



## **Geochemical Source Rock Evaluation in the Lusitanian Basin (Portugal) using TG/DSC Analysis**

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Thesis to obtain the Master of Science Degree in

### **Energy Engineering and Management**

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## Resumo

Um dos passos essenciais na exploração e exploração de hidrocarbonetos é compreender a evolução da rocha geradora e do sistema petrolífero relacionado. Ao compreender as condições em que os hidrocarbonetos são formados, é possível prever com maior exactidão os locais onde estes poderão ser encontrados. Através da avaliação geoquímica da rocha geradora é possível obter informações importantes a serem utilizadas na definição de áreas de prospeção, e na localização de actividades de exploração, reduzindo os riscos das mesmas.

O objectivo deste estudo é caracterizar a composição da matéria orgânica de seis rochas geradoras recolhidas em três afloramentos diferentes da Bacia Lusitana em Portugal, estimar a sua maturação térmica bem como o seu potencial de geração de hidrocarbonetos recorrendo a análises de TG/DSG. Uma nova metodologia foi introduzida baseada nesta técnica analítica avançada.

Em todas as amostras foram medidos valores elevados de riqueza orgânica. Valores de TOC de 2,73 % e 6,65 % em peso foram medidos nas formações de Coxos e de Vale das Fontes respectivamente. Os valores de S<sub>2</sub> indicam ainda que existe potencial petrolífero muito bom ou excelente entre as amostras analisadas. Valores elevados de T<sub>max</sub> indicam um estado de pós-maturidade observada em todas as rochas geradoras. Pode, assim, concluir-se que é provável que uma quantidade considerável de petróleo tenha sido gerado nas rochas geradoras analisadas, assim como a existência de alguma possibilidade para geração de petróleo no futuro. De acordo com os índices estimados foi identificado querogénio de tipos I e II nas diferentes amostras, indicando rochas geradoras com potencialidade de geração de petróleo.

**Palavra-chave:** *Matéria Orgânica, Petróleo, Rocha Geradora, Análise TG/DSC*

## Abstract

One of the essential steps in hydrocarbon exploration and exploitation is to understand the source rock evolution and the related petroleum system. Understanding how and where hydrocarbons were originated, help to comprehend and predict where they can be discovered. Geochemical source rock evaluation provides valuable information ready to be used for upgrading areas under investigation, concentrating exploration activities in particular places and reducing risks.

The purpose of this thesis is to characterize the organic matter content of six source rocks collected from three different outcrops within the Lusitanian Basin in Portugal, define their thermal maturation and their hydrocarbon generation potential using TG/DSC analysis. Thus, a new methodology is used based on this powerful analytical technique.

High organic richness has been measured in each source rock sample. TOC values of 2,73 wt.% and 6,65 wt.% have been measured in Coxos and Vale das Fontes Formation, respectively. In addition, S2 values indicates very good and excellent petroleum potential among the samples. Postmaturity has been reported in each source rock sample, as indicated by high  $T_{max}$  values. Thus, a considerably amount of petroleum has already been generated from them, as well as there is still a window for more petroleum generation. Type I and II kerogen haven reported within the different samples, indicting oil-prone source rocks.

**Keyword:** *Organic Matter, Petroleum, Source Rock, TG/DSC Analysis*

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## **List of Abbreviations**

HI – Hydrogen Index

OI – Oxygen Index

PP – Petroleum Potential

TG/DSC – Thermogravimetric/Differential Scanning Calorimetry

TOC – Total Organic Carbon

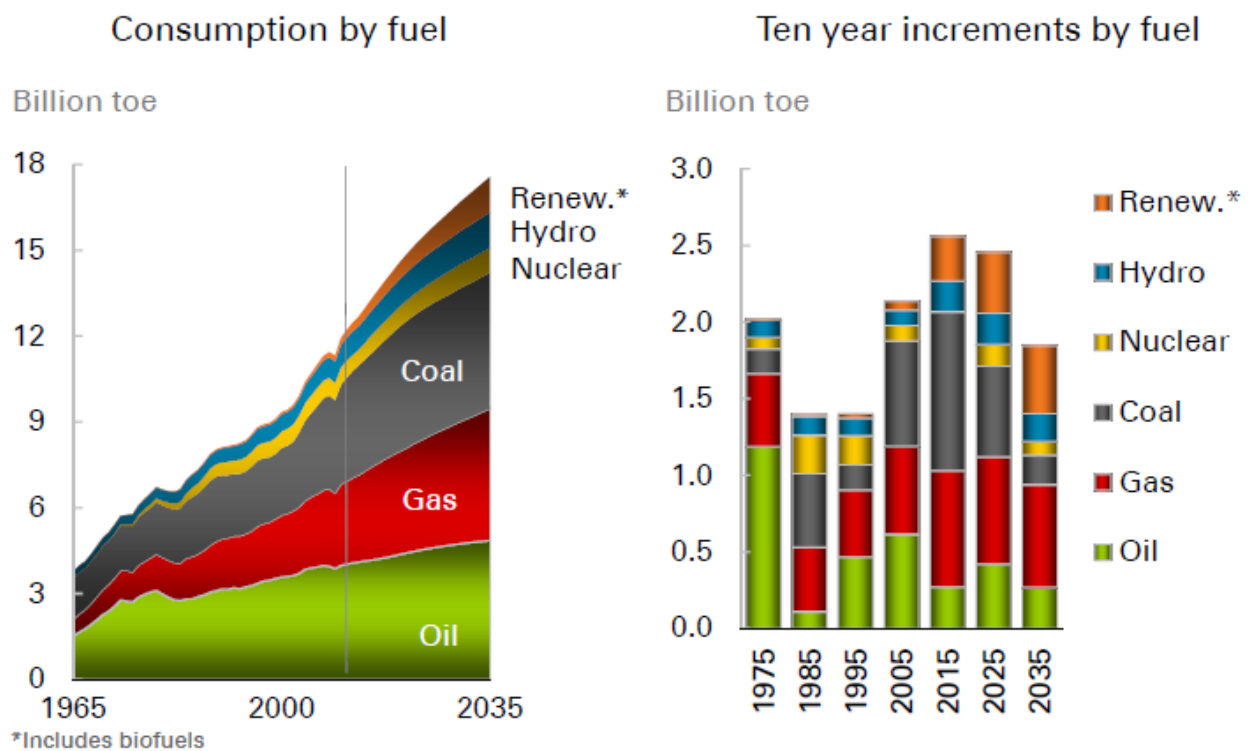
TOM – Total Organic Matter

# 1 INTRODUCTION

## 1.1 Scope of the Thesis

Primary energy demand is increasing fast and it is expected to grow by 41 % from 2012 until 2035, according to BP Outlook 2035 presented on January 2014. In addition, the increment in the industrialization and electrification of non-OECD countries as well as the fast population growth, is causing an increase of energy consumption (Bp, 2014). Therefore, new energy challenges are needed to provide such amount of energy.

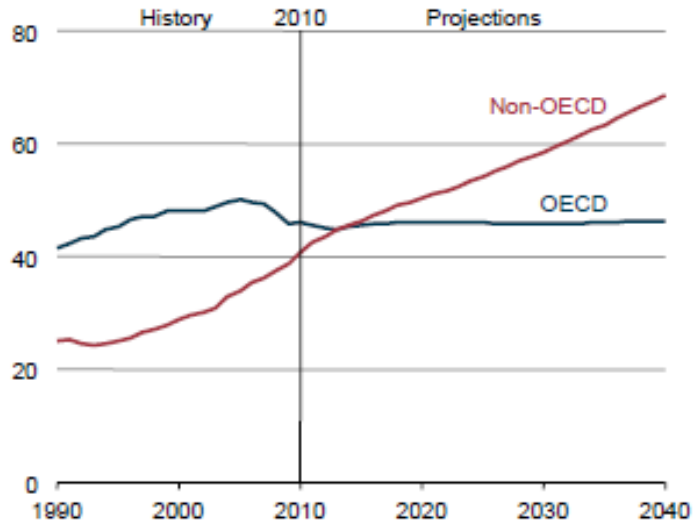
Figure 1 shows the expected energy consumption from 1965 until 2035. Even though there is an increment in renewable energies consumption, oil and gas still have a predominant proportion as an energy resource.



**Figure 1. Expected Energy Consumption (Bp, 2014)**

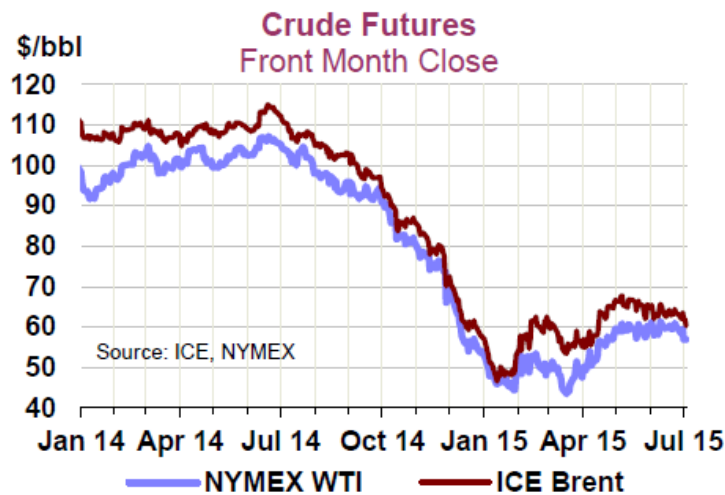
On the other hand, total world proved oil reserves reached 1700,1 billion barrels at the end of 2014, which means there is enough hydrocarbons to meet 52,5 years of global production (Bp, 2014).

Figure 2 shows OECD and non-OECD liquids consumption by region. The expectations for OECD oil consumption is 46,4 million barrels per day in 2040, whereas Non-OECD countries are expected to increase up to 68 million barrels per day (U.S. Energy Information Agency, 2013).



**Figure 2. OECD and non-OECD Liquids Consumption by Region, 1990-2040 (MBOEd)** (U.S. Energy Information Agency, 2013)

Even though oil prices have decreased significantly during the past few months, motivated by an oversupply, the financial crisis and an unstable world market (Arabia, 2015), the searching for new reserves, as well as continuous investments must be done in order to reach the global oil demand for the future. Figure 3 shows oil prices in dollars per barrel from January 2014 until July 2015. The peak price in Brent per barrel is found in July 2014, reaching 115 \$/barrel. On the contrary, the lowest price can be found in January 2015 with 48 \$/barrel.



**Figure 3. Oil prices along time for WTI and Brent** (Arabia, 2015)

One of the essential steps in hydrocarbon exploration and exploitation is to understand the source rock evolution and the related petroleum system. Understanding where hydrocarbons were originated, how and where they migrate, help to comprehend and predict where they can be found. Geochemical source

rock evaluation provides valuable information ready to be used for upgrading areas under investigation, concentrating exploration activities in particular places and reducing risks.

One of the most important aspects, which is investigated during a geochemical analysis in a source rock, is the characterization of organic matter (Lafargue, Marquis, & Pillot, 1998). Thus, with the appropriate conditions such as thermal evolution, geological time and burial depth, the organic matter can produce oil and gas (Nordeng, 2012). Depending of the amount and type of the organic matter deposited in the source rock, the quantity and nature of petroleum generated are different (Lafargue et al., 1998).

Pyrolysis is the decomposition of the organic material in the absence of oxygen at elevated temperatures. This method is used nowadays for the characterization of organic matter in petroleum exploration phase and provide information regarding petroleum potential, maturity and type of source rock in a sedimentary basin (Lafargue et al., 1998). TG/DSC analysis is a powerful analytical technique that can be used to obtain pyrolysis information.

TG/DSC (Thermogravimetric/Differential Scanning Calorimetry) analysis is presented as a geochemical source rock evaluation method. On the one hand, TG is a technique in which the mass change of a material is measured as a function of temperature and time in a controlled atmosphere (Rostek & Biernat, 2011). On the other hand, DSC is a thermal analysis technique in which the apparent heat capacity of a material is measured as a function of temperature and time, allowing the observation of the heat flow rate differences that are originated during chemical or physical changes (Gill, Moghadam, & Ranjbar, 2010).

Pyrolysis analysis is currently a standard technique for source rock characterization. Rock-Eval™ is the common device used, but in this case it monitors the resulting gas evolution of the samples, instead of measuring the weight of it.

Broadly, these pyrolysis techniques simulate, in a short period of time, the geological process that source rocks are subjected to when buried with the corresponding increase in temperature. By means of this approach, if a particular source rock is subjected to these techniques along with their specific temperature programs, the thermochemical changes, at which organic matter would be subjected under geological conditions, can be simulated. Hence, what it was supposed to occur over millions of years ago, happens approximately in a three hours test (Vandenbroucke, 2003). Taking into account the results obtained during these processes, the amount of oil and gas, which could have been generated, can be estimated. In addition, knowing the composition of the organic material in the rock, a measure of its maturity, among others, can be obtained. As a consequence, these methods provide one more step for the searching of oil and gas and other tool for the characterization of its corresponding petroleum system. It should be taken into consideration that these techniques must be complemented with others in order to support the results obtained, not forgetting that they can serve as the first contact with the geochemical evaluation. For instance, once there is a clear understanding of the results, other exploration tools such as seismic surveys can be performed to add value and guarantee, as well as reducing risks to the exploration activities.

Performing TG/DSC analysis helps to understand and answer some basic questions while applying geochemistry source rock evaluations. For example, how much organic matter content is found in the rock? Which is the organic matter generating capability? Has the organic matter generated any petroleum? Has petroleum migrated out of the source rock? Is the rock oil-prone or gas-prone?

Equally important is the onsite analysis. One of the advantages of using TG/DSC analysis is that the device, which is used for developing this technique, is quite portable, hence it could be used directly onsite location during exploration activities.

In this master thesis six source rock samples, collected from the outcrops within the Lusitanian basin in Portugal, were analyzed using TG/DSC analysis. Good results are expected to be achieved, which would bring an important and positive economic impact in Portugal, if the research is to continue. Thus, complementary techniques supporting the results obtained will be also used. In a big picture, new oil and gas reserves could be discovered, which would mean job creation, foreign energy dependency reduction and ultimately economic growth.

## **1.2 Objectives**

The purpose of this thesis is to characterize the organic matter content of six source rocks, define their thermal maturation and their hydrocarbon generation potential using TG/DSC analysis. Source rock samples were collected from three different outcrops within the Lusitanian Basin in Portugal. Even though, there have been some researches led in the Lusitanian basin in terms of geochemical source rock evaluation, there are no studies using TG/DSC analysis that were reported. Thus, a new approach in terms of geochemical source rock evaluation is used in this thesis. The specific objectives of this study are the following:

- Propose a new methodology based on TG/DSC analysis in geochemical source rock evaluation.
- Characterize the organic matter content of source rock samples.
- Define the source rocks maturation.
- Determine the source rocks hydrocarbon generation potential.

Summarizing, this work aims to evaluate the quantity of organic matter, characterize the type of kerogen, as well as determining its maturity status in order to deduce the hydrocarbon potential, using geochemical parameters based on accepted indexes that are calculated using the pyrolysis based Rock-Eval methodology.

## **1.3 Structure of the Thesis**

The thesis is structured in eight chapters. The first chapter corresponds to the introductory section, which is composed basically of the scope of the thesis and objectives. The second chapter covers the state of the art in the geochemical source rock evaluation field. Different definitions and explanation are described

in this chapter in order to clarify some concepts, aspects and processes. Furthermore, a brief explanation regarding previous studies reported within the source rock evaluation field in the Lusitanian basin is described. The third chapter describes to some extent the core of this thesis work, which is the methodology used to develop it. TG/DSC analysis and its experimental setup, assumptions and the references for the result evaluations are presented in this chapter. The fourth chapter covers the geological setting, sample definition and location, and the TG/DSC results for each source rock sample. The fifth chapter presents the discussion, based on the results obtained. The sixth chapter covers conclusions of the thesis. The seventh chapter is focused in the future development work. The eighth chapter contains the references used in this thesis work.

## **2. STATE OF THE ART**

The aim of this chapter is to cover the literature review of this thesis work, providing some descriptions and explanations such as the oil and gas formation, the petroleum system concept and the source rock fundamentals, among others. Thus, it might help to understand in a better manner the contents of this research thesis.

### **2.1 Formation of Oil and Gas Overview**

Petroleum formation might be understood as a relatively simple process. Basically, the organic matter contained within the source rock is “cooked” due to an increase of temperature during sediment burial, subjecting it to the thermal cracking and eventually leading to the release of hydrocarbons (Bordenave, 1993). It should be noticed that different types of organic matter generate different quantities and types of hydrocarbons (B. P. Tissot & Welte, 1984). Several millions of year ago, plants, plankton species and microorganisms lived and died in the oceans. As a result, they were decomposed and settled on the sea bottom, becoming accumulated organic matter and forming organic rich layers of sediments over geological time. As more sediments layers were accumulated, burial depth, pressure and temperature increased, inducing slow thermal cracking reactions that occurred along long periods of time and thus forming hydrocarbons (Legault, 2008). Finally, these petroleum migrated into the reservoir rocks by a porous and permeable carrier bed.

Oil and gas formations differ from basin to basin and depend on several factors such as burial history, tectonic movements, sedimentary facies and other geological processes. Living or dead organic matter, as well as dissolved organic matter can be supplied into the sediments. When organic-rich sediments are deposited at the bottom of the oceans, seas or lakes, biogenic methane gas is generated from the organic matter by microbial anaerobic processes. Heat increases with burial depth, causing the organic matter to transform progressively into insoluble organic matter called kerogen. As heat increases, kerogen undergoes further transformation into hydrocarbons (B. P. Tissot & Welte, 1984). In order to continue with a proper explanation, it is necessary to introduce a fundamental concept within the oil and gas exploration point of view, the petroleum system.

### **2.2 Petroleum System**

The definition of petroleum system is extremely important, since it involves the elements and processes needed so that hydrocarbons can be generated and accumulated. Thus, a clear definition of it is fundamental in order to comprehend, locate and analyze a source rock. A petroleum system is composed basically of a source rock, where hydrocarbons are generated and eventually are expelled and migrate to a reservoir rock, where oil and gas are accumulated, a seal rock, an impermeable rock which does not allow oil and gas to go up to the surface, and an overburden rock. The term petroleum includes hydrocarbons in the form of liquid or gas, whereas the term system involves the elements mentioned above, as well as the processes which are needed so that petroleum can be accumulated, such as generation,

migration, trap formation and accumulation. Petroleum system formation takes long periods of time. The age of a petroleum system can be reported using geochemical studies and tracking the burial history. On the other hand, after generation, migration and accumulation of hydrocarbons occur, preservation time starts, leading to the preservation itself, modification or destruction of petroleum. Thus, time and entrapment are two key factors for a petroleum system to exist (Magoon & Dow, 2009). Petroleum systems are located in sedimentary basins, but it is important to mention that not all sedimentary basins contain it (K. Peters, Schenk, & Wygrala, 2009). Figure 4 represents a typical petroleum system where the different elements and processes can be distinguished.

