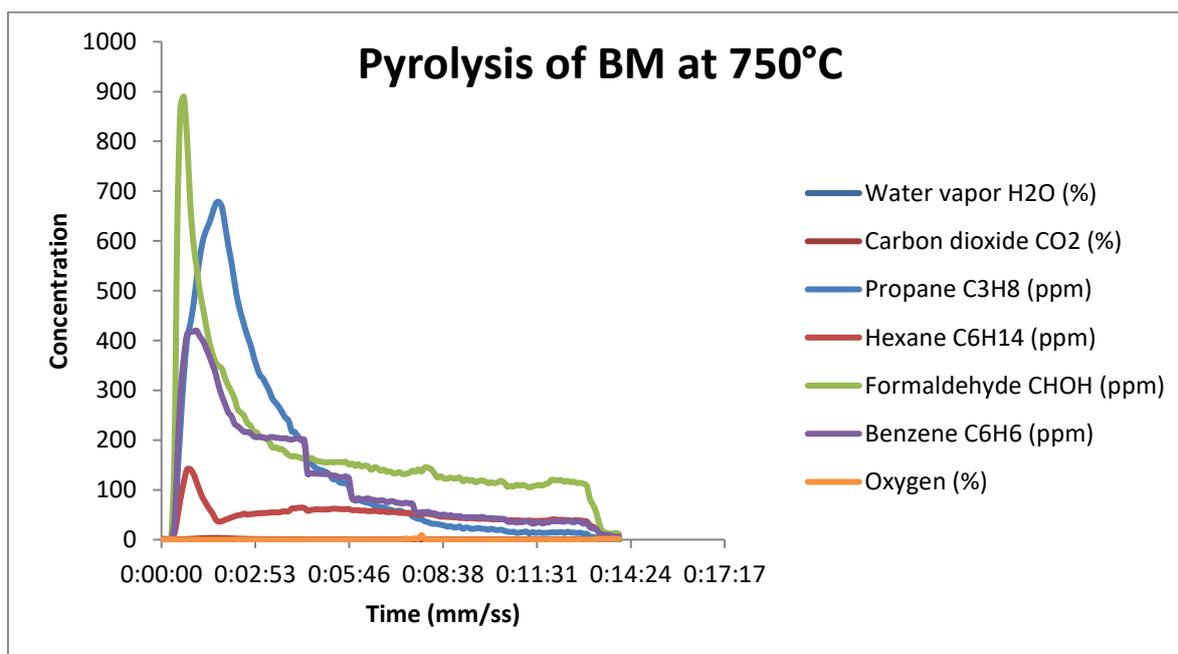
Figure 25. Pyrolysis evolved gas compounds of biomass at 750°C (2)

The main components obtained in the pyrolysis of biomass at 750°C are carbon monoxide (CO), mixture of hydrocarbons (TOC's), methane (CH_4), ethylene (C_2H_4) and ethane (C_2H_6). These components have also been obtained with other temperatures (550°C and 900°C) but

due to the fact that they work at different temperatures, reactions are different as it was expected. It should be added that the mixture of hydrocarbons are volatile organic compounds (VOC) with the exception of methane (CH_4).
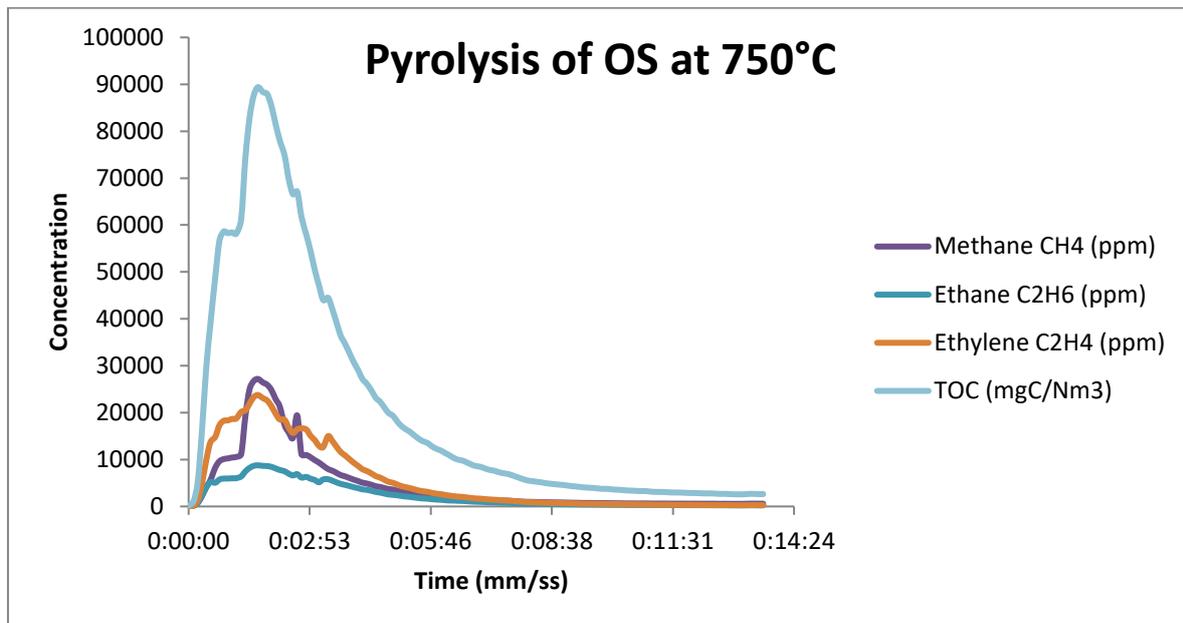
Figure 26. Pyrolysis evolved gas compounds of oil shale at 750°C (1)
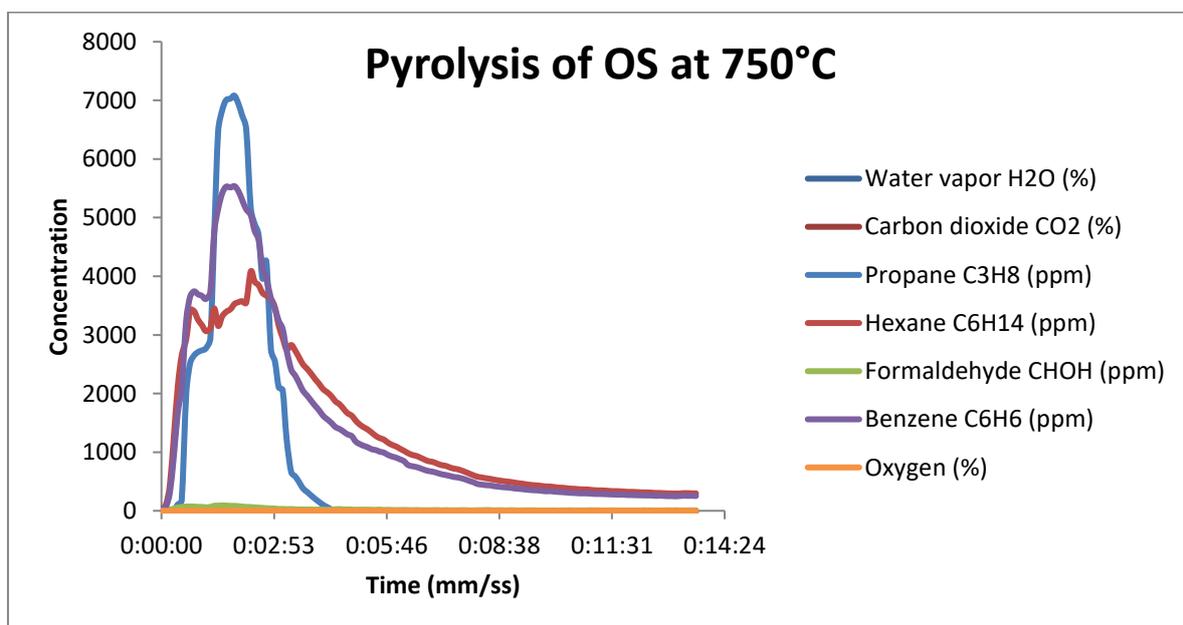
Figure 27. Pyrolysis evolved gas compounds of oil shale at 750°C (2)

