GEOCHEMICAL SOURCE ROCK EVALUATION IN THE LUSITANIAN BASIN (PORTUGAL) USING TG/DSC ANALYSIS

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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 Tmax values. Thus, a considerably amount of petroleum has already been generated from the source rock samples, 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.

Keywords: Organic Matter, Petroleum, Source Rock, TG/DSC Analysis

1. INTRODUCTION

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 [1]. Therefore, new energy challenges are needed to provide such amount of energy. 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 [1].

Even though oil prices have decreased significantly during the past few months, motivated by an oversupply, the financial crisis and an unstable world market [2], the searching for new reserves, as well as continuous investments must be done in order to reach the global oil demand for the future.

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 [3]. Thus, with the appropriate conditions such as thermal evolution, geological time and burial depth, the organic matter can produce oil and gas [4]. Depending of the amount and type of the organic matter deposited in the source rock, the quantity and nature of petroleum generated are different [3].

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 [3]. TG/DSC analysis is a

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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 [5]. 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 [6].

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 [7]. 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? 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 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.

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.

2. METHODOLOGY

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 [8]. Figure 1 shows a Perkin-Elmer STA 6000 Simultaneous Thermal Analyzer.

Figure 1. TG/DSC STA 6000 Simultaneous 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 [9]. In addition, the sample and experimental conditions are the same if both techniques are used simultaneously, providing comparative data and saving testing time [10].

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 [8]. 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 [9]. 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.

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 [11]. 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 [6], [12].

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 [8], [9]. 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 [9]. 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 [11]. 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.

The apparatus used for the purpose of the thesis is a Perkin-Elmer STA 6000 simultaneous thermal analyzer shown in Figure 1, and the corresponding Pyris software [13]. 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 N2. 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.

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

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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.

The temperature program is established using Pyris software [13], 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. Penteado, 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, N2 Atmosphere:

1. Hold for 10 min at 30 ^{o}C
2. Heat from 30 ^{o}C to 110 ^{o}C at 25 ^{o}C /min
3. Hold for 10 min at 110 ^{o}C
4. Heat from 110 ^{o}C to 300 ^{o}C at 25 ^{o}C /min
5. Hold for 10 min at 300 ^{o}C
6. Heat from 300 ^{o}C to 650 ^{o}C at 25 ^{o}C /min
7. Hold for 10 min at 650 oC
8. Cool from 650 ^{o}C to 30 ^{o}C at 25 ^{o}C /min

Oxidation Process, Air Atmosphere:

1. Hold for 10 min at 30 ^{o}C
2. Heat from 30 ^{o}C to 850 ^{o}C at 25 ^{o}C /min
3. Hold for 10 min at 850 ^{o}C
4. Cool from 850 ^{o}C to 30 ^{o}C at 25 ^{o}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, CO2 and CO [14]. Thus, to avoid any misunderstanding, the nomenclature used in Rock-Eval Pyrolysis such as S1, S2, S3, S4, S5,

T_{max}, 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 2 illustrates the controlled temperature program used in each experiment for the overall process. Parameters such as S1, S2 and S3 are calculated by mass loss during the programmed heating phase. A heating rate of 25 ^{o}C /min is set for each phase transition.

Firstly, the sample is heated from 30 ^{o}C to 110 ^{o}C in order to vaporize any water contained in the source rock sample [8]. 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 thermo-vaporization process quantified by S1, occurring between 110 ^{o}C and 300 ^{o}C [15]. 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 between 300 ^{o}C and 650 ^{o}C. This is quantify by S2 and S3 respectively (Behar et al., 2001).
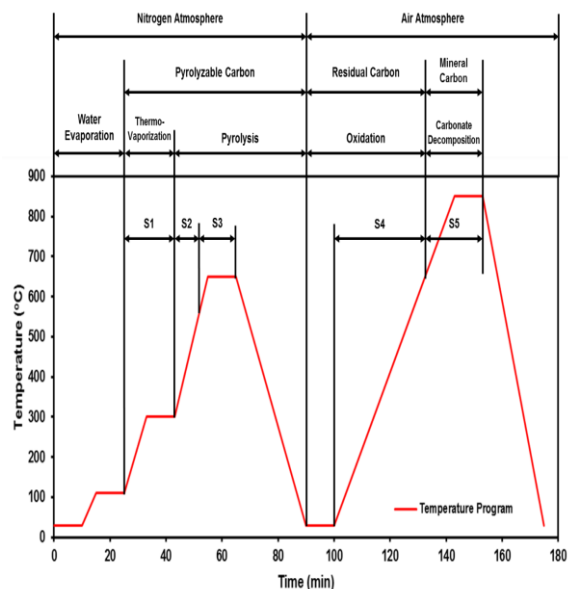

Figure 2. Overall Temperature Program used in TG/DSC Experiment

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 [16]. 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 [15]. In another words, S2 measures the source rock potential for generating hydrocarbons if thermal maturation undergoes. Equally important is Tmax value, which is related to S2. Tmax is the temperature at which the maximum amount of hydrocarbons are generated during the thermal cracking of kerogen. Tmax represents the thermal maturity of the organic matter [14]. 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, Tmax is reached when a peak in DSC signal is measured within the S2 mass loss range.