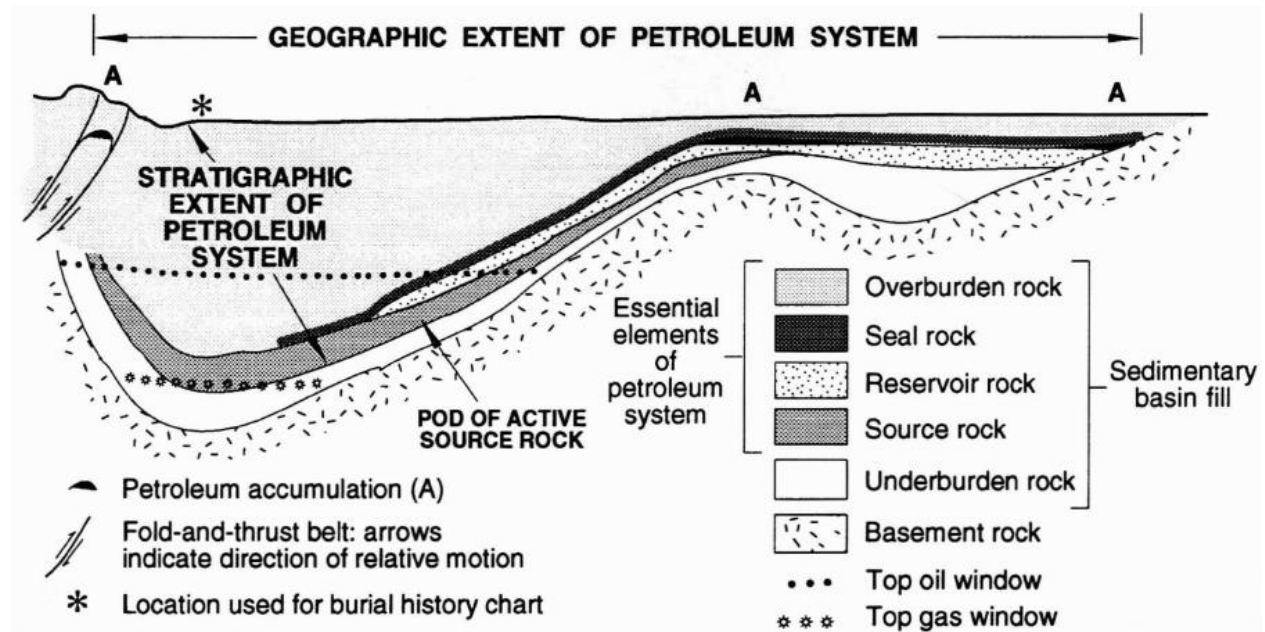


Figure 4 Petroleum System (Magoon & Dow, 2009)

One of the aims of petroleum geochemistry is to evaluate and characterize the source rocks, thereby a few fundamentals about its formation and development should be introduced.

## 2.3 Source Rock Fundamentals

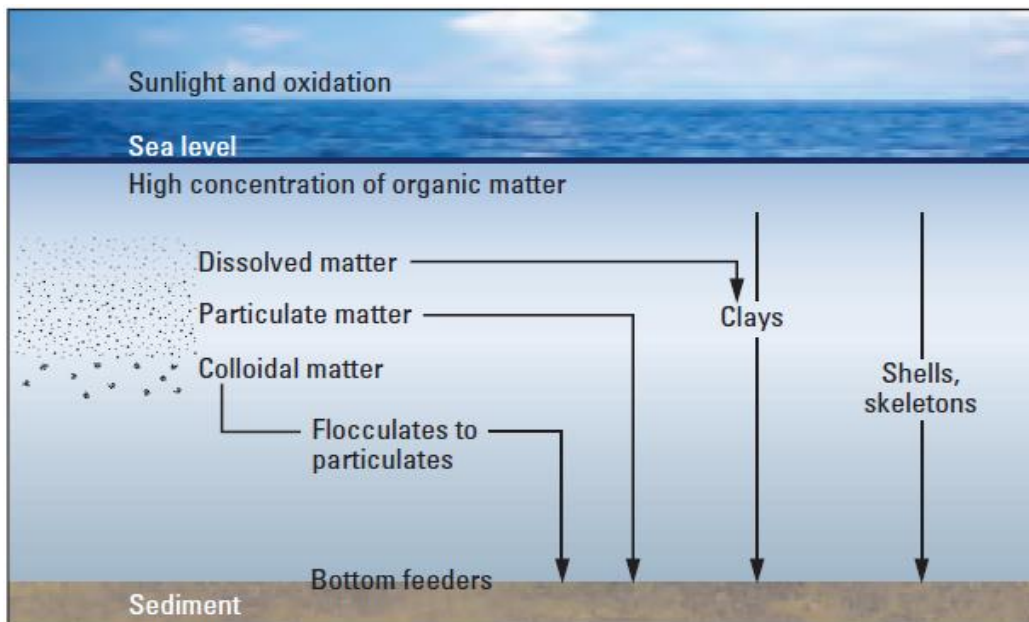
A fine-grained rock rich in organic matter capable of generating petroleum in commercial quantities given the proper temperature and pressure is called source rock (Katz, 1995). Source rocks can be originated in different paleo-environments such as deep marine, lacustrine and deltaic (Suárez-Ruiz, 2012). Among others, shales and carbonates rocks are the sedimentary rocks which can become good petroleum source rocks (Zimmerle, 1995). Shales rocks may contain less than 5% TOC, whereas carbonates source rocks may contain as much as 10% to 30 % TOC (Palacas, 1988).

Three main aspects are to be taken into account when characterizing a source rock: the amount and type of organic matter present at any given time, and the thermal maturity (Carvajal-Ortiz & Gentzis, 2015). A proper evaluation of the source rocks is crucial to reach the hydrocarbons reservoirs.



Four types of source rocks can be found in terms of petroleum generation potentiality. Effective, active, inactive and spent source rocks. Firstly, a potential source rock can be any rock that contains sufficient organic matter to generate petroleum (Suárez-Ruiz, 2012). An effective source rock is a potential source rock which has reached an adequate thermal maturity to generate petroleum. When a source rock is generating and expelling hydrocarbons either biological or by temperature at the critical moment, it is called active. An inactive source rock might show petroleum potential but it stopped generating oil and gas. Finally, a spent source rock reached postmaturity stage and might generate wet or dry gas, but it cannot generate any oil (Magoon & Dow, 2009).

Physical, biochemical and geological processes are behind the creation of a source rock, resulting in the formation of a fine-grained sedimentary rock rich in organic matter, mainly carbon and hydrogen elements (Martinelli, 2009; Mendonça Filho et al., 2012). A few phases need to be taken into account when a source rock is formed such as production, accumulation and preservation of the organic matter (Mackenzie, 2005). Thus, the amount and type of organic matter found in a source rock are subjected to environmental and depositional conditions. Biological activities take part in the production and transformation of organic matter. On the other hand, depositional conditions develop the concentration of the organic matter and finally the post-depositional conditions preserve it (S. R. Jacobson, 1991). Figure 5 shows the organic matter in the water column.



**Figure 5. Organic Matter in the Water Column** (McCarthy et al., 2011)

Biologic productivity, sediment mineralogy and oxidation of the water column play a key role in controlling the organic matter content. Highest concentrations of organic matter can be found near the water surface, both in colloidal or particulate form (Barker, 1979). From the water surface to the water-sediment interface, the organic matter pass through chemical and biological processes.

The role of oxygen in the water column is significantly important. On the one hand, it permits the biological productivity of organic matter. On the other hand, it supports biodegradation and oxidation. In addition, physical abrasion or chemical changes led by water Eh and pH can alter the organic matter (S. R. Jacobson, 1991). Once in the bottom of the sea, some of the matter is converted into simple molecules due to the action of bacteria, worms and bottom feeders. A reduction of organic richness is produced as a result of biodegradation and oxidation, separating only resistant organic material. This remaining matter is incorporated into the sediments (B. P. Tissot & Welte, 1984).

Concentration and preservation of organic matter in the sediments are controlled mainly by oxygen and energy levels. Low oxygen or anoxic environment improves the preservation of organic matter, creating reducing environments which protect organic materials from oxidation and the action of bottom feeders, which implies the absence of bioturbation (Bjørlykke, 2010; B. P. Tissot & Welte, 1984).

Low water circulation affects positively to create anoxic conditions, as it reduces the exchange of oxygen and organic matter. Furthermore, this low-energy environments allow a better deposition of sediments. Thus, source rocks are formed in low-energy environments (S. R. Jacobson, 1991).

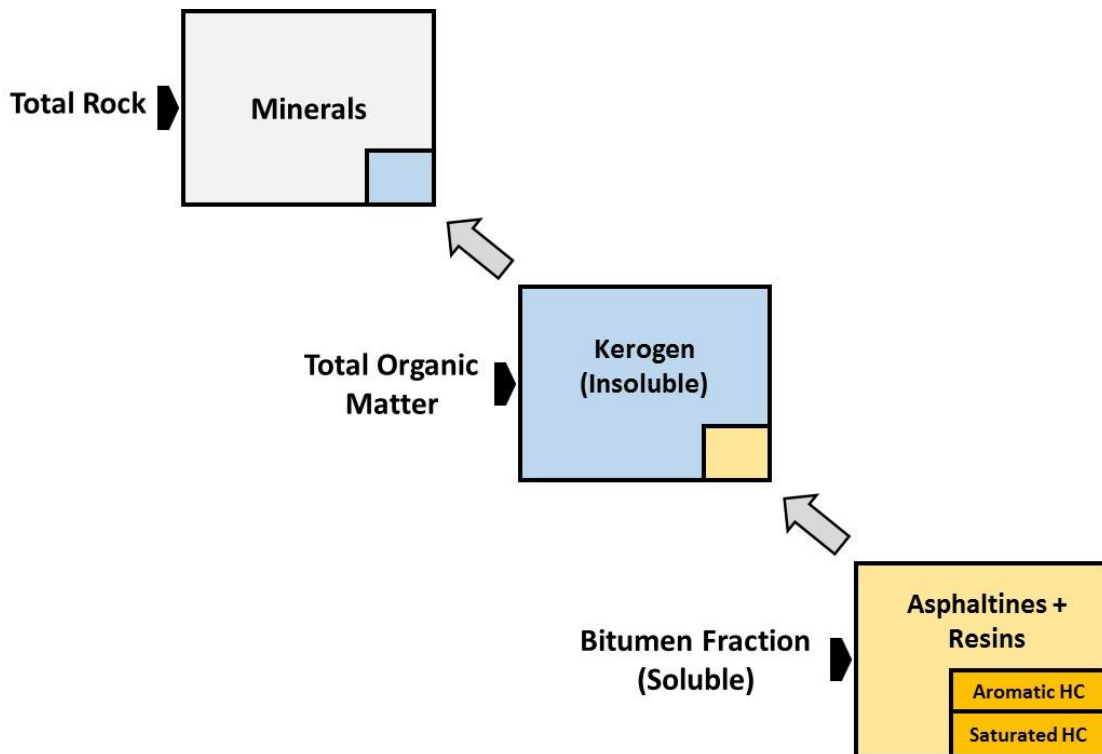
Equally important is the mineralogy role in the source rock development. Minerals, which are transported and precipitated in the sediments, might react with organic compounds and dilute a portion of organic matter, affecting the source rock ability to generate and expel hydrocarbons (McCarthy et al., 2011).

## **2.4 Kerogen and its Thermal Transformation**

The portion of sedimentary organic matter which survived the initial decomposition process and is able to generate petroleum is called kerogen (Vandenbroucke, 2003). It is insoluble in organic solvents and represents “the major organic carbon reservoir in the Earth’s crust” (Engel & Macko, 1993). On the other hand, bitumen is the organic matter that is soluble in organic solvents. The elemental analysis of kerogen encompasses the following elements: C, H, N, O, S, and probable Fe from pyrite (Vandenbroucke & Largeau, 2007). Figure 6 represents a schematic illustration of the organic matter classification within a source rock.

Biological activity at the early stage, following by temperature and pressure are responsible for the physiochemical transformation of organic matter in a sedimentary basin (B. P. Tissot & Welte, 1984). Higher temperatures and long period of geological time are involved in the transformation of kerogen into oil and gas (Bjørlykke, 2010). Thus, increments in burial depth increase temperature and pressure, which along with geological time play an important role in the organic matter transformation (McCarthy et al., 2011). It should be mentioned that the amount of hydrocarbons that might be generated in a source rock is exposed to kerogen composition and concentration, as well as the geothermal gradient evolution during burial history (Engel & Macko, 1993).

The thermal maturation process, by which organic matter is altered changing its chemical composition and creating hydrocarbons, can be divided into three consecutively stages, diagenesis, catagenesis and metagenesis.

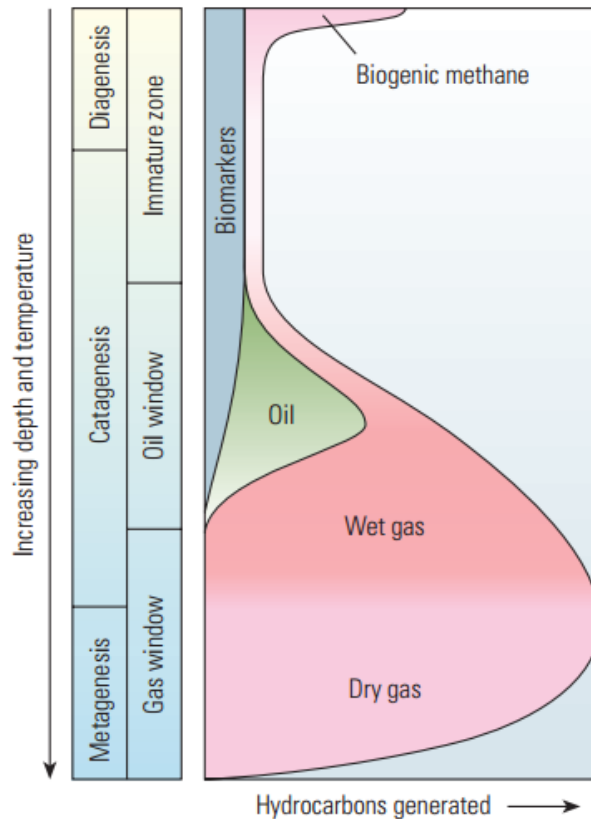


**Figure 6. Sedimentary Organic Matter Composition in a Source Rock** (Modified from Tissot & Welte, 1984)

Diagenesis is the first stage of thermal maturation process of organic matter. It comprises the natural changes occurring from the moment of sediment depositions until the first signal of thermal alteration process (Ali, Clark, Moore, & Dribus, 2010). Thus, this alteration starts in the water column (Magoon & Dow, 2009), being microbial activity the first process taking place (B. P. Tissot & Welte, 1984). The temperature, at which the alteration of organic matter in source rocks takes place, is ranged below 50 °C (Magoon & Dow, 2009). With reference to the depth interval, this phase is extended from one hundred to one thousand meters (B. P. Tissot & Welte, 1984). In this stage, oxidation along with other chemical process decompose the material. On the one hand, anoxic deposition conditions might convert the material from biogenic gas into dry gas. The term biogenic gas is referred to the gas generated during the degradation of organic matter in anaerobic conditions by bacterial microorganisms (Rice & Claypool, 1981). On the other hand, the increase of temperature and pH promote the transformation of organic matter into kerogen and bitumen. Figure 7 illustrates a general scheme of the evolution of the organic matter during its thermal maturation process.

Increasing burial depth due to successive sediment depositions, causes increment in pressure and temperature and the source rock undergoes catagenesis. During this phase, hydrocarbons are generated

at temperatures range from 50 °C to 150 °C and at several kilometers beneath the surface (B. P. Tissot & Welte, 1984). As a consequence, a thermal decomposition causes chemical bonds of kerogen breaks down, creating mostly oil but also gas (K. E. Peters, Walters, & Moldowan, 2007). A secondary cracking of oil molecules takes place during this phase due to the increment in temperature, generating wet gas such as methane, ethane, propane and heavier hydrocarbons (McCarthy et al., 2011).



**Figure 7. Thermal Transformation of Kerogen** (McCarthy et al., 2011)

The last step in the thermal transformation of kerogen is called metagenesis. Temperature ranges from 150 °C to 200 °C. In addition, higher burial depth might cause source rock be influenced by magma and hydrothermal effects (B. P. Tissot & Welte, 1984). Thus, at this stage, the increment in heat causes chemical changes within the kerogen, transforming it into methane and a carbon residue. Furthermore, late methane, or dry gas along with non-hydrocarbons gases such as carbon dioxide (CO<sub>2</sub>), nitrogen (N<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S) might be generated as the source rock moves further down (McCarthy et al., 2011).

Source rocks are said to be thermally immature, or potential source rocks, as the rocks have to be exposed to more heat in order to generate petroleum. Source rocks, which are found at the oil window, are said to be thermally mature, or effective source rocks, as the rocks have been generating petroleum, or are actively generating it. The last but not the least, source rocks are said to be thermally postmature, or spent source rocks, as the rocks have entered at the gas window and have already generated petroleum. Thus,

they have consumed all the hydrogen necessary for further oil and gas generation (McCarthy et al., 2011). On the other hand, it should be mentioned that maturation process can be also altered due to the influence of heat arising from the crustal tectonics or igneous bodies.

## 2.5 Kerogen Classification

In order to evaluate a source rock properly, a differentiation between kerogen types must be performed. As different types of organic matter have different chemical structures, the hydrocarbon potential varies (B. P. Tissot & Welte, 1984). Thus, four types of kerogen are distinguished based on its origin. Furthermore, the hydrogen, carbon and oxygen content can be used for such classification. Each type of kerogen can produce or generate different types of petroleum (B. Tissot, Durand, Espitalie, & Combaz, 1974). Figure 8 shows the van Krevelen diagram used to classify kerogen types and its level of thermal maturation. In earlier times, kerogen classification used to be made based on its elemental composition, as shown in Figure 8. As soon as Rock-Eval Pyrolysis was developed, it was found that HI and OI parameters are directly proportional to H/C and O/C ratios, thus HI and OI replaced them on the Van Krevelen diagram, respectively (Mackenzie, 2005).

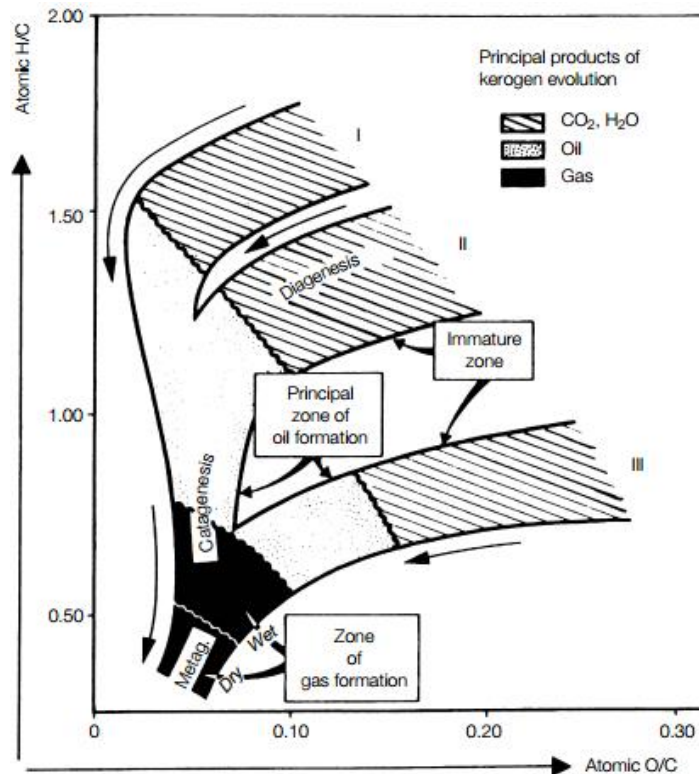


Figure 8. Van Krevelen Diagram (B. P. Tissot & Welte, 1984)

Type I kerogen originates mainly from lacustrine environments, although it can also be originated from marine environments. It is composed of algae, plankton and other matter which were reworked by bacteria and microorganisms. It shows high H/C atomic ratio and low O/C atomic ratio (B. P. Tissot & Welte,

1984). It is oil-prone, but depending on the thermal maturation phase can also generate gas. Type I kerogen is not usual and represents less than 3 % of oil and gas reserves in the world (Baskin, 1997), although it presents high hydrocarbon potential (B. P. Tissot & Welte, 1984).

