

Study of water-oil interface (exchange of compounds) by potentiometric titrations, FTIR and mass spectroscopy

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ABBREVIATIONS

ESI: Electrospray ionization

FTIR: Fourier transform infrared spectroscopy

HPLC: High performance liquid chromatography

IR: Infrared

LiCl: lithium chloride

MS: Mass spectrometry

NA: Naphthenic acid

S.A.R.A.: Saturated, aromatic, resins and asphaltenes

SAT: Saturated

TAN: Total acid number

TBAH: Tetrabutylammonium hydroxide.

UPLC: Ultra performance liquid chromatography

W/O: Water/oil

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1. INTRODUCTION

1.1. CONTEXT

Petroleum is the main source of energy in developed countries, despite the development of other sources such as nuclear, hydroelectric or renewable energies. In 2013, petroleum demand showed a new historical hit, around 90 millions of barrels per day according to International Energy Agency (IEA) and Opep, which supposed to triple the demand levels for half a century, when normally it was growing in a continuous way, 54 millions in 1975, 59 millions in 1985, etc... Despite the crisis, it was possible that consumption has continued growing in the last decades, and therefore the fossil energies will continue dominating the global market; although petroleum can be followed by coal and natural gas[1].

Regarding to the geographical distribution of consumers, (*Figure 1*) in the twentieth century, United States started being the main consumer of petroleum, following by Europe, but nowadays countries from Asia-Pacific region are on the top of the consumer list[2].

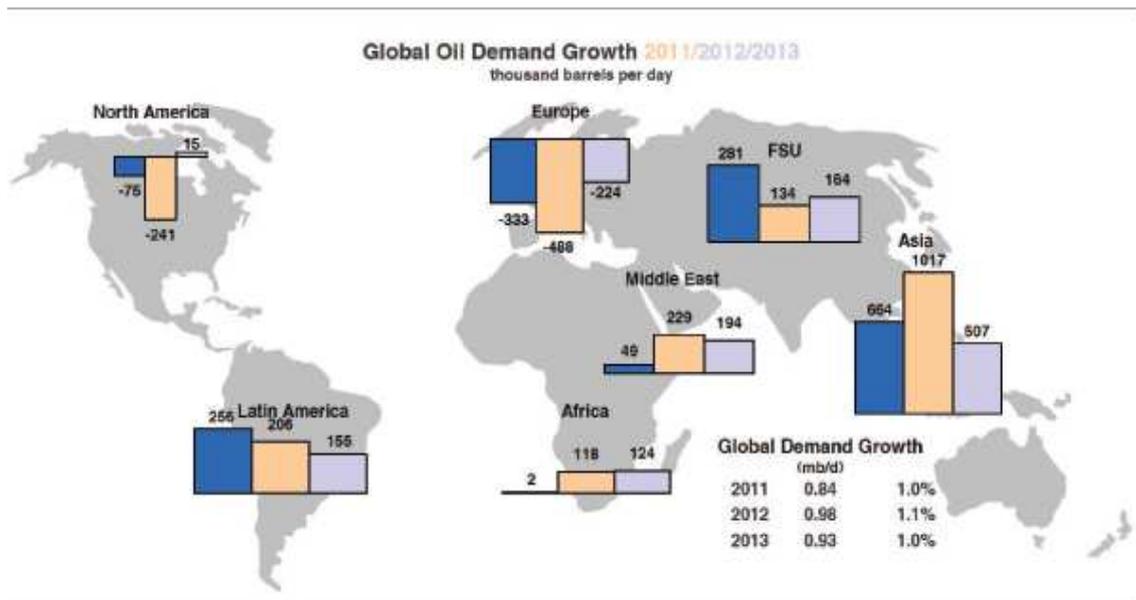


Figure 1 : Global Oil Demand[2].

This source of fossil energy is used in several and diverse fields such as transports, heating and cooling or in the generation of electricity, due to his high energetic content. In addition to these direct applications, oil is also employed in the obtaining of all types of industrial and consumer products (*Figure 2*) such as plastics, textiles or certain products of the cosmetic industry[3].