In this case, the main components obtained in the pyrolysis of oil shale at 750°C are mixture of hydrocarbons (TOC's), methane (CH_4), ethylene (C_2H_4) and ethane (C_2H_6). As in the previous case, these components have also been obtained with the other temperatures (550°C and 900°C) but the reactions are different for the same reason as before.
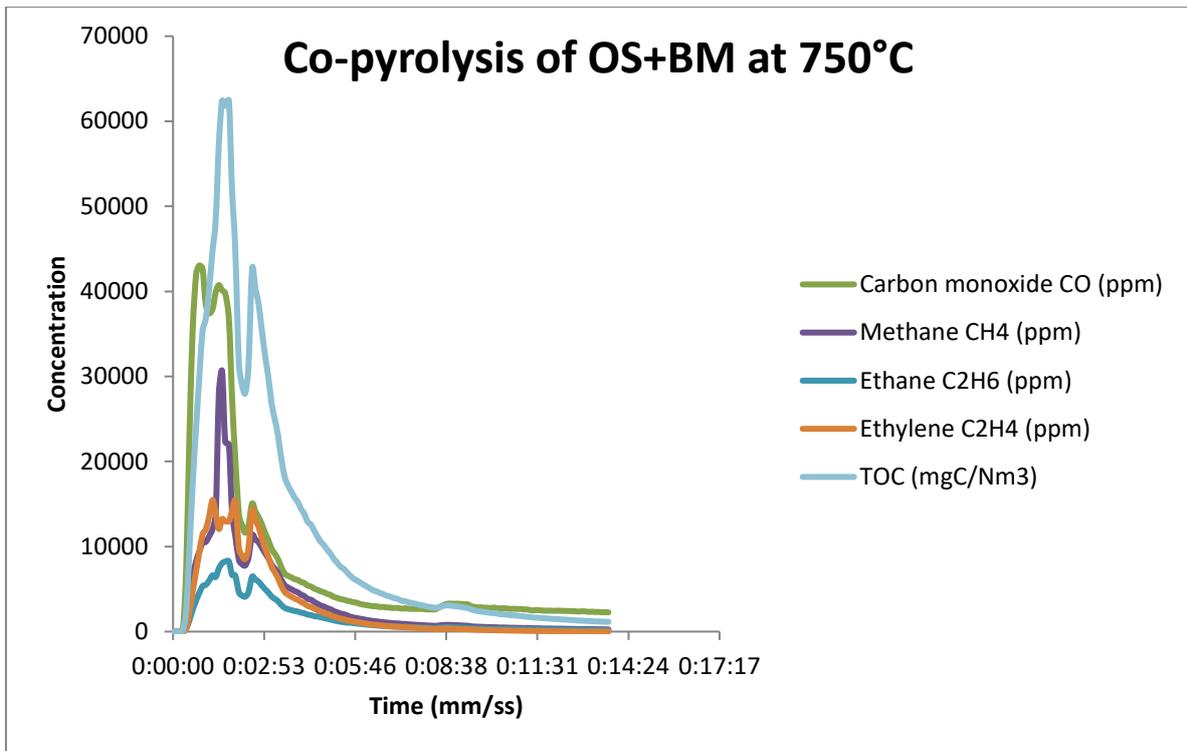
Figure 28. Co-pyrolysis evolved gas compounds of oil shale and biomass at 750°C (1)
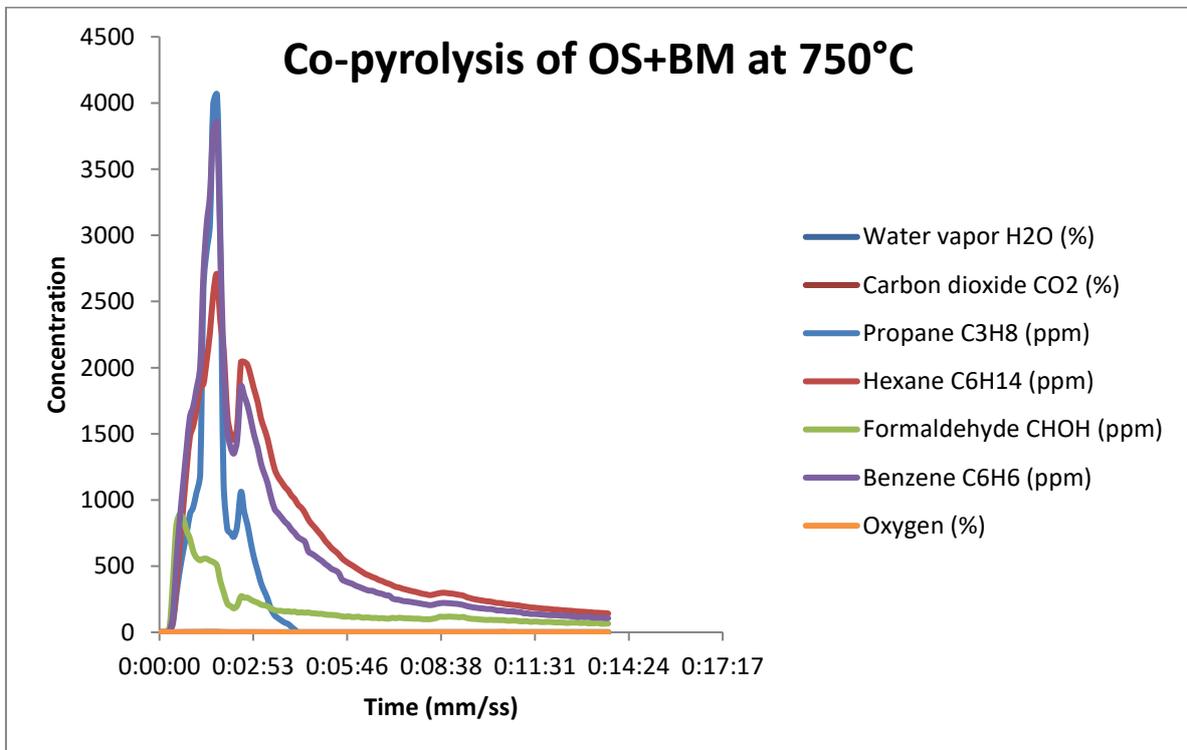
Figure 29. Co-pyrolysis evolved gas compounds of oil shale and biomass at 750°C (2)