Type II kerogen originates in reducing environments from deep marine settings. Remains of plankton, among others, reworked by bacteria compose this kind of kerogen. It shows high H/C and low O/C ratios (B. P. Tissot & Welte, 1984). Type II kerogen can generate mainly oil, but also gas, providing enough heating and maturation (Vandenbroucke, 2003).

Type III kerogen derives from continental plants and contains vegetal debris. It has been deposited in shallow to deep marine or non-marine environments. It shows low initial H/C ratio and high initial O/C ratio (B. P. Tissot & Welte, 1984). This sort of kerogen usually generates dry gas (McCarthy et al., 2011).

Type IV kerogen derives from residual organic matter which might have been altered by weathering, combustion or biologic oxidation in swamps or soils (McCarthy et al., 2011). It shows very low H/C ratio and a relatively high O/C ratio. This kind of kerogen is referred as a “dead carbon”, having no potential for petroleum generation (B. P. Tissot & Welte, 1984). It should be noted that this type of kerogen is not represented in Figure 8, as it does not present any information regarding petroleum potentiality.

Equally important is the degree of hydrogen content in kerogens. Hydrogen-rich kerogens generate both oil and gas, nevertheless, hydrogen-poor kerogens generates mainly gas. Additionally, when hydrogen is depleted from kerogen, petroleum generation ceases, despite the amount of available carbon (Baskin, 1997).

## **2.6 Previous Studies**

Several research papers have been performed in the geochemical source rock evaluation field within the Lusitanian basin, but none of them using TG/DSC analysis, which makes this thesis work unique in terms of methodology used to perform such research work. On the contrary, Rock-Eval Pyrolysis, among others, is the main technique used to develop such evaluations. It should be noted that no information, regarding geochemical source rock evaluation in Coxos Formation, appears to be reported in the literature. Thus, taking into account the results obtained, this thesis work can put a step forward for further geochemical investigations in this particular formation, as well as in the overall Lusitanian basin itself.

A really interesting investigation is developed by both, Professor Nuno Pimentel from the University of Lisbon and Professor Rui Penas Dos Reis from the University of Coimbra. In their article (Pena dos Reis & Pimentel, 2014), an overall explanation of the Lusitanian basin characteristics is presented, covering the source rocks found in Agua de Madeiros Formation (Praia do São Pedro de Moel) and Vale das Fontes Formation. According to the study, TOC values for Agua de Madeiros Formation range between 7 wt.% and 22 wt.%. With reference to Vale das Fontes Formation, specifically in the outcrops of Peniche, TOC values range from 0 wt. % to 25 wt. %. On the other hand, kerogen type I and type IV are present, but the

major presence is kerogen type III. From the thermal maturation point of view, this article designates non-mature source rocks in the outcrops of Peniche and São Pedro de Moel sections (Pena dos Reis & Pimentel, 2014).

Special attention should be given to a research article, which puts into practice the core of this thesis work, performed in real time onsite location during oil and gas exploration activities. The reason to state such affirmation resides in the fact that TG/DSC analysis could be used as an alternative technique for in-situ geochemical source rock evaluation, not forgetting that other techniques should be used to complement it. This investigation is performed by Gionata Ferroni, Konrad Rockenbauch, Fabio Rivolta and Ron McWhorter (Ferroni, Rockenbauch, Rivolta, & Mcwhorter, 2013). Several companies are involved in this project such as Sorgenia, RAG, PortoEnergy and Geolog International. In this paper, 500 rock samples within the Lusitanian basin are analyzed by geochemical techniques, performing TOC measurements and pyrolysis. Thus, providing information about TOC, S<sub>2</sub>, T<sub>max</sub> and HI values.

Another interesting paper is presented by André Luiz Durante Spigolon, Rui Paulo Bento Pena dos Reis, Nuno Lamas Pimentel and Vasco Gonçalo Alves Esteves de Matos (Spigolon, Dos Reis, Pimentel, & De Matos, 2010). A geochemical evaluation is performed in this study, collecting 76 source rock samples from the surface in different locations within the Lusitanian basin. The results shows that there is a low maturation level within the samples in general, as well as two intervals of petroleum source rock potential corresponding to Água de Madeiros and Vale das Fontes Formations. Kerogen types II and III were found in both formations. With reference to TOC values, 2,9 wt.% TOC and 3,3 wt.% TOC can be found in two samples from Vale das Fontes and Água de Madeiros Formations respectively. T<sub>max</sub> values of 425 °C in a sample from Água de Madeiros Formation and 429 °C in a sample of Vale das Fontes Formation are measured (Spigolon et al., 2010).

Água de Madeiros Formation is investigated by L. V. Duarte, R. L. Silva, J. G. Mendonça Filho, N. Poças Ribeiro and R.B.A. Chagas (Duarte, Silva, Filho, Ribeiro, & Chagas, 2012), specifically in São Pedro de Moel region. In this paper, 200 samples were analyzed, performing TOC and Rock-Eval pyrolysis measurements, among others. Maximum TOC values reached 22 wt. %. Furthermore, S<sub>2</sub> value of 78 mg HC/g rock was reached by one sample. With reference to maturity, T<sub>max</sub> values below 437 °C indicate that the study area is immature or early mature. Taking into account all measurements, these scientists state that Água de Madeiros Formation has a high source rock potential in terms of oil generation, indicating a major presence of type II kerogen (Duarte et al., 2012).

On the contrary, according to an article published by Paula Alexandra Gonçalves, Taís Freitas da Silva, Joao Graciano Mendonça Filho and Deolinda Flores, the organic matter content and the petroleum generation potential are not well known and evaluated within the Lusitanian basin. Thereby, several investigations have been performed, trying to evaluate them (Gonçalves, Silva, Mendonça Filho, & Flores, 2015).

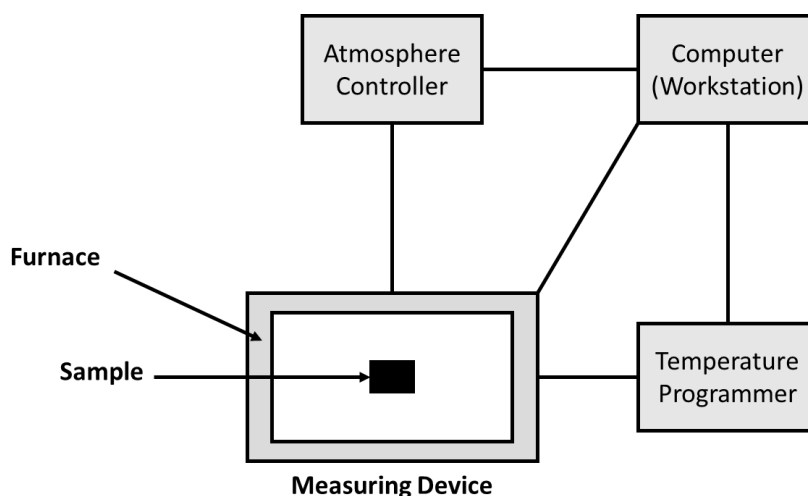
### 3. METHODOLOGY

This chapter describes the methodology used in this thesis work. It includes the TG/DSC working principle and experimental setup, the temperature program used to obtain the measurements, the TOC assumption and the references used to evaluate the results obtained.

#### 3.1 TG/DSC Analysis

A thermal analyzer device is composed commonly of a sensor to measure the temperature, a furnace in which the atmosphere is controlled, a temperature programmer and a recording device associated to a computer or workstation (Hatakeyama & Liu, 1998). Figure 9 shows a block diagram of a thermal analyzer.

The meaning, working principle and experimental setup of TG/DSC analysis are described below. These thermal analysis technique can be also used separately, nevertheless the device used in this thesis work provides the possibility to implement both methods, and thus complement one to another in order to characterize the material studied (Hammer et al., 2013). In addition, the sample and experimental conditions are the same if both techniques are used simultaneously, providing comparative data and saving testing time (Hatakeyama & Quinn, 1999).



**Figure 9. Block Diagram of Thermal Analyzer Device (Modified from Hatakeyama & Liu, 1998)**

An important point should be highlighted, the instrument used in this work cannot measure the volatile products evolved from the sample as a consequence of the increment in temperature during the experiment. A Mass Spectrometer (TG/DSC-MS), a Fourier Transform Infrared Spectrometer (TG/DSC-FTIS) or a Gas Chromatograph (TG/DSC-GC) need to be coupled to TG/DSC device in order to measure such volatile products (Hatakeyama & Liu, 1998). These set of techniques are called Evolved Gas Analysis (EGA), in which the volatile products evolved from a sample are measured as a function of temperature (Hammer et al., 2013). The use of these techniques, among others, are recommended in future



developments chapter, as there is a need to improve and progress in the current investigation, as well as making comparisons and correlations of the results obtained.

### **3.1.1 Working Principle**

Thermogravimetric (TG) is a thermal technique in which the mass change of a material is measured as a function of temperature and time in a controlled atmosphere (Menczel & Prime, 2009; Vaimakis, 2013). With reference to Differential Scanning Calorimetry (DSC), it is a thermal technique in which the heat capacity of a material is measured as a function of temperature and time by observing at the heat flow rate differences during chemical or physical changes (Crompton, 2013; Gill et al., 2010).

TG/DSC curves are obtained. On the one hand, TG curves show the mass changes, mainly loss in this case, as a consequence of the release of volatile compounds such as moisture or hydrocarbon gases, molecular decomposition such as kerogen, combustion of carbon black and residues (Hammer et al., 2013; Hatakeyama & Liu, 1998). On the other hand, DSC curves show the heat exchange (endothermic or exothermic) effects, thus the heat absorption, the heat released from the sample or the heat involved in the molecular decomposition (Hammer et al., 2013). It should be mentioned that in this particular thesis work, DSC curves are used as qualitative information, since no calculation are expected from them. Perhaps, in further investigations might be used.

Several aspects must be taken into account before running a TG/DSC experiments, such as sample pan, sample size, temperature program and the gas atmosphere. In relation to gas atmosphere, a purge gas flows through the furnace, creating an inert atmosphere, using for instance nitrogen, or a reactive atmosphere, using air (Menczel & Prime, 2009). Thus, two processes can be distinguished. If an inert atmosphere is settled, pyrolysis takes place, on the contrary, if air is settled, oxidation process occurs. It should be mentioned that TG/DSC apparatus provides the opportunity to switch the gases without altering the sample. In another words, once pyrolysis takes place, by switching the gas by air, oxidation follows.

### **3.1.2 Experimental Setup**

The apparatus used for the purpose of the thesis is a Perkin-Elmer STA 6000 simultaneous thermal analyzer shown in Figure 10, and the corresponding Pyris software (PerkinElmer, 2015). The sample used in the experiments correspond to six source rocks, which have been grinded and powdered in order to obtain a proper sample in terms of shape and size. The samples powdered ranges between 32 mg to 50 mg, with a sample average weight equals to 40 mg. A ceramic pan has been used in the experiments, which can supports higher temperatures up to 900 °C. After concluding every experiment, the ceramic pan is treated with acetone in order to remove any residue. TG/DSC analysis has been performed in an inert and reactive atmosphere under 20 ml/min flow rate. Pressure has been set to 0,5 bar .Firstly, an inert atmosphere is set using N<sub>2</sub>. Thus, pyrolysis process is performed. Then, a reactive atmosphere is set by switching the gas to air, thus oxidation process takes place. It should be noted that during the gas switching, the sample remains at the simultaneous analyzer device. The heating rate is established at 25 °C/min

during each phase transition. In the next section, the temperature program is explained in details, covering the heating rate purpose. It should be noted that the temperature program was set in order to closely follow the protocol used in Rock-Eval 6 apparatus.



**Figure 10. TG/DSC STA 6000 Simultaneous Thermal Analyzer**

TG/DSC procedure is performed using a sample pan which is held by a precision balance. The sample pan is located in a furnace where the sample itself is placed. The sample is heated and cooled during the experiment, following the temperature program. The powdered samples range between 32 mg and 50 mg. The sample weight and heat flow are continuously measured throughout the entire experiment and as a results TG/DSC curves are shown. The results obtained can be used to characterize the organic matter content, define the source rock maturation and determine the hydrocarbon generation potential.

### **3.2.3 Temperature Program and Measurement Evaluations**

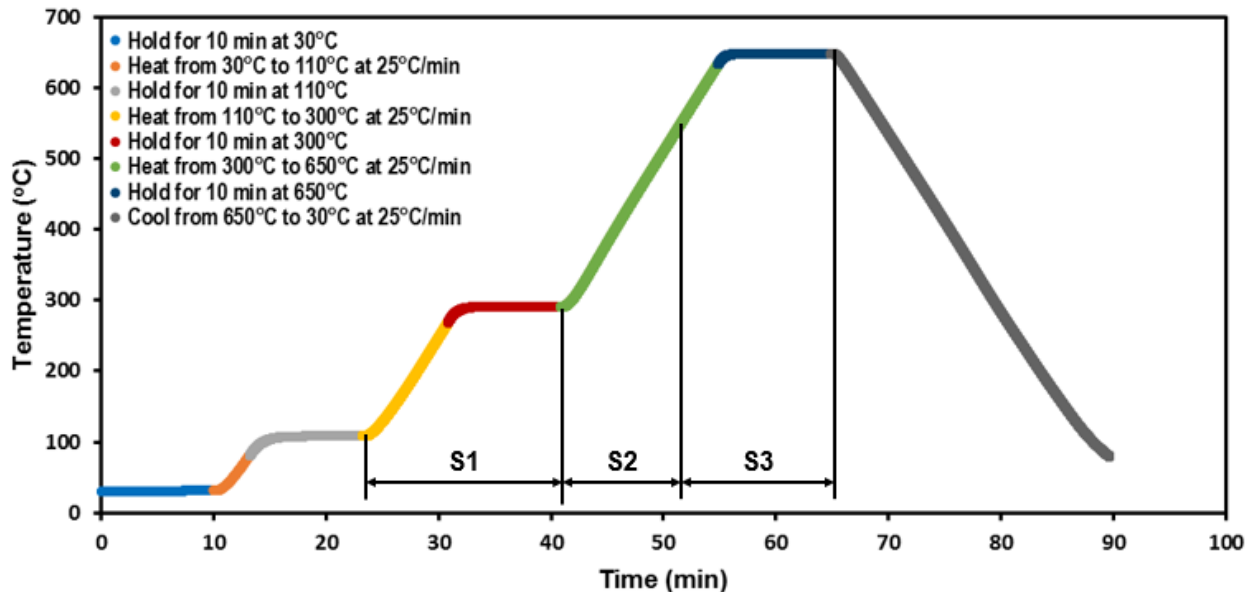
The temperature program is established using Pyris software (PerkinElmer, 2015), being an important aspect to be taken into account, among others. For more on the effect of experimental conditions such as heating rates, sample mass, among others: Hatakeyama, T., & Liu, Z. (1998), Handbook of Thermal Analysis. Depending on it, different results are obtained. For the purpose of the thesis, the temperature program has been standardized as Rock-Eval Pyrolysis experiment. For more on Rock-Eval Pyrolysis: Behar, Beaumont, & De B. Pentead, 2001, Rock-Eval 6 Technology: Performances and Developments. In this case, there is just one difference in terms of temperature program, the isothermal time has been set to 10 minutes for each phase transition, while Rock-Eval Pyrolysis establishes 3 minutes. The temperature program used in both pyrolysis and oxidation processes is described below:

- **Pyrolysis Process, N<sub>2</sub> Atmosphere:**
  1. Hold for 10 min at 30 °C
  2. Heat from 30 °C to 110 °C at 25 °C/min
  3. Hold for 10 min at 110 °C

4. Heat from 110 °C to 300 °C at 25 °C/min
  5. Hold for 10 min at 300 °C
  6. Heat from 300 °C to 650 °C at 25 °C/min
  7. Hold for 10 min at 650 °C
  8. Cool from 650 °C to 30 °C at 25 °C/min
- **Oxidation Process, Air Atmosphere:**
    1. Hold for 10 min at 30 °C
    2. Heat from 30 °C to 850 °C at 25 °C/min
    3. Hold for 10 min at 850 °C
    4. Cool from 850 °C to 30 °C at 25 °C/min

It is important to mention that TG/DSC analysis and Rock-Eval Pyrolysis can be compared. To some extent, both techniques aims the same, but there are some differences in terms of working principle and therefore the manner in which the measurements are performed. For instance, Rock-Eval Pyrolysis utilizes a flame ionization detector (FID) to measure the evolved hydrocarbons, CO<sub>2</sub> and CO (Behar et al., 2001). Thus, to avoid any misunderstanding, the nomenclature used in Rock-Eval Pyrolysis such as S1, S2, S3, S4, S5, T<sub>max</sub>, Production Potential (PP), Hydrogen Index (HI), Oxygen Index (OI), and Total Organic Carbon (TOC) is also used for TG/DSC analysis in this thesis work.

Figure 11 illustrates the controlled temperature program used in each experiment for Pyrolysis process. Parameters such as S1, S2 and S3 are calculated by mass loss during the programmed heating phase. A heating rate of 25 °C/min is set for each phase transition.