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 ^{o}C to 650 ^{o}C (Behar et al., 2001). S5 represents the mineral carbon from the carbonate decomposition of the source rock, between 650 ^{o}C to 850 ^{o}C [14]. Figure 20 shows the overall temperature program, representing all the stages in which the source rock sample is subjected during the entire experiment.

3. RESULTS AND DISCUSSIONS

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 km2 [17] and its sedimentary thickness is approximately 5 km [18]. 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

[17]. Figure 3 shows the Lusitanian basin location, as well as the place where the samples were collected (red arrow).
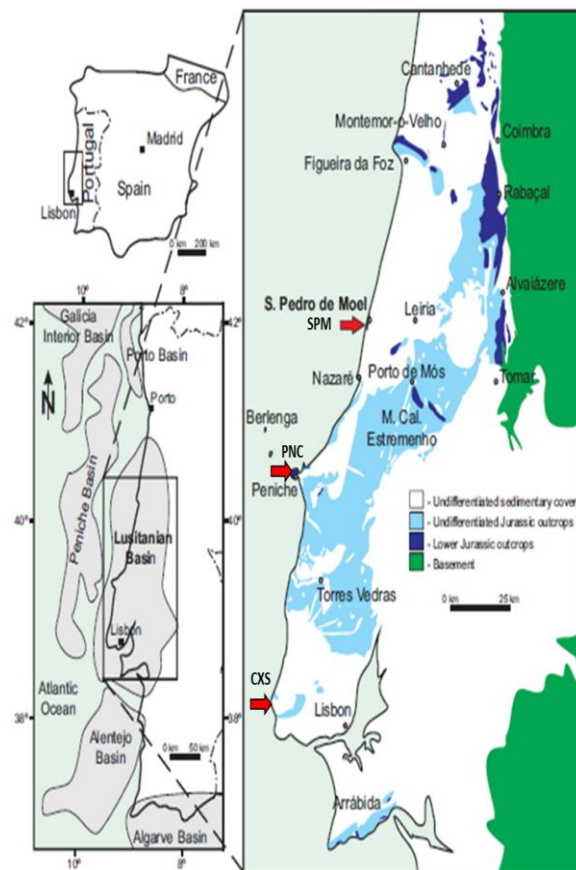

Figure 3. Lusitanian Basin Location (Modified from Ribeiro & Chagas, 2012)

3.1 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.

Samples SPM-004/006 correspond to Água de Medeiros Formation (in Portuguese Formação Água de Medeiros - 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 [17].

Samples PNC-008/009 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 [17].

Samples CXS-013/014 correspond 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.

3.2 SAMPLE RESULTS AND EVALUATIONS

Table 1 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 CO2/g of rock to 72,2 mg CO2/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. lowest. T_{max} values vary from 505 oC to 530,77 oC. Sample CXS-013 has the highest T_{max} value, while sample SPM-006 has the lowest.

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_{max}. Thus, based on TOC results, a further geochemical investigation is strongly suggested for each sample.

Table 1 Geochemical Parameters determined using TG/DSC Analysis for each Sample

SAMPLE	TOM (wt.%)	TOC (wt.%)	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	S4 (mg/g)	S5 (mg/g)	T_{max} (ºC)
SPM-004	10,66	5,4	3,38	31	72,2	5,76	100,8	520,3
SPM-006	7,74	4,21	2,07	18,6	56,8	9,45	216,25	505
PNC-008	11	6,65	6,3	40,97	62,7	10,16	39,5	512,13
PNC-009	8,92	4,91	2,2	27,68	59,3	8,09	114,74	523,64
CXS-013	5	2,73	1,17	19,85	29,3	1,85	91,15	506,22
CXS-014	5,86	3,86	1,61	37,07	20	1,08	6,78	530,77

With reference to S1 values, the second formation has the highest rating in terms of petroleum potential, specially sample PNC-008, which has an excellent 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.

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 when looking S2 values. 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.

Maturity indicates the source rock ability to generate petroleum. DSC signal has shown T_{max} values higher than 500 ^{o}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 Tmax values might suggest that theses 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.

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.

4. 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 systems into the reservoir rock. On the contrary, samples from Coxos Formation have shown the lowest petroleum potential, which cannot be underestimated, as it is classifies 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 ^{o}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 theses 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 advance 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 stop generating petroleum whereas spent source rock are said to be in postmature stage and can still generate wet or dry gas.

Kerogen types are describe 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.

5. 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 method 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 S2 and S3. Thus, the evaluation of the decarboxylation and depolymerization reactions would be clarify. 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 [19]. 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. Penteado, 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 [20]. 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 [19]. 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 [21]. 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 Ro [15]. 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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