In this case, the main components obtained in co-pyrolysis of oil shale and biomass at 750°C are mixture of hydrocarbons (TOC's), carbon monoxide (CO), methane (CH_4), ethylene (C_2H_4) and ethane (C_2H_6). As in the previous cases, these components have also been

obtained with the other temperatures (550°C and 900°C) but reactions are different for the same reason as before.

Once the components obtained in pyrolysis processes have been seen, now differences in the pyrolysis between the different temperatures would be analyzed. In order to do this, it is compared the evolution of methane gas in different environments.
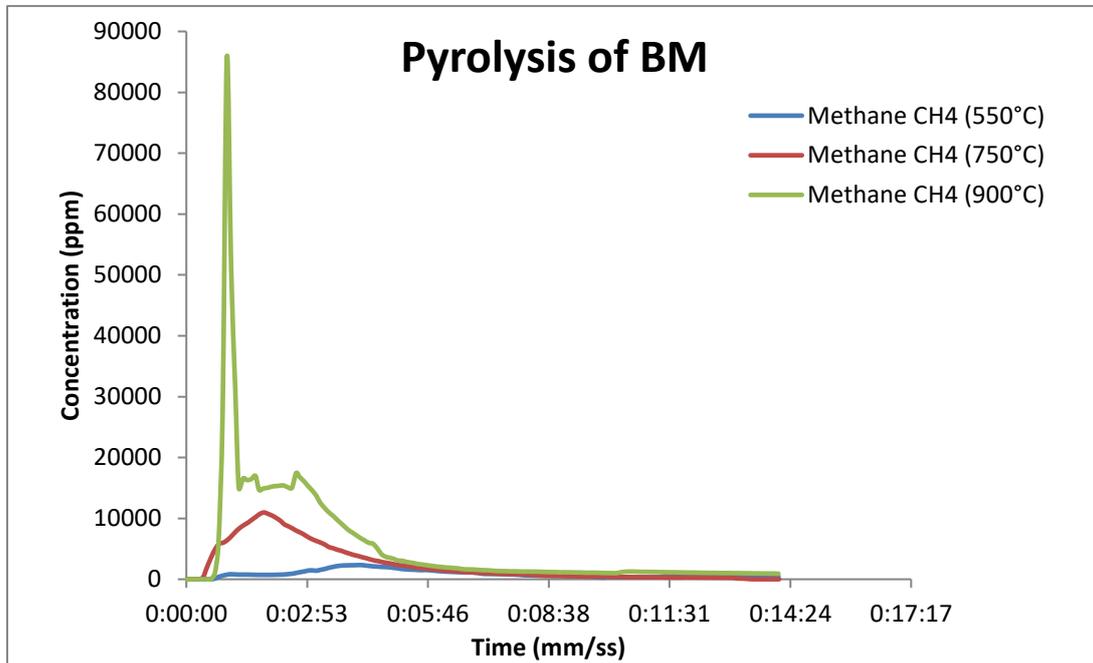
Figure 30. Pyrolysis of biomass