**Figure 11. Controlled Temperature Program for Pyrolysis Stage**

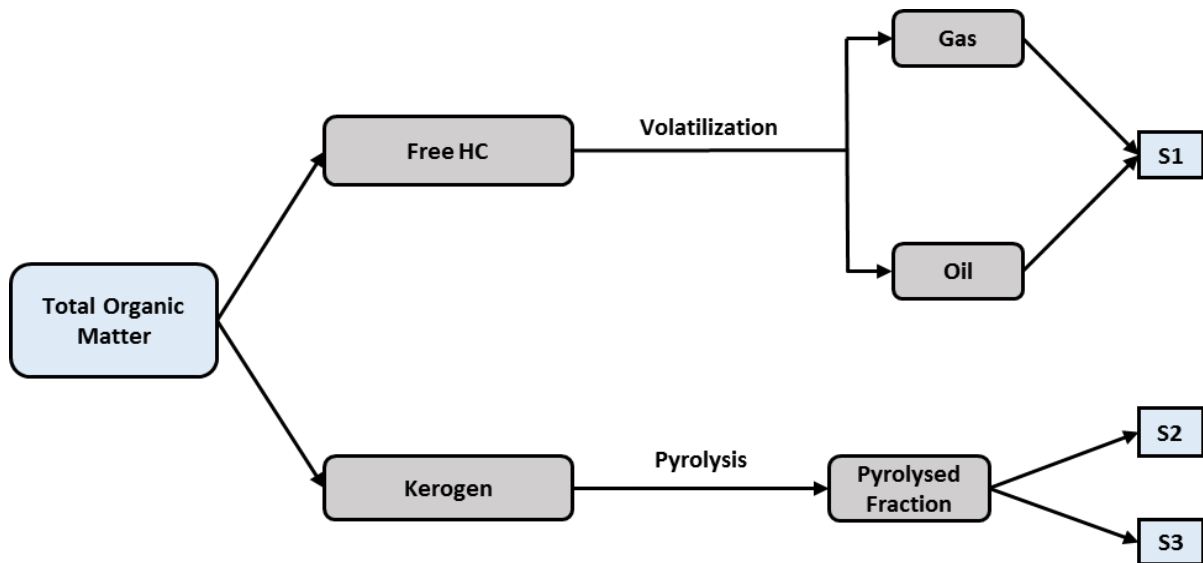
Firstly, the sample is heated from 30 °C to 110 °C in order to vaporize any water contained in the source rock sample (Hatakeyama & Liu, 1998). During the first phase of pyrolysis, free oil and gas contained

within the soluble organic matter (bitumen) is expelled from the source rock sample by the thermovaporization process quantified by S1, occurring between 110 °C and 300 °C (McCarthy et al., 2011). It should be noted that S1 represents the hydrocarbons already generated in the subsurface, but are expelled from the source rock during pyrolysis process. During the next stage of controlled heating program, the thermal cracking of insoluble organic matter (kerogen) in the source rock occurs, releasing hydrocarbons and CO<sub>2</sub> between 300 °C and 650 °C. This is quantify by S2 and S3 respectively (Behar et al., 2001).

It should be mentioned that S2 and S3 are challenging to measure using TG/DSC analysis due to the technique limitations and a lack of information in the literature. Chemical reactions such as decarboxylation and depolymerization occur at this phase. Thus, as decarboxylation occurs at low temperatures, as it is easier to take place due to the less activation energy required, it might start first. On the other hand, depolymerization dominates at high heating rates, as this is the case, then, depolymerization might start first. Thus, it is assumed in this work that depolymerization occurs first and then decarboxylation takes place (Basu, 2013). This aspect should be further investigated in future developments, for instance, coupling a mass spectrometer to measure the evolved products.

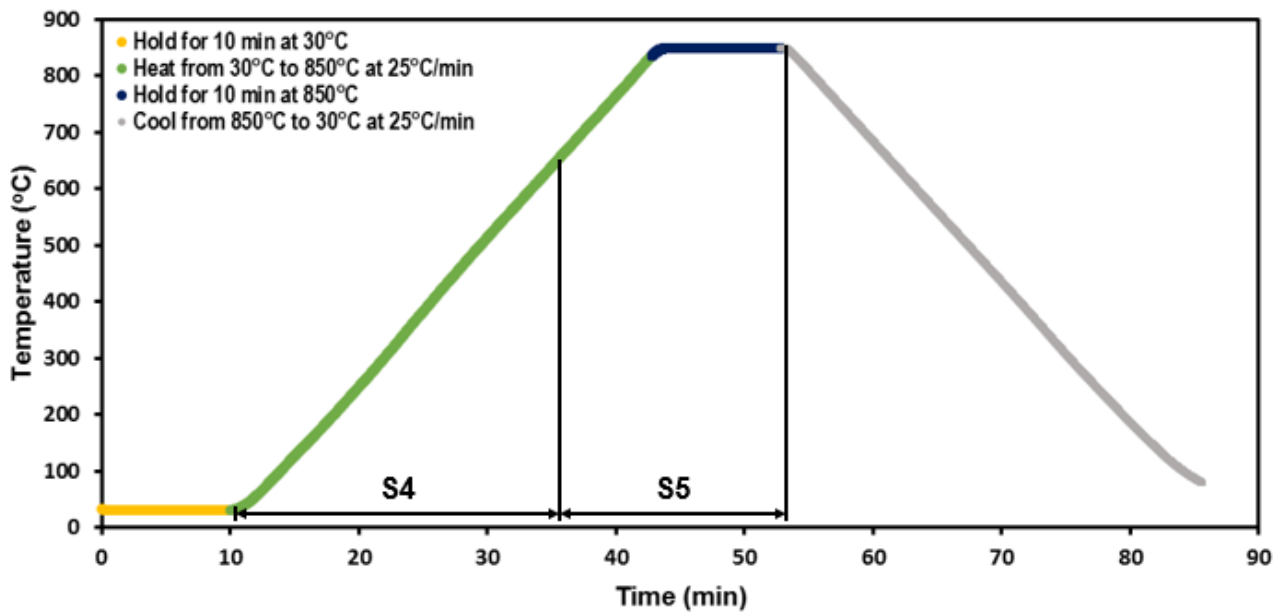
It should be noted that S2 is a key parameter within geochemical source rock evaluation. It represents the amount of oil and gas which can still be produced from the source rock if the thermal maturation continues (McCarthy et al., 2011). In another words, S2 measures the source rock potential for generating hydrocarbons if thermal maturation undergoes. Equally important is  $T_{max}$  value, which is related to S2.  $T_{max}$  is the temperature at which the maximum amount of hydrocarbons are generated during the thermal cracking of kerogen.  $T_{max}$  represents the thermal maturity of the organic matter (Behar et al., 2001). In order to calculate this parameter DSC signal must be taken into account, as well as the range of S2 mass loss. During this stage,  $T_{max}$  is reached when a peak in DSC signal is measured within the S2 mass loss range.

Figure 12 shows a scheme summarizing the total organic matter decomposition within a source rock when the first heating program is applied. Firstly, a physical change occurs by volatilization of bitumen, thus S1 is measured. Then, a chemical change occurs by thermal cracking of kerogen, releasing hydrocarbons and CO<sub>2</sub>, represented by S2 and S3 respectively (Bordenave, 1993).



**Figure 12. Organic Fraction measured by TG/DSC Analysis** (Modified from Bordenave, 1993)

Figure 13 illustrates the controlled heating program used in each experiment for oxidation process. As it is described above, pyrolysis is completed using nitrogen as inert gas. Once this process is finished, the gas is switched into air via Pyris software. Then, oxidation process starts. At this step, the rock sample remains at the apparatus.



**Figure 13. Controlled Temperature Program for Oxidation Stage**

At this point, S4 and S5 are calculated during the controlled heating phase. S4 corresponds to the residual carbon which remains after pyrolysis, thus under oxidation conditions, between 30 °C to 650 °C (Behar et al., 2001). S5 represents the mineral carbon from the carbonate decomposition of the source

rock, between 650 °C to 850 °C (Behar et al., 2001). Figure 14 shows the overall temperature program, representing all the stages in which the source rock sample is subjected during the entire experiment.

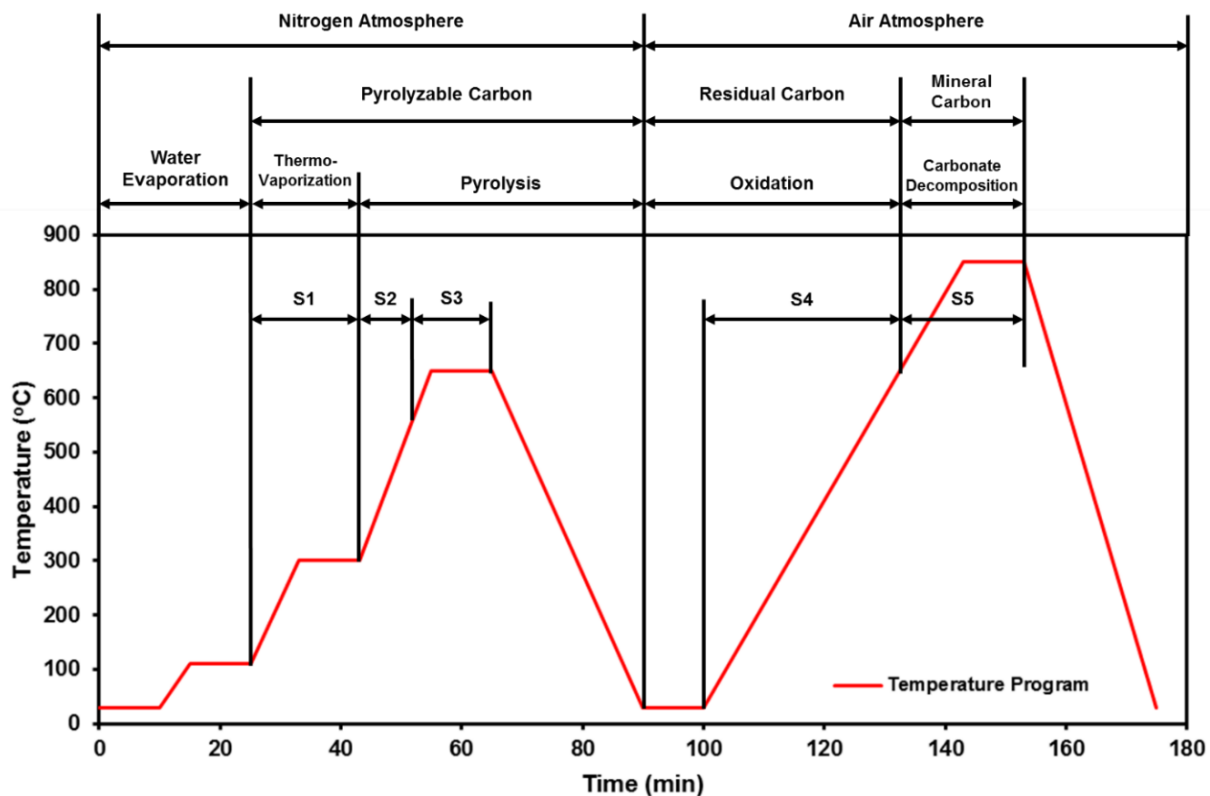


Figure 14. Overall Temperature Program used in TG/DSC Experiment

Summarizing the figure above, two physical processes are produced under N<sub>2</sub> atmosphere, water evaporation and free hydrocarbons volatilization from the soluble bitumen. Then, the thermochemical cracking of kerogen occurs, releasing hydrocarbons and CO<sub>2</sub>. By switching N<sub>2</sub> by air, oxidation process occurs. At this point, the residual carbon is measured, as well as the mineral carbon from the carbonate decomposition of the source rock. Total Organic Matter content (TOM) is the first geochemical parameter calculated as shown in Equation 1.

**Total Organic Matter:**

$$TOM (\%) = S1 + S2 + S3 \quad (1)$$

Other geochemical parameters can also be calculated such as Petroleum Potential (PP), which describes the maximum amount of petroleum that a mature source rock might generate. PP is shown in Equations 2 (McCarthy et al., 2011).

**Petroleum Potential:**

$$PP \left( \frac{kg\ HC}{ton\ of\ rock} \right) = S1 + S2 \quad (2)$$

Hydrogen Index (HI) and Oxygen Index (OI) are related to the Total Organic Carbon (TOC), as it is used for their calculation. Thus, a proper TOC determination is key in order to evaluate them. The next section aims to calculate TOC, taking into account some assumptions according to TG/DSC analysis limitations. Hydrogen Index (HI) "is proportional to the amount of hydrogen contained within the kerogen", high HI values indicates greater potential to generate oil. Oxygen Index (OI) is related to the amount of oxygen contained within the kerogen. Both indices are used for defining the type of kerogen contained within the source rocks and their thermal maturation, and are plotted in the Van Krevelen diagram (McCarthy et al., 2011). Equations 3 and 4 show HI and OI respectively (Behar et al., 2001).

**Hydrogen Index:**

$$HI \left( \frac{mg\ HC}{g\ TOC} \right) = \frac{S2 * 100}{TOC} \quad (3)$$

**Oxygen Index:**

$$OI \left( \frac{mg\ CO_2}{g\ TOC} \right) = \frac{S3 * 100}{TOC} \quad (4)$$

### 3.2 TOC Assumption

It is highly important to mention that some assumptions must be considered when calculating Total Organic Carbon (TOC) values, due to TG/DSC limitations. In order to avoid such assumptions, further studies should be developed using different geochemical techniques, as it is explained in the seventh chapter of this thesis work. Thus, it should be noted that the results obtained as a consequence of the assumptions are merely indicative. Therefore, assuming these parameters, the organic matter characterization, the maturation definition and the petroleum potential determination can be calculated for each source rock sample. The method used for TOC calculation is called "The Basic Method" (Behar et al., 2001) which it is used in Rock-Eval analysis. It should be mentioned that the equations used in this study have been modified according to TG/DSC measurements. Equations 5, 6 and 7 are described below.

**TOC: Total Organic Carbon:**

$$TOC\ (wt\%) = PC + RC \quad (5)$$

**PC: Pyrolysable Organic Carbon:**

$$PC \text{ (wt\%)} = \frac{[(S1 + S2) * 0,83] + \left(S3 * \frac{12}{44}\right)}{10} \quad (6)$$

**RC: Residual Organic Carbon:**

$$RC \text{ (wt\%)} = \frac{S4}{10} \quad (7)$$

### 3.3 References for the Result Evaluations

A proper evaluation of the results obtained from the measurements and calculations are considered in this section. To perform such appraisal, references tables are used. Thus, the organic matter characterization, thermal maturation and petroleum potential for each source rock sample are evaluated by an adequate analysis of it. Once again, it should be highly noted that the results should be taken as merely indicative, recommending the used of other geochemical techniques to complement it and compare it.

Table 1 shows the geochemical parameters describing the petroleum potential.

**Table 1. Geochemical Parameters Describing the Petroleum Potential (Magoon & Dow, 2009)**

Petroleum Potential	TOC (wt. %)	S1 (mg HC/g of rock)	S2 (mg HC/g of rock)
Poor	0-0,5	0-0,5	0-2,5
Fair	0,5-1	0,5-1	2,5-5
Good	1-2	1-2	5-10
Very Good	2-4	2-4	10-20
Excellent	>4	>4	>20

Table 2 illustrates the kerogen type classified by its source of material and its general environment of deposition.

**Table 2. Kerogen Type Classified by its Source of Material (McCarthy et al., 2011)**

Kerogen Type	Source Material	General Environment of Deposition
I	Mainly algae	Lacustrine settings
II	Mainly plankton, some contribution from algae	Marine settings
III	Mainly higher plants	Terrestrial settings
IV	Reworked, oxidized material	Varied settings

Table 3 illustrates the geochemical parameter describing the kerogen type and the main expelled product.



**Table 3. Geochemical Parameter Describing the Kerogen Type and the Expelled Product (Magoon & Dow, 2009)**

<b>Kerogen Type</b>	<b>HI (mg HC/g TOC)</b>	<b>Main Expelled Product</b>
I	> 600	Oil
II	300-600	Oil
II/III	200-300	Mixed Oil and Gas
III	50-200	Gas
IV	< 50	None

Table 4 shows the geochemical parameters describing the level of thermal maturation of the source rock.

**Table 4. Geochemical Parameter Describing the Level of Thermal Maturation (Magoon & Dow, 2009)**

<b>Stage of Thermal Maturity</b>	<b>T<sub>max</sub> (°C)</b>
<b>Immature</b>	< 435
<b>Mature</b>	---
<i>Early</i>	435-445
<i>Peak</i>	445-450
<i>Late</i>	450-470
<b>Postmature</b>	> 470

## 4. RESULTS

In this chapter, the geological settings of the Lusitanian basin, the samples definition and location and the results obtained from the source rock evaluation using TG/DSC analysis are presented. Following the temperature program and taking into account all measurements and assumptions, S1, S2, S3, S4, S5, TOM, TOC, HI, OI, PP and  $T_{max}$  have been calculated. Hence, the characterization of the organic matter content, the source rock maturation definition and the hydrocarbon generation potential determination have been performed for each sample.

### 4.1 Geological Settings

The Lusitanian Basin is located in Portugal, but more exactly it is placed in the west part of the Iberian margin. It covers around 22000 km<sup>2</sup> (Spigolon et al., 2010) and its sedimentary thickness is approximately 5 km (Gonçalves et al., 2015). It was formed as a consequence of the opening of the North Atlantic Ocean. It represents a Mesozoic rift basin. The basin evolution started in the Upper Triassic. The sedimentation process was developed with a rich organic matter content, resulting generally in a good basin capable of generating hydrocarbons (Spigolon et al., 2010). Figure 15 shows the Lusitanian basin location, as well as the place where the samples were collected (red arrow).

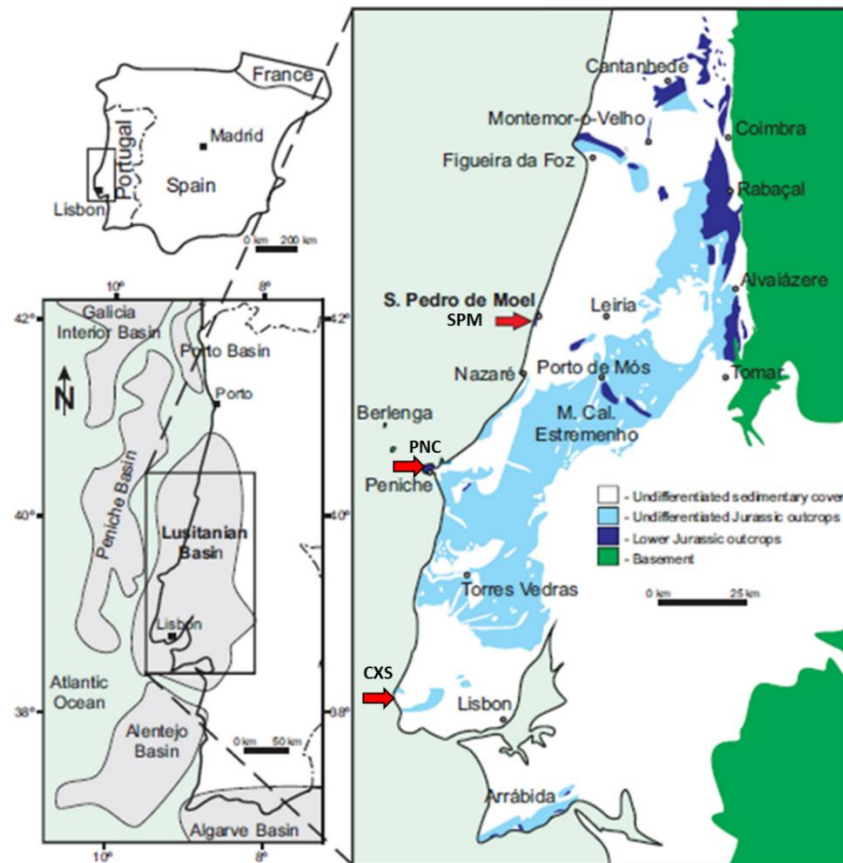


Figure 15. Lusitanian Basin Location (Modified from Ribeiro & Chagas, 2012)

## 4.2 Sample definition and Location

Six source rock samples collected from the outcrops of the Lusitanian basin are investigated in this work. Three places were selected, Água de Medeiros Formation (SPM), Vale das Fontes Formation (PNC) and Praia dos Coxos Formation (CXS). From each place, two samples were considered. A general description of the source rocks are presented below.

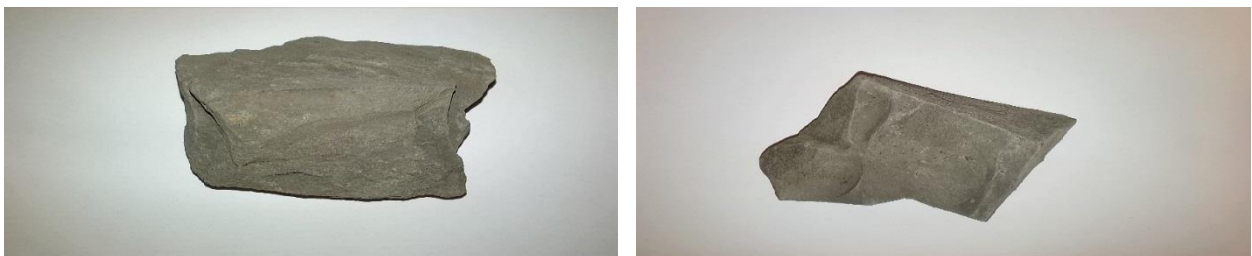
### 4.2.1 Samples SPM 004/006

These source rocks corresponds to Água de Madeiros Formation (in Portuguese Formação Água de Madeiros - Membro da Pedra Lisa), specifically from Praia da Pedra Lisa Member. This formation was formed during the Lower Jurassic. These source rocks are characterized by marine paleoenvironment with high organic matter content, corresponding to calcareous marls (Spigolon et al., 2010). Figure 16 shows the Água de Madeiros Formation, where SPM-004 (Left) and SPM-006 (Right) were collected.



**Figure 16. Source Rock Location. Água de Madeiros Formation. Praia da Pedra Lisa Member**

Figure 17 illustrates the source rock samples, SPM-004 (Left) and SPM-006 (Right).



**Figure 17. Source Rock Samples. SPM-004 (Left), SPM-006 (Right)**

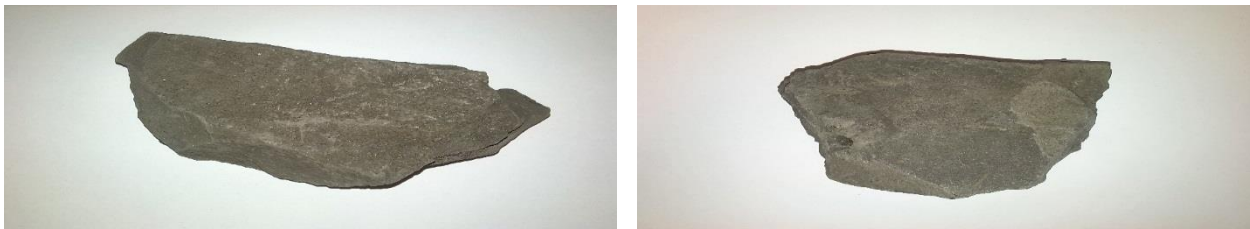
### 4.2.2 Samples PNC 008/009

These source rocks belong to Vale das Fontes Formation, specifically in Peniche. The age comprises the Lower Jurassic. These rocks are characterized by a deep marine paleoenvironment with high organic matter content, which correspond to calcareous marls (Spigolon et al., 2010). Figure 18 shows the Vales das Fontes Formation, where PNC-008 and PNC-009 were collected.



**Figure 18. Source Rock Location. Vale das Fontes Formation**

Figure 19 illustrates the source rock sample, PNC-008 (Left) and PNC-009 (Right).



**Figure 19. Source Rock Samples. PNC-008 (Left), PNC-009 (Right)**

#### **4.2.3 Samples CXS 013/014**

These source rocks belong to Praia dos Coxos Formation. The age is specified at the Lower Cretaceous. These rocks correspond to infralitoral marls. It should be mentioned that there is no geochemical information reported in this particular formation. Thus, this thesis work aims to give some clues about the hydrocarbon generation potential, organic matter characterization and thermal maturity of it. Figure 20 shows the Praia do Coxos Formation, where CXS-013 and CXS-014 were collected.



**Figure 20. Source Rock Location. Praia dos Coxos Formation**

Figure 21 illustrates the source rock sample, CXS-013 (Left) and CXS-014 (Right).



Figure 21. Source Rock Samples. CXS-013 (Left), CXS-014 (Right)

### 4.3 Sample Results and Evaluations

It is important to mention that basically, all physical and chemical processes occurring for each sample during the experiments are produced at the same phase, as the temperature program followed is the same. The only differences are in the amount of mass loss and the energy absorbed or released from the samples. Two processes take place during each experiment. First pyrolysis using  $N_2$  and then, oxidation using air. For each sample, mass loss as a function of temperature has been measured using TG technique. The energy absorbed or released when samples are heated or cooled has been measured using DSC technique, providing information regarding endothermic (heat absorption) and exothermic (heat released) processes. In addition, DSC signal has been useful for tracking  $T_{max}$  peaks, corresponding to the thermal maturation of source rocks.

#### 4.3.1 Sample SPM-004

This source rock sample corresponds to Água de Medeiros Formation, specifically from Praia da Pedra Lisa Member. Figure 22 shows TG/DSC curves during pyrolysis stage for sample SPM-004.

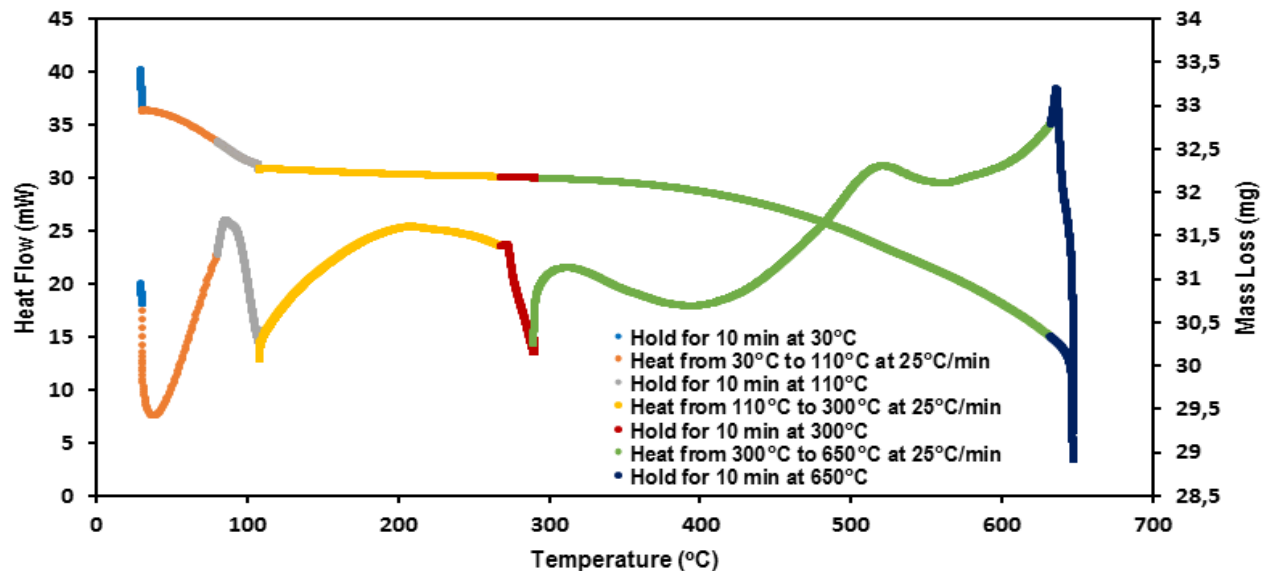


Figure 22. TG/DSC Curves during Pyrolysis Stage for Sample SPM-004

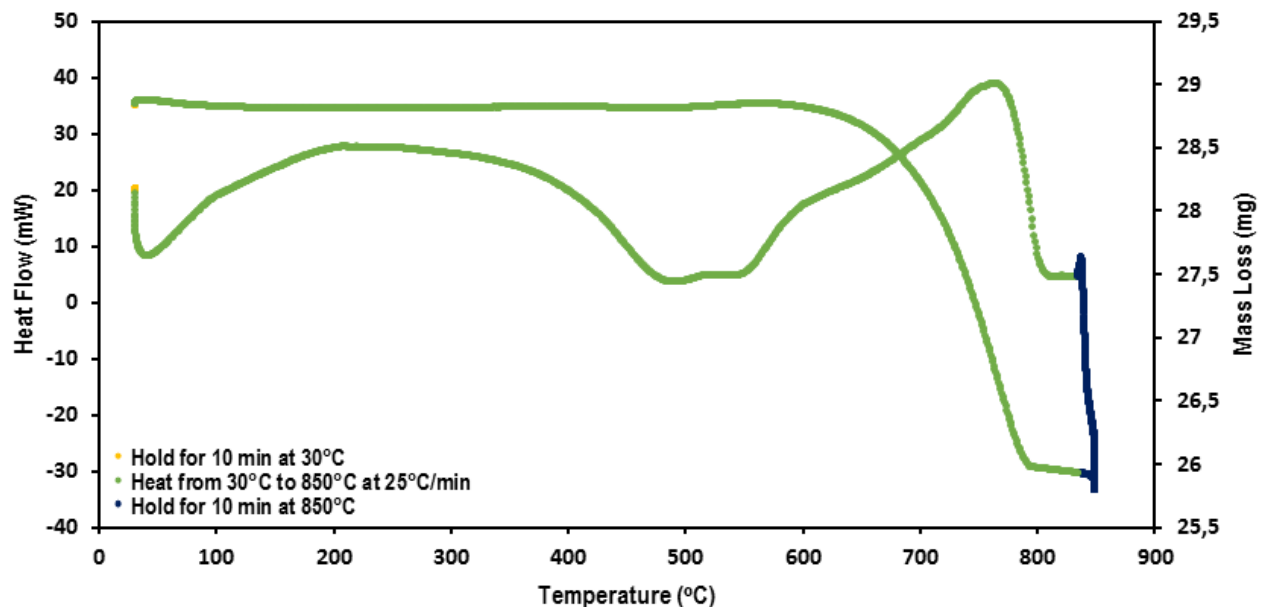
Heat flow and mass loss curves are distinguished in Figure 22. The graph legend shows the complete temperature program followed through the entire experiment. A consider amount of mass is lost from the source rock sample during the first heating phase due to water evaporation between 30 °C to 110 °C. At the same time, an endothermic peak is appreciated it following the physical change, which means the sample absorbed energy as water evaporation took place. Then, a small amount of mass is lost during the thermo-evaporation of free hydrocarbons from bitumen (S1), followed by another endothermic process between 110 °C to 300 °C. It is appreciated how the sample releases energy (exothermic process) during the isothermal phase at 300 °C. Between 300 °C to 650 °C, a new highly amount of mass is lost from the sample as a consequence of the thermal cracking of kerogen, releasing hydrocarbons (S2) and CO<sub>2</sub> (S3). At the same time, endothermic peaks are produced at that stages as a result of the energy absorbed from the sample during the chemical changes.

At the beginning of the experiment, the mass sample was 33,40 mg. During the experiment, 13,88 wt.% of the sample mass has been lost. DSC curve shows that T<sub>max</sub> value corresponds to 520,3 °C. Table 5 shows the geochemical parameters determined during pyrolysis process for sample SPM-004.

**Table 5. Geochemical Parameters determined during Pyrolysis Phase for Sample SPM-004**

SAMPLE	S1 (mg HC/g rock)	S2 (mg HC/g rock)	S3 (mg CO <sub>2</sub> /g rock)	T <sub>max</sub> (°C)
SPM-004	3,38	31	72,2	520,3

Figure 23 shows TG/DSC curves during oxidation stage for sample SPM-004.



**Figure 23. TG/DSC Curves during Oxidation Stage for Sample SPM-004**

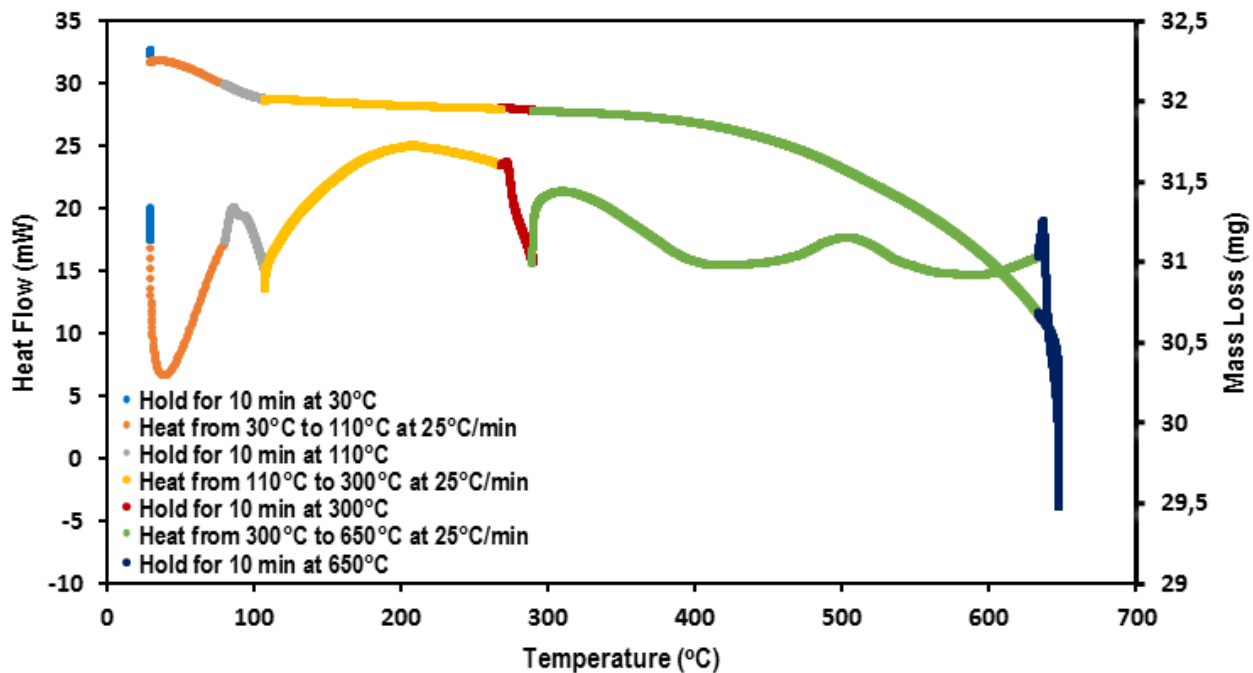
Heat flow and mass loss curves are distinguished in Figure 23. The graph legend shows the complete temperature program followed through the entire experiment. A notably amount of mass is lost between 650 °C and 850 °C. S4 and S5 are therefore calculated, corresponding to the residual carbon remaining after pyrolysis process, and the mineral carbon from the carbonate decomposition respectively. Endothermic and exothermic peaks are shown as a results of absorption and release of energy throughout the decomposition. During this phase, 11,24 wt.% of sample mass has been lost. Table 6 shows the total mass loss from the sample and the geochemical parameters determined during oxidation phase for sample SPM-004.

**Table 6. Geochemical Parameters determined during Oxidation Phase for Sample SPM-004**

SAMPLE	S4 (mg C/g rock)	S5 (mg CO <sub>2</sub> /g rock)
SPM-004	5,76	100,8

#### 4.3.2 Sample SPM-006

This source rock sample corresponds to Água de Medeiros Formation, specifically from Praia da Pedra Lisa Member. Figure 24 shows TG/DSC curves during pyrolysis stage for sample SPM-006.



**Figure 24. TG/DSC Curves during Pyrolysis Stage for Sample SPM-006**

Heat flow and mass loss curves are distinguished in Figure 26. The graph legend shows the complete temperature program followed through the entire experiment. Similarly to sample SPM-004, a consider amount of mass is lost from the source rock sample during the first heating phase due to water evaporation between 30 °C to 110 °C. Simultaneously, an endothermic peak is appreciated it following the

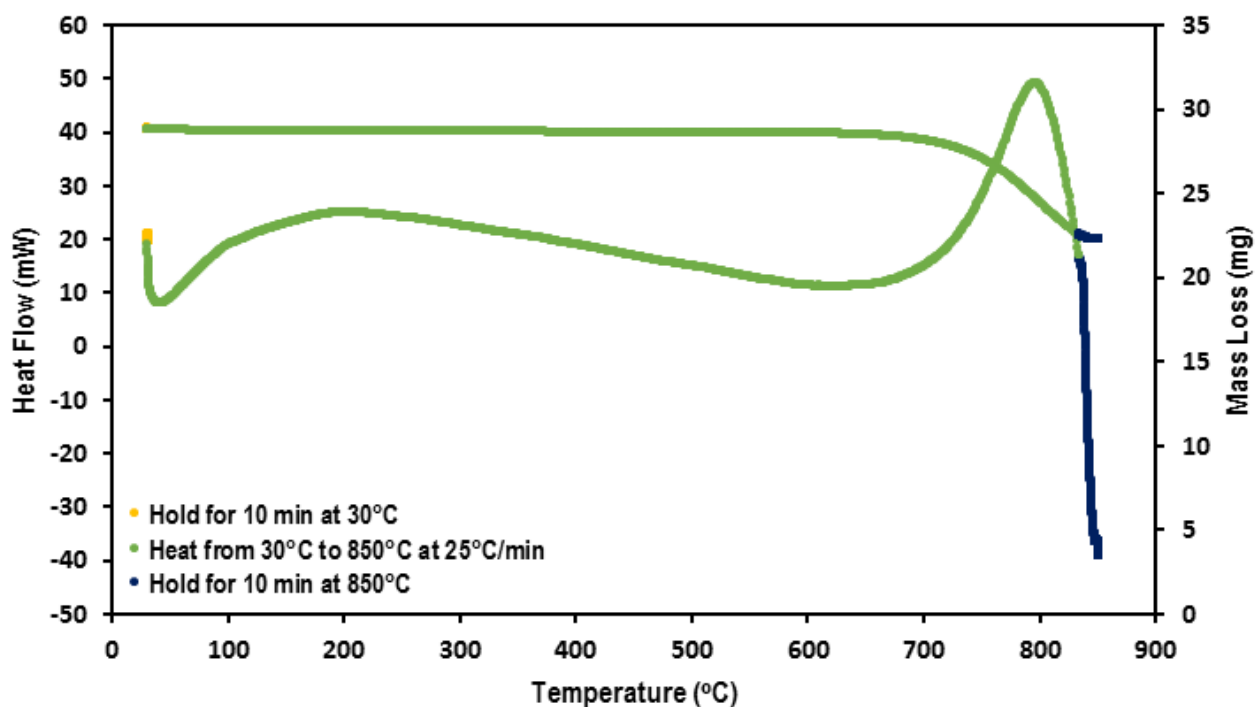
physical change, which means the sample absorbed energy as water evaporation took place. Then, a small amount of mass is lost during the thermo-evaporation of free hydrocarbons from bitumen (S1), followed by an endothermic process between 110 °C to 300 °C. It is appreciated how the sample releases energy (exothermic process) during the isothermal phase at 300 °C. Between 300 °C to 650 °C, a new highly amount of mass is lost from the sample as a consequence of the thermal cracking of kerogen, releasing hydrocarbons (S2) and CO<sub>2</sub> (S3). At the same time, endothermic peaks are produced at that stages as a result of the energy absorbed from the sample during the chemical changes.