As it can be seen in Figure 30, as the temperature of the process is increased, reaction time decreases according to what has been mentioned in the theoretical part. These times are approximately 18 minutes for the temperature of 550°C, 14 minutes for the temperature of 750°C and 10 minutes for temperature of 900°C. In addition, it can be observed that when the temperature increases, the concentration increase is pronounced. This is because reaction time is smaller at higher temperatures and, therefore, reaction evolves faster.
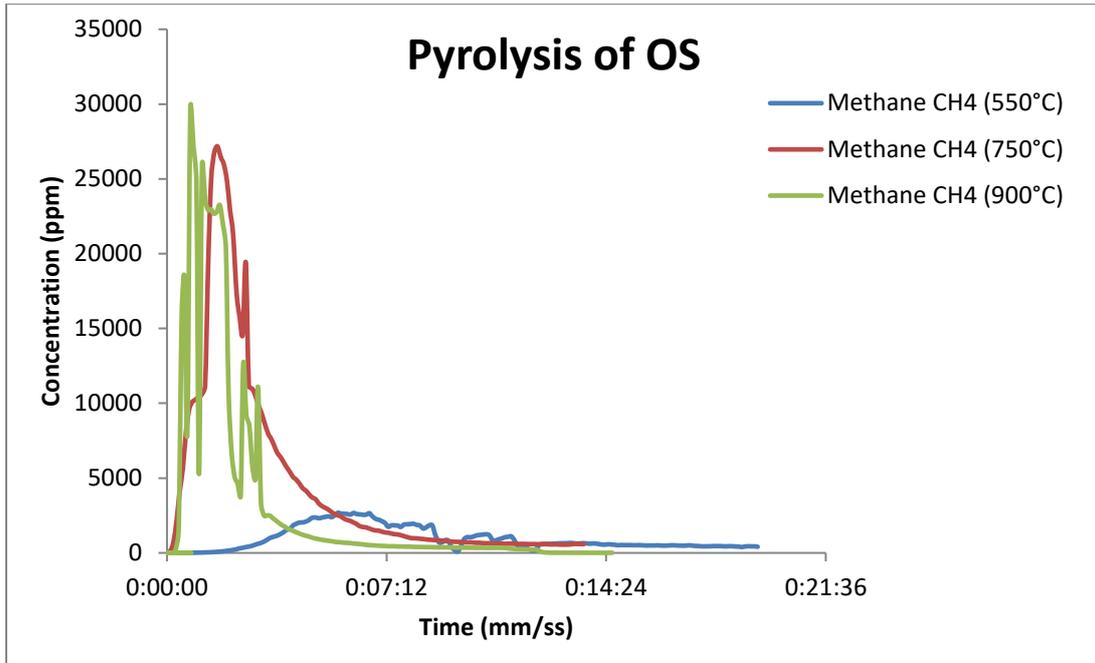
Figure 31. Pyrolysis of Oil Shale

As it can be perceived in Figure 31, as the temperature of the process is increased, reaction time also decreases. These times are approximately 21 minutes for the temperature of 550°C, 17 minutes for the temperature of 750°C and 14 minutes for the temperature of 900°C. Like in pyrolysis of the biomass, it can be seen that when the temperature increases, the concentration increase is pronounced. In this case, the difference between concentrations at temperatures of 750°C and 900°C is not as pronounced as in the previous case.
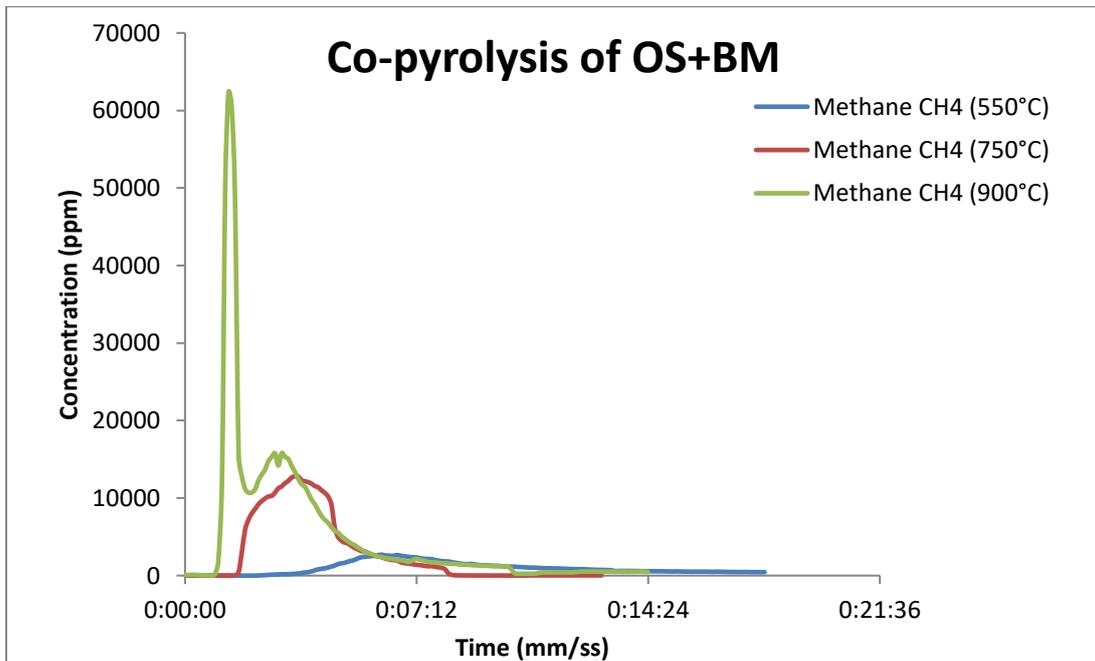
Figure 32. Co-pyrolysis of Oil Shale and Biomass