At the beginning of the experiment, the mass sample was 32,53 mg. During the experimentation, 9,66 wt.% of the sample mass has been lost. DSC curve shows that T<sub>max</sub> value corresponds to 505 °C. Table 7 shows the geochemical parameters determined during pyrolysis process for sample SPM-006.

**Table 7. Geochemical Parameters determined during Pyrolysis Phase for Sample SPM-006**

SAMPLE	S1 (mg HC/g rock)	S2 (mg HC/g rock)	S3 (mg CO <sub>2</sub> /g rock)	T <sub>max</sub> (°C)
SPM-006	2,07	18,6	56,8	505

Figure 25 shows TG/DSC curves during oxidation stage for sample SPM-006.



**Figure 25. TG/DSC Curves during Oxidation Stage for Sample SPM-006**

Heat flow and mass loss curves are distinguished in Figure 27. The graph legend shows the complete temperature program followed through the entire experiment. A notably amount of mass is lost between 690 °C and 850 °C. S4 and S5 are therefore calculated, corresponding to the residual carbon



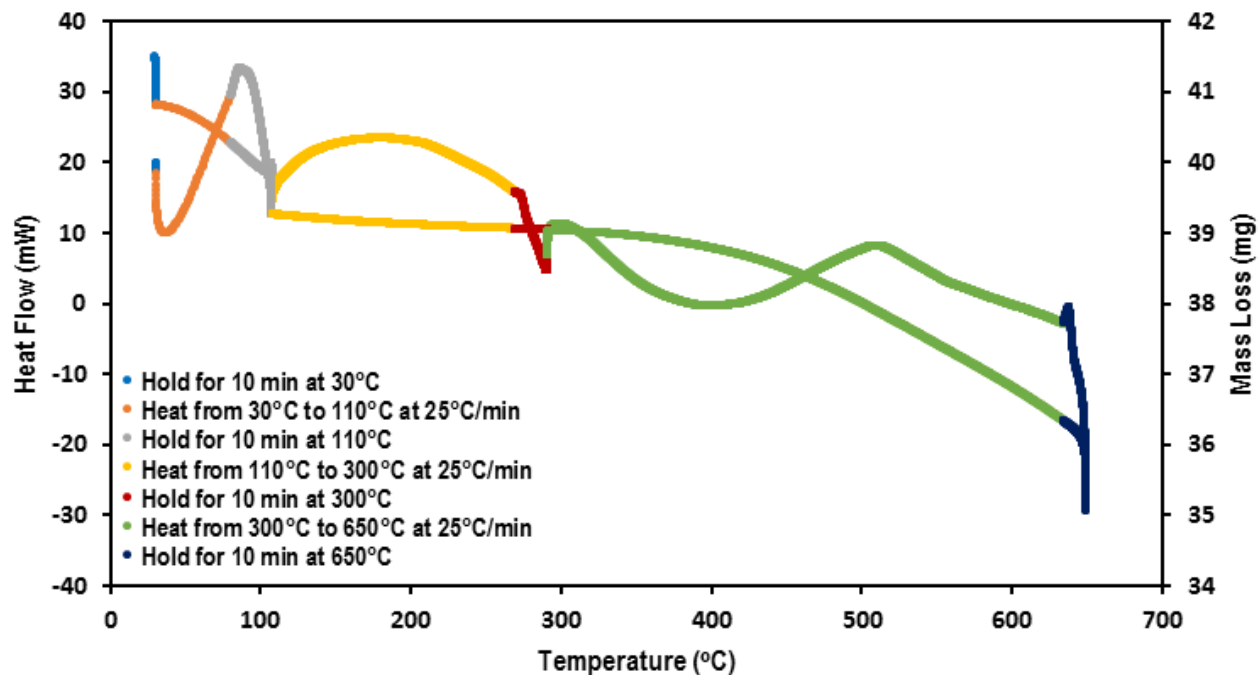
remaining after pyrolysis process, and the mineral carbon from the carbonate decomposition respectively. Endothermic and exothermic peaks are shown as a results of absorption and release of energy throughout the decomposition. During this phase, 23,27 wt.% of sample mass has been lost. Table 8 shows the total mass loss from the sample and the geochemical parameters determined during oxidation phase for sample SPM-006.

**Table 8. Geochemical Parameters determined during Oxidation Phase for Sample SPM-006**

SAMPLE	S4 (mg C/g rock)	S5 (mg CO <sub>2</sub> /g rock)
SPM-006	9,45	216,25

### 4.3.3 Sample PNC-008

This source rock sample corresponds to Vale das Fontes Formation. Figure 26 shows TG/DSC curves during pyrolysis stage for sample PNC-008.



**Figure 26. TG/DSC Curves during Pyrolysis Stage for Sample PNC-008**

Heat flow and mass loss curves are distinguished in Figure 26. The graph legend shows the complete temperature program followed through the entire experiment. Similarly to sample SPM-004 and SPM-006, a consider amount of mass is lost from the source rock sample during the first heating phase due to water evaporation between 30 °C to 110 °C. Simultaneously, an endothermic peak is appreciated it following the physical change, which means the sample absorbed energy as water evaporation took place. Then, a small amount of mass is lost during the thermo-evaporation of free hydrocarbons from bitumen (S1), followed by an endothermic process between 110 °C to 300 °C. It is appreciated how the sample

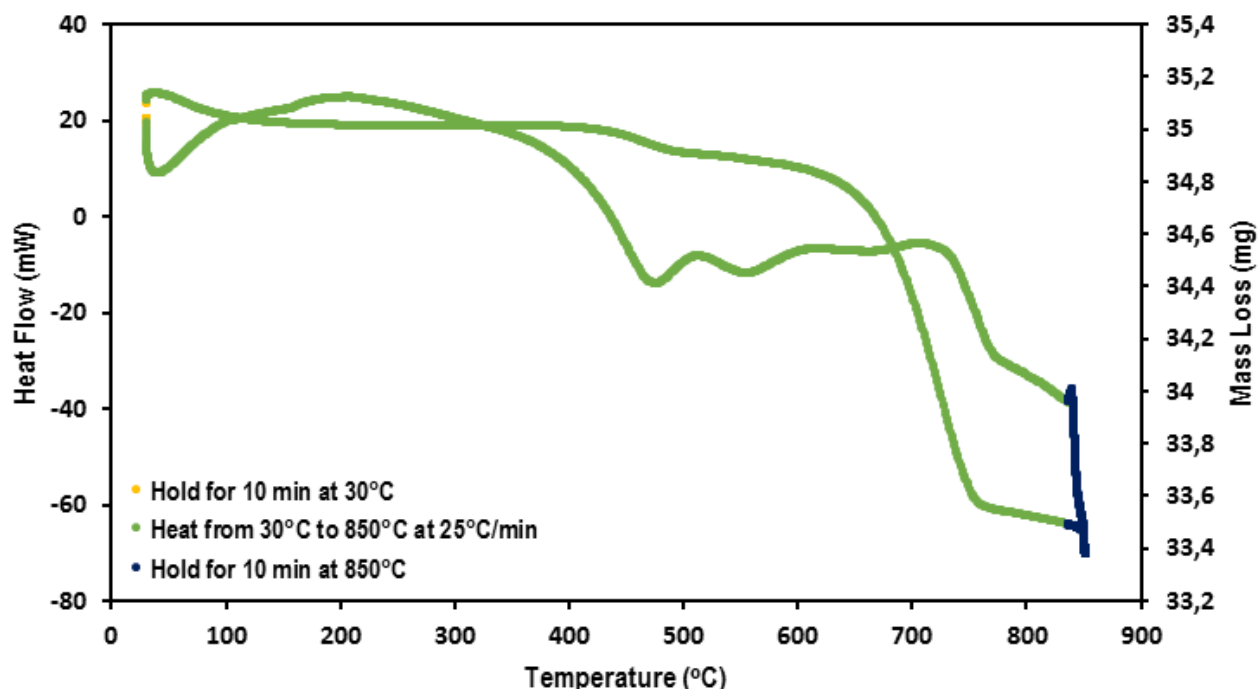
releases energy (exothermic process) during the isothermal phase at 300 °C. Between 300 °C to 650 °C, a new highly amount of mass is lost from the sample as a consequence of the thermal cracking of kerogen, releasing hydrocarbons (S2) and CO<sub>2</sub> (S3). At the same time, endothermic peaks are produced at that stages as a result of the energy absorbed from the sample during the chemical changes.

At the beginning of the experiment, the mass sample was 41,48 mg. During the experimentation, 15,68 wt.% of the sample mass has been lost. DSC curve shows that T<sub>max</sub> value corresponds to 512,13 °C. Table 9 shows the geochemical parameters determined during pyrolysis process for sample PNC-008.

**Table 9. Geochemical Parameters determined during Pyrolysis Phase for Sample PNC-008**

SAMPLE	S1 (mg HC/g rock)	S2 (mg HC/g rock)	S3 (mg CO <sub>2</sub> /g rock)	T <sub>max</sub> (°C)
PNC-008	6,3	40,97	62,68	512,13

Figure 27 shows TG/DSC curves during oxidation stage for sample PNC-008.



**Figure 27. TG/DSC Curves during Oxidation Stage for Sample PNC-008**

Heat flow and mass loss curves are distinguished in Figure 31. The graph legend shows the complete temperature program followed through the entire experiment. In this case, a little increase in mass is appreciated due to oxidation itself. Then, a notably amount of mass is lost between 600 °C and 750 °C. S4 and S5 are therefore calculated, corresponding to the residual carbon remaining after pyrolysis process, and the mineral carbon from the carbonate decomposition respectively. Endothermic and exothermic peaks are shown as a results of absorption and release of energy throughout the decomposition. During this

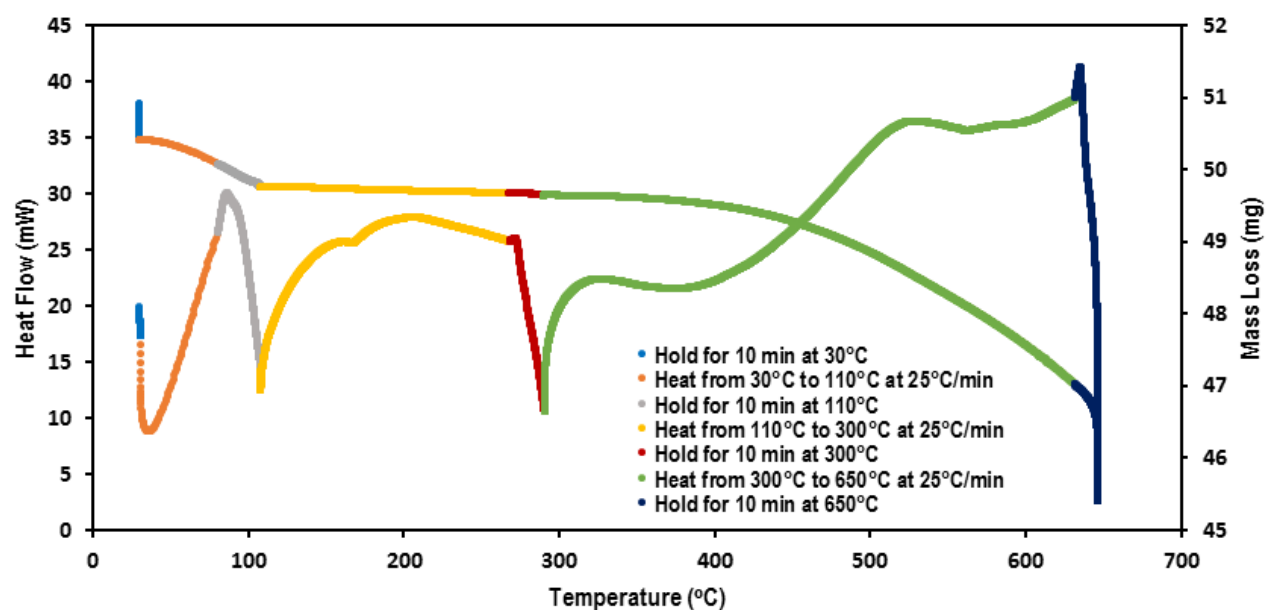
phase, 23,27 wt.% of sample mass has been lost. Table 10 shows the total mass loss from the sample and the geochemical parameters determined during oxidation phase for sample PNC-008.

**Table 10. Geochemical Parameters determined during Oxidation Phase for Sample PNC-008**

SAMPLE	S4 (mg C/g rock)	S5 (mg CO <sub>2</sub> /g rock)
PNC-008	10,16	39,5

#### 4.3.4 Sample PNC-009

This source rock sample corresponds to Vale das Fontes Formation. Figure 28 shows TG/DSC curves during pyrolysis stage for sample PNC-009.



**Figure 28. TG/DSC Curves during Pyrolysis Stage for Sample PNC-009**

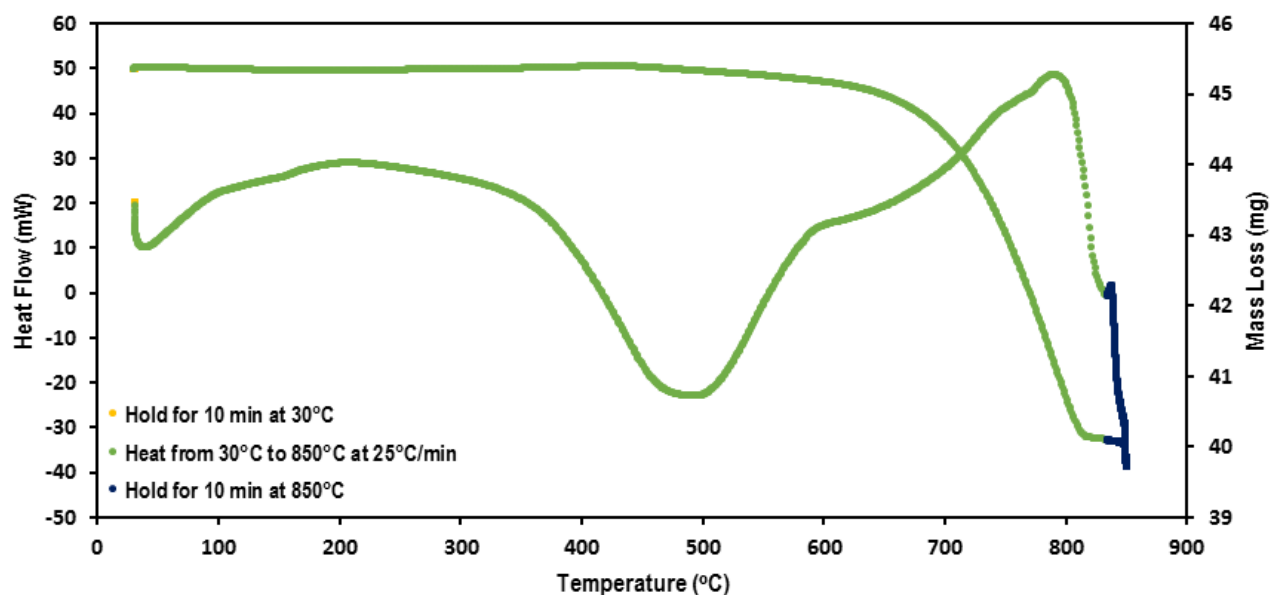
Heat flow and mass loss curves are distinguished in Figure 28. The graph legend shows the complete temperature program followed through the entire experiment. Similarly to sample SPM-004, SPM-006 and PNC-008, a consider amount of mass is lost from the source rock sample during the first heating phase due to water evaporation between 30 °C to 110 °C. Simultaneously, an endothermic peak is appreciated it following the physical change, which means the sample absorbed energy as water evaporation took place. Then, a small amount of mass is lost during the thermo-evaporation of free hydrocarbons from bitumen (S1), followed by an endothermic process between 110 °C to 300 °C. It is appreciated how the sample releases energy (exothermic process) during the isothermal phase at 300 °C. Between 300 °C to 650 °C, a new highly amount of mass is lost from the sample as a consequence of the thermal cracking of kerogen, releasing hydrocarbons (S2) and CO<sub>2</sub> (S3). At the same time, endothermic peaks are produced at that stages as a result of the energy absorbed from the sample during the chemical changes.

At the beginning of the experiment, the mass sample was 50,89 mg. During the experimentation, 11,04 wt.% of the sample mass has been lost. DSC curve shows that  $T_{max}$  value corresponds to 523,64 °C. Table 11 shows the geochemical parameters determined during pyrolysis process for sample PNC-009.

**Table 11. Geochemical Parameters determined during Pyrolysis Phase for Sample PNC-009**

SAMPLE	S1 (mg HC/g rock)	S2 (mg HC/g rock)	S3 (mg CO <sub>2</sub> /g rock)	T <sub>max</sub> (°C)
PNC-009	2,2	27,68	59,28	523,64

Figure 29 shows TG/DSC curves during oxidation stage for sample PNC-009.



**Figure 29. TG/DSC Curves during Oxidation Stage for Sample PNC-009**

Heat flow and mass loss curves are distinguished in Figure 29. The graph legend shows the complete temperature program followed through the entire experiment. Then, a notably amount of mass is lost between 650 °C and 820 °C. S4 and S5 are therefore calculated, corresponding to the residual carbon remaining after pyrolysis process, and the mineral carbon from the carbonate decomposition respectively. Endothermic and exothermic peaks are shown as a results of absorption and release of energy throughout the decomposition. During this phase, 12,6 wt.% of sample mass has been lost. Table 12 shows the total mass loss from the sample and the geochemical parameters determined during oxidation phase for sample PNC-009.

**Table 12. Geochemical Parameters determined during Oxidation Phase for Sample PNC-009**

SAMPLE	S4 (mg C/g rock)	S5 (mg CO <sub>2</sub> /g rock)
PNC-009	8,09	114,74

#### 4.3.5 Sample CXS-013

This source rock corresponds to Praia dos Coxos Formation. Figure 30 shows TG/DSC curves during pyrolysis stage for sample CXS-013.