As it can be seen in Figure 32, as the temperature of the process is increased, reaction time also decreases. These times are approximately 18 minutes for the temperature of 550°C, 10 minutes for the temperature of 750°C and 7 minutes for the temperature of 900°C. Like in the last cases, when the temperature increases can be seen, concentration increases pronounced. In order to demonstrate this last phenomenon in Figure 33 evolution of the average concentration is shown according to the temperature for carbon monoxide (CO) and for methane (CH4).
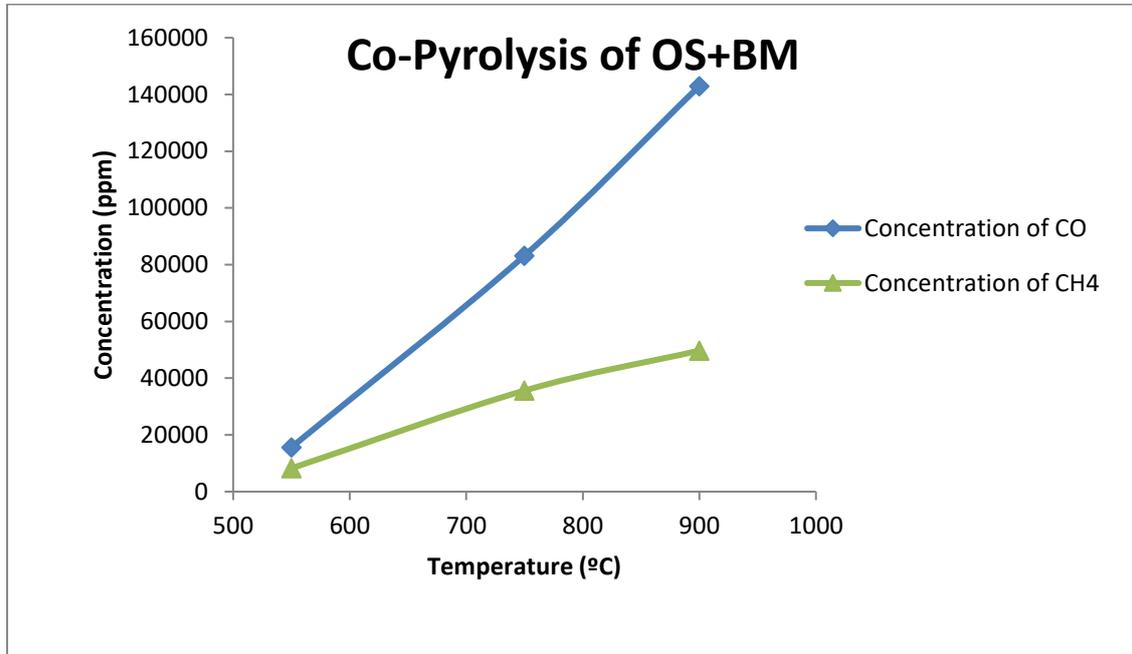

Figure 33. Evolution of the average concentration according to the temperature

3.2.2 Concentration per mass of organic matter

In this point, concentration of some of the gases per unit of organic mass is calculated using the data obtained in the FTIR. The gases that are calculated are carbon monoxide (CO), methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4) and propane (C_3H_8).

In order to achieve this purpose, what is needed to do is to calculate the average value of the concentration of each gas during reaction time and divide this value into the mass of organic matter.

$$\frac{Concentration\ of\ gas}{Mass\ of\ organic} = \frac{Average\ value\ of\ concentration}{(S_i - S_f)} \left[{ppm}/{g} \right] \tag{12}$$

Solving the equation (12) for each gas the values obtained are in Table 6.

Table 6. Concentration per mass of organic

Sample	Temperature (°C)	Concentration/mass of organic [ppm/g]				
		Carbon monoxide (CO)	Methane (CH_4)	Ethane (C_2H_6)	Ethylene (C_2H_4)	Propane (C_3H_8)
BM	550	22013	6205	1502	659	360
	750	68193	18138	5110	4491	1058
	900	175496	33219	7376	13184	956
OS	550	4215	7683	8161	15155	1938
	750	23265	34370	17473	41812	6445
	900	22498	16346	6541	26465	371
OS + BM	550	12783	6729	4628	4704	659
	750	57079	24444	11522	25995	2273
	900	76390	26561	8151	22655	1269

As it can be perceived in the last table (Table 6), as the temperature increases, the concentration of lower molecular weight compounds is increased. In order to check this data, what is done is to compare them with what is said in the literature [43].
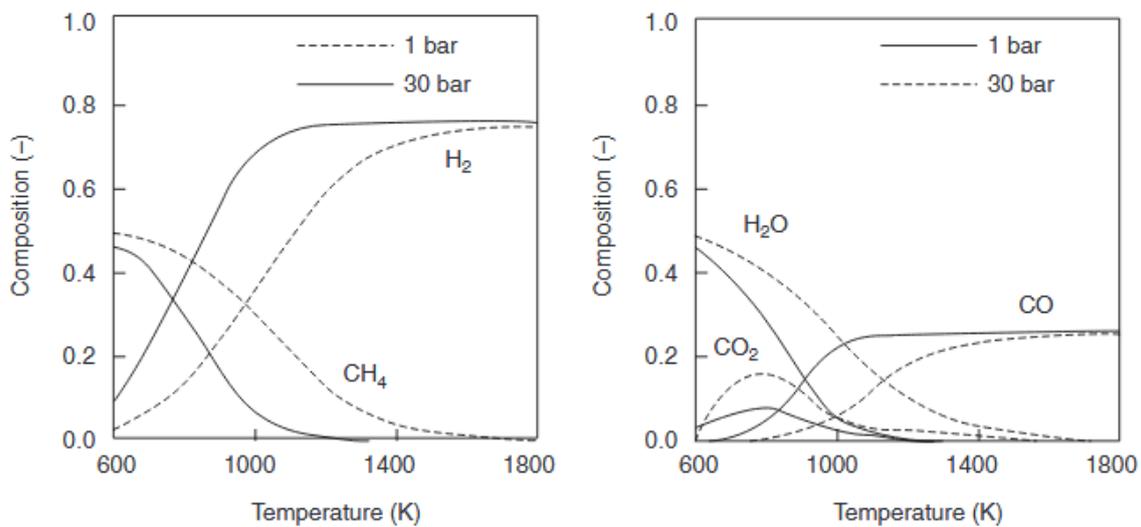
Figure 34. Effect of temperature and pressure on equilibrium gas composition [43]

As it can be seen in the previous figure (Figure 34), this phenomenon is confirmed since as the temperature increases, the concentration of lower molecular weight compounds is increased. Therefore, the results can be considered as valid.

3.2.3 Comparison between the concentration measured and calculated in the co-pyrolysis

In this section, comparison between the concentrations measured and calculated using the FTIR data in co-pyrolysis is analysed. In order to achieve this purpose, the amount of organic mass of biomass (Equation (13)) and oil shale (Equation (14)) is calculated for each temperature, knowing that the sample of oil shale is 2.1 g and the sample of Scots pine is 1 g. Sample masses before (S_i) and after (S_f) pyrolysis are used for oil shale and biomass.

$$Organic\ mass\ of\ biomass\ (OMBM) = \frac{1}{S_i} \cdot \left(S_i - S_f\right) [g] \tag{13}$$

$$Organic\ mass\ of\ oil\ shale\ (OMOS) = \frac{2.1}{S_i} \cdot \left(S_i - S_f\right) [g] \tag{14}$$

It should be added that, as for oil shale, the equation (14) is not met when the temperature is 900°C due to carbonates has begun to decompose. Therefore, by this temperature the organic mass is calculated from ignition losses obtained in chemical composition of the Kukersite Oil Shale (41.4%).

$$Organic\ mass\ of\ oil\ shale\ (OMOS) = 2.1 \cdot 0.414 [g] \tag{15}$$

Once this clarification has been made, in order to determine theoretical concentrations, the concentration measured in pyrolysis has to be multiplied by organic mass of each component for each temperature according to the equation (16).

$$Concentration = OMBM \cdot CBM + OMOS \cdot COS [ppm] \tag{16}$$

Where OMBM is the organic mass of biomass (g), CBM is the measured concentration of biomass in each temperature (ppm/g), OMOS is organic mass of oil shale (g) and COS is measured concentration of oil shale in each temperature (ppm/g).

So, the results obtained for the co-pyrolysis are shown in Table 7:

Table 7. Concentration calculated in the co-pyrolysis

Sample	T (°C)	OMOS (g)	OMBM (g)	Concentration (ppm)				
				Carbon monoxide (CO)	Methane (CH_4)	Ethane (C_2H_6)	Ethylene (C_2H_4)	Propane (C_3H_8)
OS + BM	550	0.52	0.81	19915	8961	5416	8341	1289
	750	0.56	0.85	71238	34653	14104	27139	4496
	900	0.87	0.88	173326	43318	12149	34561	1160

In Table 8 the measured results are shown for co-pyrolysis:

Table 8. Concentration measured in the co-pyrolysis

Sample	T (°C)	Concentration (ppm)				
		Carbon monoxide (CO)	Methane (CH₄)	Ethane (C₂H₆)	Ethylene (C₂H₄)	Propane (C₃H₈)
	550	15662	8245	5670	5764	807
OS + BM	750	83215	35636	16797	37898	3314
	900	142995	49720	15257	42408	2375

As it can be seen in both tables above (Table 7 and Table 8), the results of the measured and calculated concentration of carbon monoxide (CO), methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄) and propane (C₃H₈) diverge. This is because there is a certain error as for accuracy due to the different devices when performing the experiment. However, it can be observed that in both cases the concentrations follow a similar trend in each gas. Therefore, the results can be valid even if this uncertain.

Finally, in order to compare the results of concentration obtained what is done is to compare them with literature. To do this, concentration obtained is used in pyrolysis of oil shale and compared to the values of the article [44]. This article states about the Huadian oil shale and in Table 3 the concentration in mg/Nm³ of the different hydrocarbon gases obtained in the pyrolysis of oil shale for different temperatures is shown. Since the results obtained in the experiments are in ppm, they must be changed to mg/Nm³ to obtain comparison. In order to achieve this, the equation (17) is used:

$$Concentration \left[{}^{mg}\!/_{Nm^3} \right] = \frac{Concentration\ [ppm] \cdot Molecular\ weight \left[{}^{g}\!/_{mol} \right]}{Molar\ volume \left[{}^{Nm^3}\!/_{mol} \right]} \qquad \textbf{(17)}$$

Table 9 shows the resolution of the equation (17) for the concentration obtained in the pyrolysis of oil shale at the temperature of 550ºC for methane, ethane and propane and Table 10 shows the results obtained in the study [44]:

Table 9. Concentration in pyrolysis of oil shale at 550ºC

Concentration (mg/Nm³)		
Methane (CH₄)	Ethane (C₂H₆)	Propane (C₃H₈)
6624	13192	4595

Table 10. Concentration in pyrolysis of oil shale at 520ºC

Concentration (mg/Nm^3)		
Methane (CH$_4$)	Ethane (C$_2$H$_6$)	Propane (C$_3$H$_8$)
8844	1114	790

Comparing the results obtained in the Table 9 with the results obtained in the article [44] at the temperature of 520ºC (Table 10) it can be perceived that there is a big difference. This is because the molecular structures (or Building blocks) of the oil shale are different.