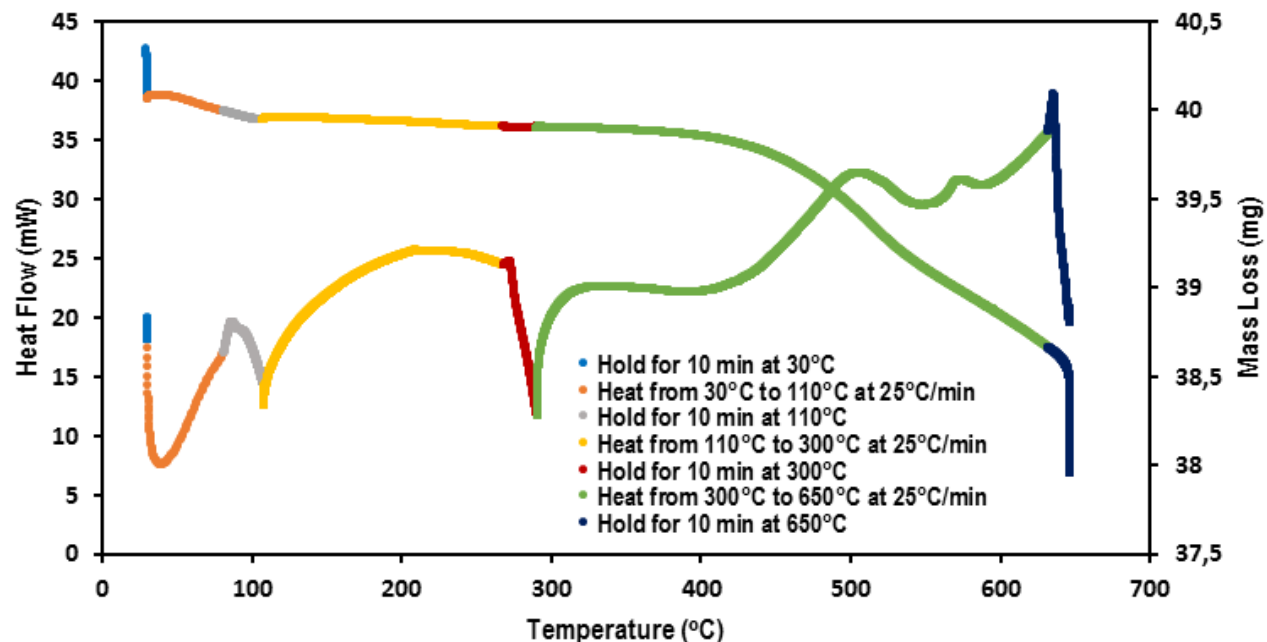


Figure 30. TG/DSC Curves during Pyrolysis Stage for Sample CXS-013

Heat flow and mass loss curves are distinguished in Figure 30. The graph legend shows the complete temperature program followed through the entire experiment. Similarly to sample SPM-004, SPM-006, PNC-008 and PNC-009, a consider amount of mass is lost from the source rock sample during the first heating phase due to water evaporation between 30 °C to 110 °C. Simultaneously, an endothermic peak is appreciated it following the physical change, which means the sample absorbed energy as water evaporation took place. Then, a small amount of mass is lost during the thermo-evaporation of free hydrocarbons from bitumen (S1), followed by an endothermic process between 110 °C to 300 °C. It is appreciated how the sample releases energy (exothermic process) during the isothermal phase at 300 °C. Between 300 °C to 650 °C, a new highly amount of mass is lost from the sample as a consequence of the thermal cracking of kerogen, releasing hydrocarbons (S2) and CO<sub>2</sub> (S3). At the same time, endothermic peaks are produced at that stages as a result of the energy absorbed from the sample during the chemical changes.

At the beginning of the experiment, the mass sample was 40,34 mg. During the experimentation, 6,35 wt.% of the sample mass has been lost. DSC curve shows that  $T_{max}$  value corresponds to 506,22 °C. Table 13 shows the geochemical parameters determined during pyrolysis process for sample CXS-013.

Table 13. Geochemical Parameters determined during Pyrolysis Phase for Sample CXS-013

SAMPLE	S1 (mg HC/g rock)	S2 (mg HC/g rock)	S3 (mg CO <sub>2</sub> /g rock)	T <sub>max</sub> (°C)
CXS-013	1,17	19,85	29,33	506,22

Figure 31 shows TG/DSC curves during oxidation stage for sample CXS-013.

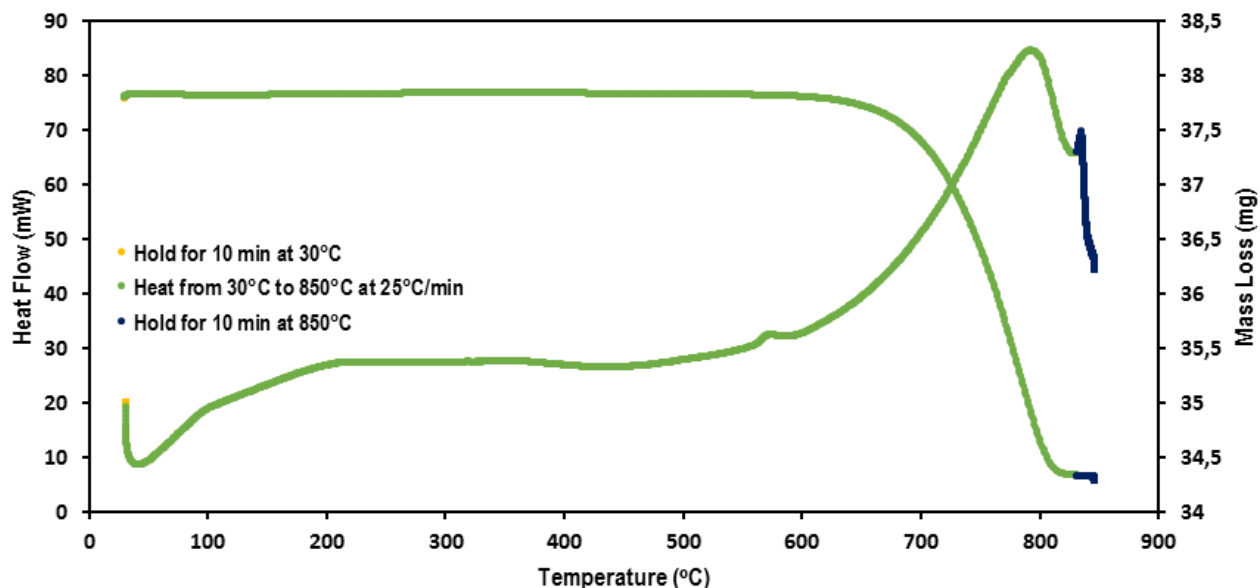


Figure 31. TG/DSC Curves during Oxidation Stage for Sample CXS-013

Heat flow and mass loss curves are distinguished in Figure 31. The graph legend shows the complete temperature program followed through the entire experiment. A notably amount of mass is lost between 660 °C and 810 °C. S4 and S5 are therefore calculated, corresponding to the residual carbon remaining after pyrolysis process, and the mineral carbon from the carbonate decomposition respectively. Endothermic and exothermic peaks are shown as a results of absorption and release of energy throughout the decomposition. During this phase, 9,65 wt.% of sample mass has been lost. Table 12 shows the total mass loss from the sample and the geochemical parameters determined during oxidation phase for sample CXS-013.

Table 14. Geochemical Parameters determined during Oxidation Phase for Sample CXS-013

SAMPLE	S4 (mg C/g rock)	S5 (mg CO <sub>2</sub> /g rock)
CXS-013	1,85	91,15

#### 4.3.6 Sample CXS-014

This source rock corresponds to Praia dos Coxos Formation. Figure 32 shows TG/DSC curves during pyrolysis stage for sample CXS-014.

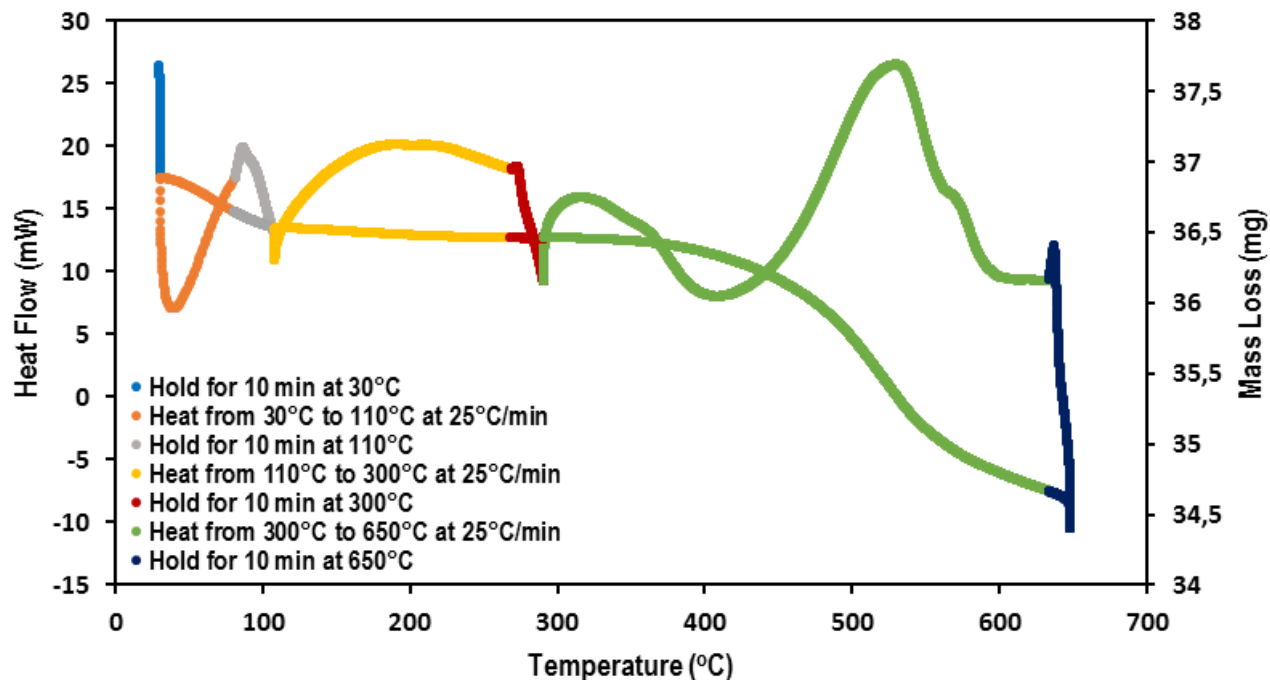


Figure 32. TG/DSC Curves during Pyrolysis Stage for Sample CXS-014

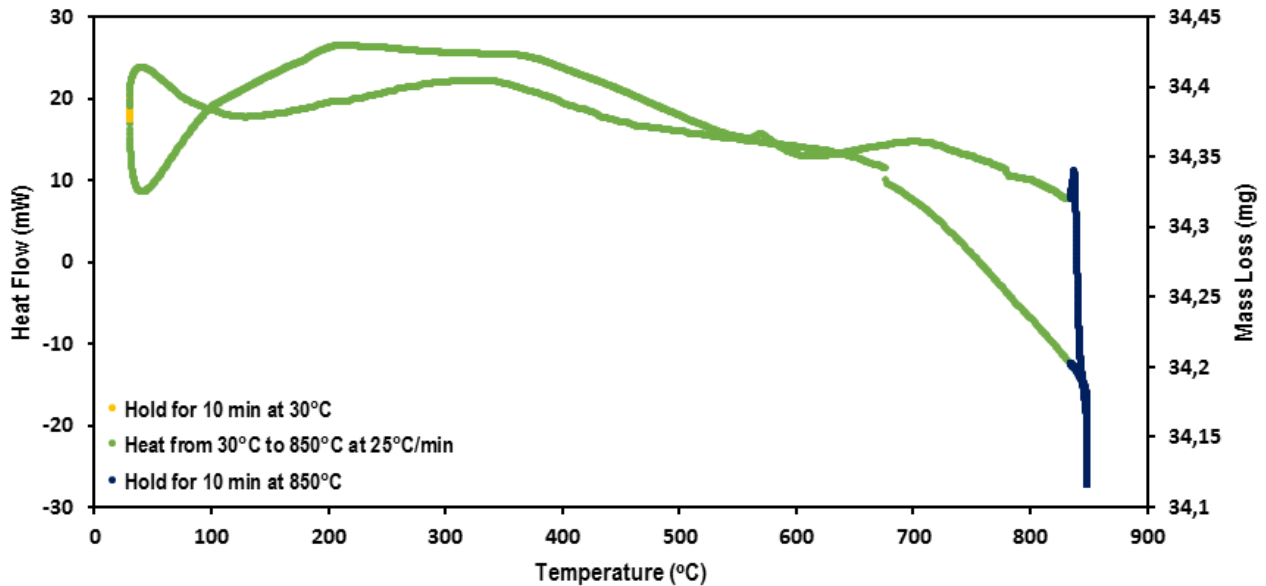
Heat flow and mass loss curves are distinguished in Figure 32. The graph legend shows the complete temperature program followed through the entire experiment. Similarly to sample SPM-004, SPM-006, PNC-008, PNC-009 and CXS-013, a consider amount of mass is lost from the source rock sample during the first heating phase due to water evaporation between 30 °C to 110 °C. Simultaneously, an endothermic peak is appreciated it following the physical change, which means the sample absorbed energy as water evaporation took place. Then, a small amount of mass is lost during the thermo-evaporation of free hydrocarbons from bitumen (S1), followed by an endothermic process between 110 °C to 300 °C. It is appreciated how the sample releases energy (exothermic process) during the isothermal phase at 300 °C. Between 300 °C to 650 °C, a new highly amount of mass is lost from the sample as a consequence of the thermal cracking of kerogen, releasing hydrocarbons (S2) and CO<sub>2</sub> (S3). At the same time, endothermic peaks are produced at that stages as a result of the energy absorbed from the sample during the chemical changes.

At the beginning of the experiment, the mass sample was 37,68 mg. During the experimentation, 8,91 wt.% of the sample mass has been lost. DSC curves shows that  $T_{max}$  value corresponds to 530,77 °C. Table 15 shows the geochemical parameters determined during pyrolysis process for sample CXS-014.

Table 15. Geochemical Parameters determined during Pyrolysis Phase for Sample CXS-014

SAMPLE	S1 (mg HC/g rock)	S2 (mg HC/g rock)	S3 (mg CO <sub>2</sub> /g rock)	$T_{max}$ (°C)
CXS-014	1,61	37,07	19,91	530,77

Figure 33 shows TG/DSC curves during oxidation stage for sample CXS-014.



**Figure 33. TG/DSC Curves during Oxidation Stage for Sample CXS-014**

Heat flow and mass loss curves are distinguished in Figure 33. The graph legend shows the complete temperature program followed through the entire experiment. A little increase in mass is appreciated due to oxidation itself. Then, a notably amount of mass is lost between 660 °C and 810 °C. S4 and S5 are therefore calculated, corresponding to the residual carbon remaining after pyrolysis process, and the mineral carbon from the carbonate decomposition respectively. Endothermic and exothermic peaks are shown as a results of absorption and release of energy throughout the decomposition. During this phase, 1,17 wt.% of sample mass has been lost. Table 12 shows the total mass loss from the sample and the geochemical parameters determined during oxidation phase for sample CXS-014.

**Table 16. Geochemical Parameters determined during Oxidation Phase for Sample CXS-014**

SAMPLE	S4 (mg C/g rock)	S5 (mg CO <sub>2</sub> /g rock)
CXS-014	1,08	6,78



## 5. DISCUSSIONS

In this chapter, a discussion of the results is described. An appropriate source rock evaluation is also presented. TG/DSC curves and its measurements achieved from the experiment have been taking into consideration, as well as the equations used to conclude an overall evaluation, not forgetting the corresponding assumptions.

Table 17 shows the source rock geochemical parameters determined during the completed experiment from TG/DSC analysis for each sample. TOM values vary from 5 wt.% to 10,66 wt.%. Sample PNC-008 has the highest TOM value whereas Sample CXS-013 has the lowest TOM value. TOC values vary from 2,73 wt.% to 6,65 wt.%. Sample PNC-008 has the highest TOC value, while sample CXS-013 has the lowest. S1 values vary from 6,3 mg HC/g of rock to 1,17 mg HC/g of rock. Sample PNC-008 has the highest S1 value, while sample SPM-004 has the lowest. S2 values vary from 18,6 mg HC/g of rock to 40,97 mg HC/g of rock. Sample PNC-008 has the highest S2 value, whereas sample SPM-006 has the lowest. S3 values vary from 20 mg CO<sub>2</sub>/g of rock to 72,2 mg CO<sub>2</sub>/g of rock. Sample SPM-004 has the highest S3 value, while sample CXS-014 has the lowest. S4 values vary from 1,08 mg C/g of rock to 10,16 mg C/g of rock. Sample PNC-008 has the highest S4 value, while sample CXS-014 has the lowest. S5 values vary from 6,78 mg C/g of rock to 216,25 mg C/g of rock. Sample SPM-006 has the highest S5 value, while sample CXS-014 has the lowest. HI values vary from 441,87 mg HC/g of TOC to 959,38 mg HC/g of TOC. Sample CXS-014 has the highest HI value, while sample SPM-006 has the lowest. OI values vary from 517,61 mg CO<sub>2</sub>/g of TOC to 1349,35 mg CO<sub>2</sub>/g of TOC. Sample SPM-006 has the highest OI value, while sample CXS-014 has the lowest. T<sub>max</sub> values vary from 505 °C to 530,77 °C. Sample CXS-013 has the highest T<sub>max</sub> value, while sample SPM-006 has the lowest. PP values vary from 20,67 kg/ton to 47,27 kg/ton. Sample PNC-008 has the highest PP value, while sample SPM-006 has the lowest.

**Table 17. Geochemical Parameters determined using TG/DSC Analysis for each Sample**

<b>SAMPLE</b>	<b>TOM (wt.%)</b>	<b>TOC (wt.%)</b>	<b>S1 (mg/g)</b>	<b>S2 (mg/g)</b>	<b>S3 (mg/g)</b>	<b>S4 (mg/g)</b>	<b>S5 (mg/g)</b>	<b>HI (mg HC/g TOC)</b>	<b>OI (mg CO<sub>2</sub>/g TOC)</b>	<b>T<sub>max</sub> (°C)</b>	<b>PP (kg/ton)</b>
<i>SPM-004</i>	10,66	5,4	3,38	31	72,2	5,76	100,8	574,18	1337,3	520,3	34,38
<i>SPM-006</i>	7,74	4,21	2,07	18,6	56,8	9,45	216,25	441,87	1349,35	505	20,67
<i>PNC-008</i>	11	6,65	6,3	40,97	62,7	10,16	39,5	616,14	942,93	512,13	47,27
<i>PNC-009</i>	8,92	4,91	2,2	27,68	59,3	8,09	114,74	564,17	1208,64	523,64	29,88
<i>CXS-013</i>	5	2,73	1,17	19,85	29,3	1,85	91,15	727,52	1073,87	506,22	21,02
<i>CXS-014</i>	5,86	3,86	1,61	37,07	20	1,08	6,78	959,38	517,61	530,77	38,68

## 5.1 Organic Richness and Petroleum Potential

Table 18 shows TOC values and its corresponding petroleum potential classification for each sample. Samples SPM-004/006 and PNC-008/009 have obtained an excellent organic richness and petroleum potential while samples CXS-013/014 have obtained a very good rate. It should be noted that sample PNC-008 has the highest petroleum potential, obtaining 6,65 wt.% TOC, while sample CXS-013 has the lowest, obtaining 2,73 wt.% TOC. Based on TOC results, it seems that no petroleum has been generated from the source rocks due to their relatively high TOC values, or they had higher TOC values and some of it has already been converted to hydrocarbons. Thus, it might indicate immature or early mature source rocks. Hence, if thermal maturation undergoes, and taking into account the positive results in terms of petroleum potential, more hydrocarbons generation might be expected for each sample. In any case, these results should be compared with others geochemical parameters already calculated such as S1, S2, and T<sub>max</sub>. Thus, based on TOC results, a further geochemical investigation is strongly suggested for each sample.

The relatively high TOC values are consistent with previous studies performed in Agua de Madeiros and Vale das Fontes Formations respectively (Duarte et al., 2012; Pena dos Reis & Pimentel, 2014; Spigolon et al., 2010). Nevertheless, TOC information has not been reported in Coxos Formation.