3.2.4 Composition of the gases

In this section the composition of the non-condensable gases obtained through the Gas chromatography – Thermal Conductivity Detector (GC-TCD) is shown. Therefore, the results obtained with this device are those that are shown in Table 11 and Table 12:

Table 11. Concentration of the gases (1)

Sample	Temperature (°C)	Concentration of the gases (vol. %)					
		H$_2$	O$_2$	N$_2$	CO	CH$_4$	CO$_2$
BM	550	0.01	2.15	91.25	1.70	0.86	3.85
	750	0.01	4.24	88.91	2.08	1.28	3.09
	900	0.05	2.61	81.23	6.61	3.81	4.11
OS	550	0.00	0.61	98.48	0.14	-	0.42
	750	0.01	3.15	90.44	0.58	1.15	2.72
	900	0.01	1.90	77.99	3.30	2.07	11.06
OS+BM	550	0.00	1.51	96.32	0.53	0.00	1.37
	750	0.01	2.97	88.60	1.84	1.80	3.12
	900	0.04	2.77	65.92	8.80	6.66	9.38

Table 12. Concentration of the gases (2)

Sample	Temperature (°C)	Concentration of the gases (vol. %)					
		C_2H_4	C_2H_6	C_3H_6	C_3H_8	$i-C_4H_{10}$	$n-C_4H_{10}$
BM	550	0.00	0.10	0.00	0.04	0.00	0.00
	750	0.21	0.13	0.00	0.05	0.00	0.00
	900	1.01	0.39	0.00	0.18	0.01	0.00
OS	550	0.08	0.11	0.04	0.11	0.11	
	750	0.79	0.66	0.04	0.34	0.07	0.06
	900	1.99	0.96	0.06	0.52	0.06	0.08
OS+BM	550	0.06	0.14	0.00	0.06	0.00	0.00
	750	0.76	0.53	0.04	0.23	0.05	0.05
	900	3.78	1.59	0.05	0.80	0.10	0.12

3.2.5 Comparison between the composition of the gases measured and calculated

In this section, is realized the comparison between the composition of the gases measured in the GC-TCD and the composition of gases calculated with the values obtained in FTIR. The composition of theoretical gases has been calculated by passing the value of the average concentration for each temperature from parts per million to percentage following the equation (18).

$$Theoretical\ composition = \frac{Average\ concentration}{10000}\ [\%]$$

(18)

So, in Table 13 the results of calculating the theoretical composition for the carbon monoxide (CO), methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4) and propane (C_3H_8) are shown:

Table 13. Concentration of the gases calculated with the data of the FTIR

Sample	Temperature (°C)	Concentration of the gases (vol. %)				
		CO	CH_4	C_2H_6	C_2H_4	C_3H_8
BM	550	2.97	0.84	0.20	0.09	0.05
	750	10.15	2.70	0.76	0.67	0.16
	900	25.86	4.89	1.09	1.94	0.14
OS	550	0.51	0.93	0.99	1.83	0.23
	750	3.07	4.54	2.31	5.52	0.85
	900	4.80	3.49	1.40	5.65	0.08
OS + BM	550	1.57	0.82	0.57	0.58	0.08
	750	8.32	3.56	1.68	3.79	0.33
	900	14.30	4.97	1.53	4.24	0.24

In order to compare the concentration of the gases measured (GC-TCD) and calculated (FTIR), Table 14 and Table 15 with the concentration ratios of each gas in function of the carbon monoxide are shown to see what the differences are.

Table 14. Concentration ratios measured

Sample	Temperature (ºC)	Concentration ratios measured			
		CH_4/CO	C_2H_6/CO	C_2H_4/CO	C_3H_8/CO
BM	550	0.51	0.06	0.00	0.02
	750	0.62	0.06	0.10	0.02
	900	0.58	0.06	0.15	0.03
OS	550	-	0.81	0.59	0.78
	750	1.98	1.14	1.36	0.59
	900	0.63	0.29	0.60	0.16
OS + BM	550	0.00	0.26	0.11	0.11
	750	0.98	0.29	0.41	0.13
	900	0.76	0.18	0.43	0.09

Table 15. Concentration ratios calculated

Sample	Temperature (ºC)	Concentration ratios calculated			
		CH_4/CO	C_2H_6/CO	C_2H_4/CO	C_3H_8/CO
BM	550	0.28	0.07	0.03	0.02
	750	0.27	0.07	0.07	0.02
	900	0.19	0.04	0.08	0.01
OS	550	1.82	1.94	3.60	0.46
	750	1.48	0.75	1.80	0.28
	900	0.73	0.29	1.18	0.02
OS + BM	550	0.53	0.36	0.37	0.05
	750	0.43	0.20	0.46	0.04
	900	0.35	0.11	0.30	0.02

As it can be seen in the two previous tables (Table 14 and Table 15) there are quite a few differences between the concentration ratios. Therefore, what follows is a table (Table 16) with the values extracted from the literature in the pyrolysis of biomass in order to be able to compare them with the results obtained.

Table 16. Concentration ratios obtained from the literature

Reference	Sample	Temperature (°C)	Concentration ratios CH_4/CO
[45]	Wood	900	0.17
[46]	Wood	900	0.73
[47]	Siberian elm	600	0.35
		700	0.46
[48]	Wood chips	500	0.93
		750	0.91
		1000	0.12

As it can be observed in Table 16, in the literature there are also some differences between the different concentration ratios. This can be seen clearly in the case of wood at a temperature of 900ºC where the difference between the concentration values is very high with values of 0.17 in the first case and 0.73 in the second one. However, if values are compared with the calculated and measured concentration ratios (Table 14 and Table 15) the values tend to be more similar to the calculated values (Table 15).