**Table 18. TOC Values and its corresponding Petroleum Potential Classification for each Sample**

	<b>SAMPLE</b>	<b>TOC (wt.%)</b>	<b>PETROLEUM POTENTIAL (QUANTITY)</b>
<i>1<sup>th</sup> Formation</i>	<i>SPM-004</i>	5,4	Excellent
	<i>SPM-006</i>	4,21	Excellent
<i>2<sup>nd</sup> Formation</i>	<i>PNC-008</i>	6,65	Excellent
	<i>PNC-009</i>	4,91	Excellent
<i>3<sup>d</sup> Formation</i>	<i>CXS-013</i>	2,73	Very Good
	<i>CSX-014</i>	3,86	Very Good

Table 19 shows S1 values and its corresponding petroleum potential classification for each sample. S1 represents the hydrocarbons already generated in the subsurface, but are expelled from the source rock during pyrolysis process.

In this case, second formation has the highest rating in terms of petroleum potential, specially sample PNC-008, which has an excellent S1 value of 6,3 mg of HC/g of rock. Third Formation has the lowest rating, obtaining a good petroleum potential in both samples. First Formation obtained a very good petroleum potential in both samples. Hence, based on S1 results, further investigation should be applied to each sample in order to compare and correlate the results.

S1 values are consistent with previous studies performed in Agua de Madeiros Formation (Duarte et al., 2012). Nevertheless, S1 information has not been adequate reported in Vale das Fontes and Coxos Formations.

**Table 19. Overall Results for each sample. S1 and its Petroleum Potential**

	<b>SAMPLE</b>	<b>S1 (mg HC/g rock)</b>	<b>PETROLEUM POTENTIAL (QUANTITY)</b>
<i>1<sup>th</sup> Formation</i>	<i>SPM-004</i>	3,38	Very Good
	<i>SPM-006</i>	2,07	Very Good
<i>2<sup>nd</sup> Formation</i>	<i>PNC-008</i>	6,3	Excellent
	<i>PNC-009</i>	2,2	Very Good
<i>3<sup>rd</sup> Formation</i>	<i>CXS-013</i>	1,17	Good
	<i>CSX-014</i>	1,61	Good

Table 20 shows S2 values and its corresponding petroleum potential classification for each sample. S2 corresponds to hydrocarbons released as a consequence of the thermal cracking of kerogen. It represents the amount of petroleum that might be generated from the source rock if thermal maturation undergoes. Thus, it is a key measurement in terms of petroleum potential.

In general, very good and excellent petroleum potential have been measured for the samples. PNC-008 and PNC-009 have the highest values corresponding to 40,97 mg HC/g of rock and 27,68 mg HC/g of rock, respectively. On the other hand, SPM-006 and CXS-013 have the lowest values corresponding to 18,6 mg HC/g of rock and 19,85 mg HC/g of rock, respectively. S2 results indicate that these source rock samples have shown excellent capabilities to generate petroleum if thermal maturation continues. Special attention should be given to sample PNC-008, which once again, it is demonstrating its excellent petroleum potential. Therefore, taking into account S2 results obtained, further investigation should be performed for each sample.

It should be noted that the relatively high S2 values are consistent with previous studies performed in Agua de Madeiros and Vale das Fontes Formations respectively (Duarte et al., 2012; Spigolon et al., 2010). Nevertheless, S2 information has not been reported in Coxos Formation.

**Table 20. Overall Results for each sample. S2 and its Petroleum Potential**

	<b>SAMPLE</b>	<b>S2 (mg HC/g rock)</b>	<b>PETROLEUM POTENTIAL (QUANTITY)</b>
<i>1<sup>th</sup> Formation</i>	<i>SPM-004</i>	31	Excellent
	<i>SPM-006</i>	18,6	Very Good
<i>2<sup>nd</sup> Formation</i>	<i>PNC-008</i>	40,97	Excellent
	<i>PNC-009</i>	27,68	Excellent
<i>3<sup>rd</sup> Formation</i>	<i>CXS-013</i>	19,85	Very Good
	<i>CSX-014</i>	37,07	Excellent

## 5.2 Thermal Maturation

Table 21 shows  $T_{max}$  values and its corresponding maturation level classification for each sample.  $T_{max}$  corresponds to the temperature at which the maximum amount of hydrocarbons are generated during

the thermal cracking of kerogen.  $T_{max}$  represents the thermal maturity of the organic matter. DSC signal has been used to track  $T_{max}$  values.

Maturity indicates the source rock ability to generate petroleum. DSC signal has shown  $T_{max}$  values higher than 500 °C, indicating postmaturity in each sample. Source rocks are said to be thermally postmature when they have entered at the gas window and have already generated petroleum. On the other hand, very good and excellent petroleum potential have been measured in the samples. Thus, high  $T_{max}$  values might suggest that these source rock samples have a considerable amount of organic matter that is hard to decompose, as well as they have already generated a large amount of petroleum. In addition, they still have a window for more hydrocarbons generation as it is indicated by TOC, S1 and S2 values.

$T_{max}$  values are not consistent with previous studies performed in Agua de Madeiros and Vale das Fontes Formation, where non-mature or early mature source rocks were reported (Duarte et al., 2012; Pena dos Reis & Pimentel, 2014; Spigolon et al., 2010). Thus, these cases should be further investigated in future studies to reach a proper evaluation, comparing with vitrinite reflectance measurements and  $T_{max}$  values from Rock-Eval apparatus.  $T_{max}$  information has not been reported in Coxos Formation.

**Table 21. Overall Results for each sample. Tmax and its Maturation Level**

	<b>SAMPLE</b>	<b><math>T_{max}</math> (°C)</b>	<b>MATURATION LEVEL</b>
<i>1<sup>th</sup> Formation</i>	<i>SPM-004</i>	520,3	Postmature
	<i>SPM-006</i>	505	Postmature
<i>2<sup>nd</sup> Formation</i>	<i>PNC-008</i>	512,13	Postmature
	<i>PNC-009</i>	523,64	Postmature
<i>3<sup>rd</sup> Formation</i>	<i>CXS-013</i>	506,22	Postmature
	<i>CSX-014</i>	530,77	Postmature

### 5.3 Kerogen Types

Table 22 shows HI values and its corresponding kerogen classification and main expelled product for each sample. HI corresponds to the amount of hydrogen contained within the kerogen. High HI values indicates greater potential to generate oil. It is useful to track kerogen type contained within the source rock and its thermal maturation.

Samples SPM-004/006 and PNC-009 contain type II kerogen. The general environment of deposition for this type of kerogen is marine. This samples were collected from Agua de Madeiros Formation, specifically from Praia de Lisa Member and Peniche, an absolutely marine environment. Type II kerogen is composed of mainly plankton with some contributions of algae. These samples are an oil-prone source rocks.

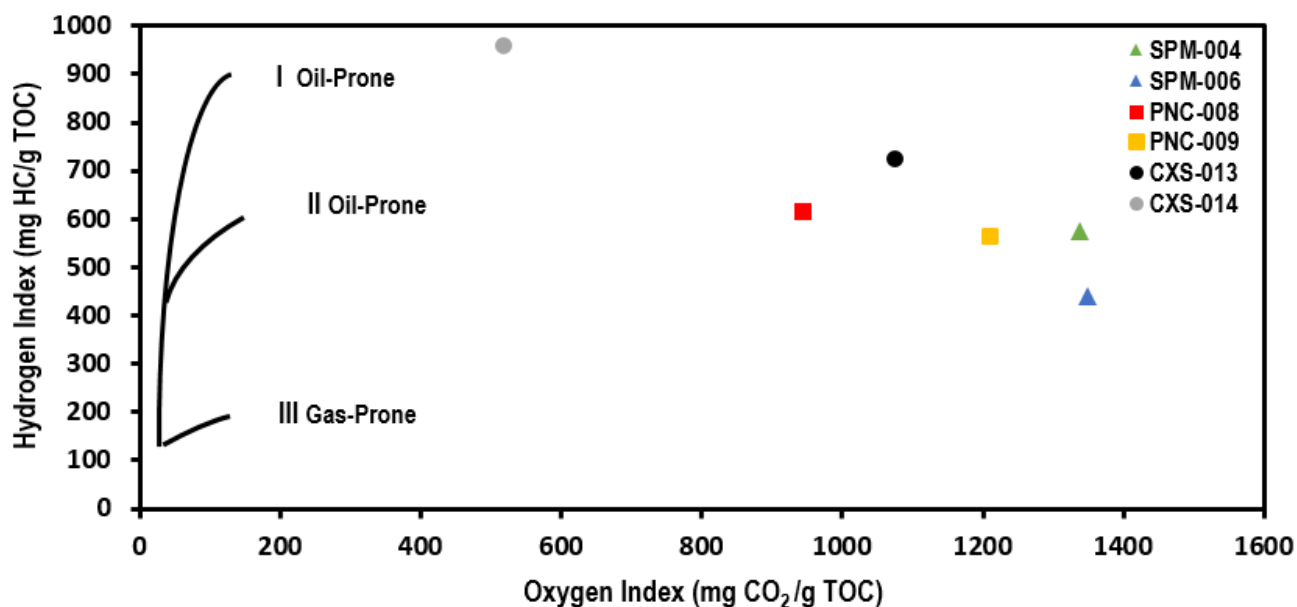
Samples PNC-008 and CXS-013/014 contain type I kerogen, which is composed of algae, plankton and other matter which were reworked by bacteria and microorganisms. It should be noted that all source rocks were collected from marine environments. Type I kerogen originates mainly from lacustrine environments, but it can also be originated from marine environments. These source rocks are oil-prone.

Kerogen type characterizations are consistent with previous studies performed in Agua de Madeiros and Vale das Fontes Formations respectively, where type I and II kerogen were reported (Duarte et al., 2012; Pena dos Reis & Pimentel, 2014; Spigolon et al., 2010). Nevertheless, kerogen type information has not been reported in Coxos Formation.

**Table 22. Overall Results for each sample. HI, Kerogen Type and its Main Expelled Product**

	SAMPLE	HI (mg HC/g rock)	KEROGEN TYPE	MAIN EXPELLED PRODUCT AT PEAK MATURITY
1 <sup>th</sup> Formation	SPM-004	574,18	II	Oil
	SPM-006	441,87	II	Oil
2 <sup>nd</sup> Formation	PNC-008	616,14	I	Oil
	PNC-009	564,17	II	Oil
3 <sup>rd</sup> Formation	CXS-013	727,52	I	Oil
	CSX-014	959,38	I	Oil

Figure 34 shows the Van Krevelen diagram determined by HI and OI parameters for each sample.



**Figure 34. Van Krevelen Diagram determined by HI and OI Parameters**

In this case, kerogen types are represented graphically using the corresponding Hydrogen and Oxygen Indexes. As it was mentioned in Table 23, samples SPM-004, PNC-008, PNC-009, CXS-013 and

CXS-014 are located within zone I kerogen. On the other hand, sample SPM-006 is located in zone II kerogen. High OI values indicate high amount of oxygen within the kerogen. As samples were collected from the outcrops, they are exposed the external environment, giving as a results those high S3 and OI values, indicating a strong influence of weathering. Thus, it is not recommended to related maturity to OI values.

## 6. CONCLUSIONS

TG/DSC analysis has shown to be a valuable technique within the geochemical source rock evaluation field, providing information regarding hydrocarbon generation potential, organic matter characterization and thermal maturation, as Rock-Eval apparatus. Thus, TG/DSC analysis provides preliminary information that can be completed and compared by other geochemical techniques. In addition, it is shown to be a relatively rapid method which can be used onsite location.

Several conclusions can be drawn based on the detailed analysis of the source rock samples, collected from three different outcrops within the Lusitanian basin, using TG/DSC analysis as a geochemical source rock evaluation technique.

High organic richness in general has been described in each sample, indicating high TOC values thus, a high petroleum potential. Agua de Madeiros and Vale das Fontes Formations show excellent petroleum potential whereas Coxos Formation has been classified as very good. Nevertheless, it should be noted that TOC contains residual carbon or as it is called “dead carbon”, which has not capacity to generate petroleum. Thus, S2 is a better petroleum potential indicator.

S1 values vary between good, very good and excellent petroleum potential as these are the hydrocarbons that have already been generated in the source rock. Sample PNC-008 has shown the highest petroleum potential, indicating an excellent petroleum generation ready to be expelled to the carrier system into the reservoir rock. On the contrary, samples from Coxos Formation have shown the lowest petroleum potential, which cannot be underestimated, as it is classified as good.

Based on S2 values, excellent and very good petroleum potential have been shown for the source rock samples. S2 represents the amount of hydrocarbons that can still be generated if thermal maturation undergoes. Again, sample PNC-008, from Vale das Fontes Formation, have shown an excellent petroleum potential, adding an enormous value to this particular sample. Overall S2 results indicate that these source rock samples have shown excellent capabilities to generate petroleum if thermal maturation continues.

Equally important to mention is the hydrocarbons migration interpretation. S2 (the amount of hydrocarbons which might be generated if thermal maturation continues) decreases when thermal transformation of kerogen increases. Prior to any hydrocarbon expulsion, the petroleum potential, quantified by S2, is transformed by natural cracking into thermo-vaporizable hydrocarbons, quantified by S1 (the amount of hydrocarbons which have already been generated in the subsurface). It should be noted that the hydrocarbons represented by S1 will eventually migrate out of the source rock throughout the carrier system into the reservoir rock. Thus, prior to any petroleum expulsion, S1 increases as S2 decreases. In this thesis work, the geochemical results have shown that S1 values are lower than S2 values in each source rock sample, which might be interpreted as hydrocarbons migrated out of the investigated source rocks into the carrier system.

DSC signal has been used for tracking  $T_{max}$  values, thus, indicating the thermal maturation of each source rock sample. Maturity indicates the source rock ability to generate petroleum. DSC signal has shown  $T_{max}$  values higher than 500 °C, indicating postmaturity in each sample. Source rocks are said to be thermally postmature, or spent source rocks, when they have entered at the gas window and have already generated petroleum. Another interpretation can be drawn. Very good and excellent petroleum potential have been reported in the samples, as indicated by TOC, S1 and S2. Thus, these high  $T_{max}$  values might suggest that these source rock samples have a considerable amount of organic matter that is hard to decompose. Furthermore, they have already generated a large amount of petroleum and there is a window for more petroleum generation.

With reference to the source rock type, all samples are potential source rock as they have shown petroleum potential. Due to their advanced thermal maturation, it is logical to think that they are spent source rocks, although they could be inactive rocks as they have shown very good and excellent petroleum potential. The difference between both of them is that inactive source rocks show petroleum potential but it stops generating petroleum whereas spent source rocks are said to be in postmature stage and can still generate wet or dry gas.

Kerogen types are described by HI parameter. Samples PNC-008 and CXS-013/014 contain type I, originated in a marine environment such as Agua de Vale das Fontes and Coxos Formation. These source rocks are classified as oil-prone. Samples SPM-004/006 and PNC-009 contain type II kerogen, also originated from a marine environment such as Agua de Madeiros and Vale das Fontes Formation. These source rocks are also classified as oil-prone.



## 7. FUTURE DEVELOPMENTS

Further investigations are considered to be applied to this thesis work, in order to compare and correlate results, as well as it would provide clues about the reliability of TG/DSC technique itself within the geochemical source rock evaluation field. Furthermore, those new studies would add value to the present work, thus an improvement in the evaluation and interpretation of the results would be expected. Several methods are described below for such purpose.

TG/DSC analysis cannot measure the volatile products evolved from the sample as a consequence of the physical and chemical changes due to the increment in temperature during the experiment. Thus, it is highly recommended to couple a Mass Spectrometer (TG/DSC-MS), a Fourier Transform Infrared Spectrometer (TG/DSC-FTIS) or a Gas Chromatograph (TG/DSC-GC) along with TG/DSC itself, in order to measure such volatile products (Hatakeyama & Liu, 1998). Including these techniques would measure, for instance, two important geochemical parameters such as S<sub>2</sub> and S<sub>3</sub>. Thus, the evaluation of the decarboxylation and depolymerization reactions would be clarified. The set of techniques in which the volatile products evolved from a sample are measured as a function of temperature is called Evolved Gas Analysis (EGA) (Hammer et al., 2013). For more on EGA techniques: Hatakeyama, T., & Liu, Z. (1998), *Handbook of Thermal Analysis*. Using EGA coupled with TG/DSC analysis would help to identify the evolved gases throughout the experiment.

The use of DSC signal can provide information about the energy needed to perform physical and chemical changes during the source rock evaluation. For instance, the energy required to breakdown the kerogen into smaller hydrocarbons can be calculated. On the other hand, it is important to mention the use of DTG signal. DTG is the derivative thermogravimetric curve and represents the rate of mass change when applying TG analysis. It is useful for tracking mass loss, which are difficult to detect by TG curve itself.

Equally important to mention is Rock-Eval technique, which has been widely used as a standard tool for hydrocarbon exploration (Lafargue et al., 1998), as it was developed by the Institut Français de Pétrole in partnership with Petrofina in the 1970's (Bordenave, 1993). Thus, the temperature program used in this research work has been standardized taking as a reference this source rock evaluation technique. Rock-Eval allows to measure the TOC content, the petroleum potential, the kerogen types and the thermal maturity. For more on Rock-Eval: Behar, Beaumont, & De B. Penteadó, 2001, *Rock-Eval 6 Technology: Performances and Developments*. Thus, it is strongly recommended to repeat the experiments for each sample and then, compare and correlate the results already obtained with TG/DSC analysis. Subsequently, a proper source rock evaluation would be provided, proving TG/DSC reliability.

TOC content is a strong indicator of the organic richness, as well as the ability of a source rock to generate hydrocarbons (Jarvie, 1991). Thus, a proper determination of this parameter is key in any geochemical source rock evaluation. In addition, other geochemical parameters can be calculated from it. TOC measurement is performed by combustion under air or oxygen atmosphere at temperatures range up

to 1500°C, depending on the method used. Furthermore, an acid treatment might be needed to reach a correct TOC measurement (Bordenave, 1993). For more on TOC measurements: Bordenave, M. L. (1993). *Applied Petroleum Geochemistry*. (Technip, Ed.). Paris. It should be noted that TOC content can be measured using TG/DSC analysis, but then, several geochemical parameters must be assumed due to the apparatus limitations. Thus, it is highly recommended to perform an individual TOC analysis for each source rock sample.

Vitrinite reflectance is another source rock evaluation tool used to assess the thermal maturation (Senftle & Landis, 1991). Vitrinite is a maceral found in coals and kerogens which is formed due to the thermal alteration of lignin and cellulose in plant cell walls. Vitrinite undergoes complex chemical reactions when temperature is increased, increasing its reflectance. Thus, reflectivity is measured under a microscope, using an oil-immersion objective lens and one photometer. This measurement is represented in percentage of light reflected in oil, named as  $R_o$  (McCarthy et al., 2011). The use of this technique in each source rock sample would provide a definitive and reliable measurement of the thermal maturation. Hence, it is highly recommended its usage.

The use of these techniques would provide a detailed geochemical source rock evaluation for each source rock sample. In addition, it would add valuable information comparable with TG/DSC technique results, as well as it would contribute with new information regarding their geological formations, especially in Coxos Formation, where no further investigation had been performed yet.

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