One the one hand, one of the reasons why measured concentration values, using Gas chromatography – Thermal Conductivity Detector (GC-TCD), may be wrong is that they have been measured much later since the experiments were performed as it is shown in the following table (Table 17):

Table 17. Measurement of the concentration

Sample	Temperature (°C)	Date of the experiment	Date of the measurement of the concentration
OS	550	17/04/2019	24/04/2019
	750	29/04/2019	09/05/2019
	900	22/04/2019	09/05/2019
BM	550	24/04/2019	14/05/2019
	750	24/04/2019	09/05/2019
	900	24/04/2019	14/05/2019
OS + BM	550	24/04/2019	14/05/2019
	750	02/05/2019	24/05/2019
	900	02/05/2019	24/05/2019

This delay between measures can cause that some gases to enter or leave from the Tedlar®
bag during the waiting days of the measures, which means that the measured composition of
gases during the experiments may change.

On the other hand, in the case of the FTIR the results are more accurate. However, this cannot
always be ensured since during the realization of the experiments, not all measures were
within the range of calibration and this is a problem. To solve this problem there are two
possible solutions. The first is to recalibrate the ranges with respect to those currently
existing. The second and most interesting one is to increase dilution so that the total
concentration values are less than the range at which they are currently calibrated. Therefore,
in conclusion it can be said that between the two measures the FTIR is the most accurate but
not in all experiments ensures that the measurements are within the range of calibration.

3.3 Char obtained

In this point, in order to see the differences of the char obtained in each experiment, this solid residue is shown in the following figures (Figure 35-Figure 43).

Figure 35. Char obtained with Biomass at 550ºC

Figure 36. Char obtained with Biomass at 750ºC

Figure 37. Char obtained with Biomass at 900ºC

Figure 38. Char obtained with Oil Shale at 550ºC

Figure 39. Char obtained with Oil Shale at 750ºC

Figure 40. Char obtained with Oil Shale at 900ºC

Figure 41. Char obtained with Biomass and Oil Shale at 550ºC

Figure 42. Char obtained with Biomass and Oil Shale at 750ºC

Figure 43. Char obtained with Biomass and Oil Shale at 900ºC

CONCLUSIONS

In this project it has been carried out the pyrolysis of oil shale, the pyrolysis of Scots pine and the co-pyrolysis of oil shale and Scots pine using the batch reactor. The conditions used to perform the experimental part have been to use nitrogen as an inert gas in order to ensure the pyrolysis at different temperatures (550ºC, 750ºC and 900ºC).

Mass losses that have been obtained in the experiments are between 80.60% and 87.62% for biomass pyrolysis, between 24.54% and 42.24% for pyrolysis of oil shale and between 39.56% and 60.46% for co-pyrolysis of oil shale and biomass. Therefore, it has been shown that these values are in agreement with the literature data, so they can be considered as valid results. In addition, it has been observed that as the temperature increases, the mass loss also increases.

Next, a gas characterization has been performed using the FTIR. In order to do this, first, it has been seen which the most important hydrocarbons during the different reactions at a temperature of 750ºC were. Based on the literature it can be said that the most important hydrocarbons are carbon monoxide (CO), carbon dioxide (CO_2), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), benzene (C_6H_6) and methane (CH_4). Noting the results obtained in the pyrolysis of biomass and co-pyrolysis of oil shale and biomass, it has been observed that the most prominent components are carbon monoxide (CO), methane (CH_4), ethylene (C_2H_4) and ethane (C_2H_6) which are the main constituents of the mixture of hydrocarbons (TOC's). In the case of pyrolysis of oil shale, it has been seen that the most important hydrocarbons are methane (CH_4), ethylene (C_2H_4) and ethane (C_2H_6) (which form most of the mixture of hydrocarbons (TOC's)). Therefore, these results agree with the literature data. In addition, it can be observed that in all three cases the most important components are very similar except for carbon monoxide (CO) in the case of pyrolysis of oil shale.

In the following part, it has been analyzed how the different pyrolysis reactions evolve at different temperatures. In order to do this, it has been compared the evolution of methane gas (CH_4) in the different environments. It has been concluded that as the temperature of the process is increased, the reaction time decreases according to what has been mentioned in the theoretical part. It also can be observed that when the temperature increases, the concentration increases sharply. This is because the reaction time is shorter at higher temperatures and therefore, the reaction evolves faster.

Also the concentration per mass of organic of the carbon monoxide (CO), the methane (CH_4), the ethane (C_2H_6), the ethylene (C_2H_4) and the propane (C_3H_8) has been calculated. Based on

the results it could be concluded that as the temperature increases, the concentration of lower molecular weight compounds is increased. In addition, measured and calculated concentrations in co-pyrolysis have been compared. In this comparison, it has been seen that although there is a small difference between the values in both cases the concentrations follow a similar trend in each gas.

Next, it has been compared the composition of the gases using the GC-TCD and the values measured with this device have been compared with those calculated from the concentration ratios (obtained in the FTIR). At this point, it has been seen a discrepancy between measured and calculated values. However, it has been shown that in the literature there are also differences between the values of concentration ratios for similar cases. In addition, the measured values (obtained in the GC-TCD) can be erroneous because the measurements were performed much later than the experiments were carried out. This may cause that some gases to enter or leave from the Tedlar® bag during the waiting days of the measures and this means that the measured composition of the gases during the experiments may change.

As for the results calculated with the FTIR these are more recommended even though this cannot always be ensured since during the realization of the experiments, not all measures were within the range of calibration and this is a problem. To solve this problem there are two possible solutions: recalibrate the ranges with respect to those currently existing or increase the dilution so that the total concentration values are less than the range at which they are currently calibrated.

Finally, the future plans for this project could be the improvement of the set-up of the reactor since there were some cold regions inside of it that caused the partial condensation of the sample during the pyrolysis process. Another possible thing to do is improve the gas analysis as there has been a significant delay between the experiments (Tedlar® bag) and the measures (GC-TCD).

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