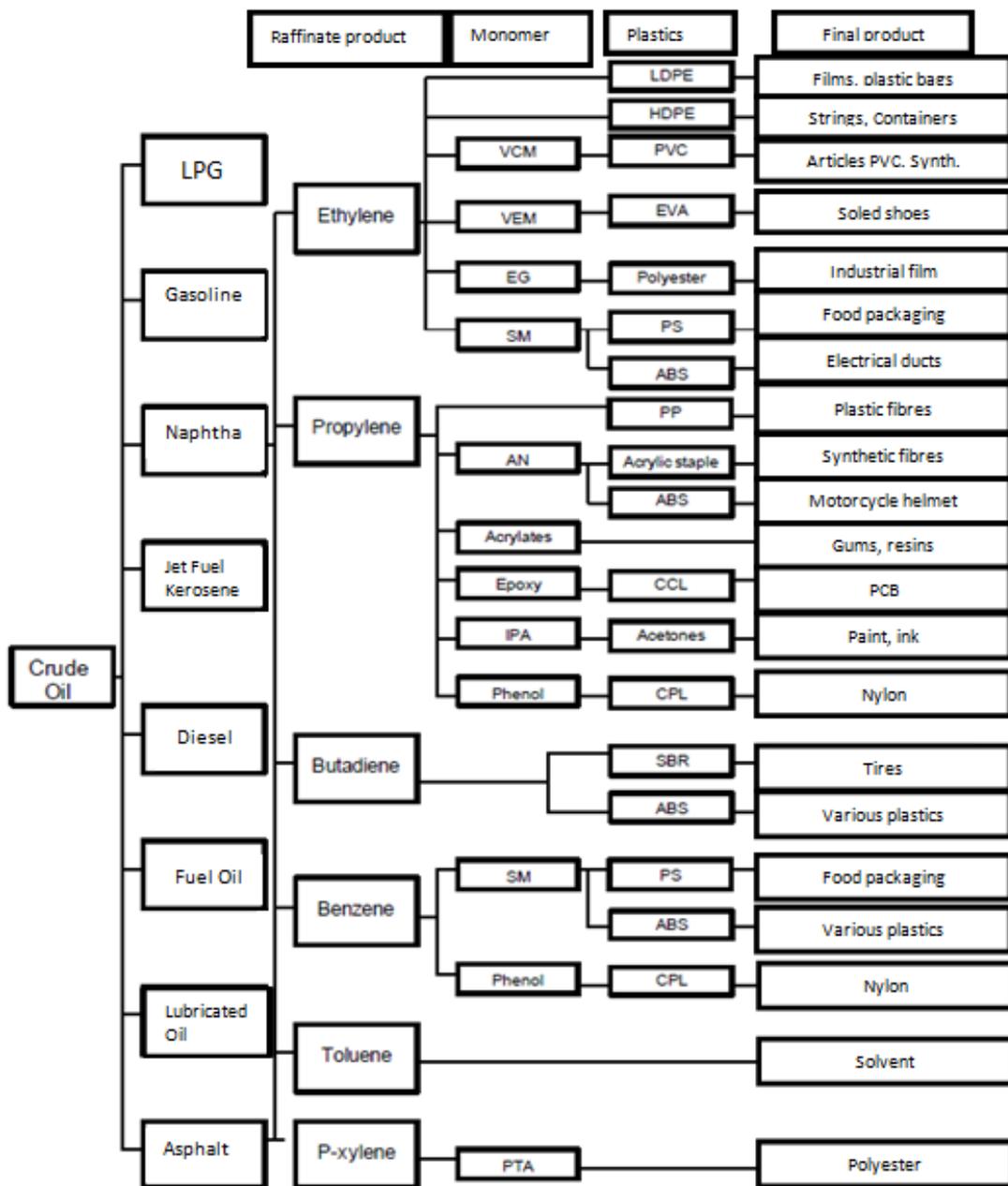


Figure 2 :Table summarizing the main products of petroleum processing[3].

As shown in this graphic, crude oil is present in all type of materials and such is its importance than an increase of oil price, can induce variations and a strong impact in both the local and the global economy.

1.2. DEFINITIONS

Crude oil is a homogeneous mixture of organic compound, mainly water insoluble hydrocarbons of various molecular weights which could contain aromatic rings. In addition, small amounts of N, O, S and metals (Ni and V) are also found.

It is generated by transformation of accumulated organic matter like zooplankton and algae and it is found in geological formations beneath the Earth's surface, buried for millions of years and also it can be accumulated in natural geological traps, from which is extracted by drilling wells (*Figure 3*). This cumulated matter is called **kerogen** and is mixed with mineral sediments to form the bedrock[4].

These sediments suffer different physical and chemical processes. In between 2500 and 5000m depth, environmental temperatures permit the thermal cracking of kerogen in petroleum hydrocarbons. Even at greater depth, it can be cracked in gas[4]. After, and because of the lower density and rock's porosity, petroleum goes up. In case of impermeable rock the products could not ascend and deposits will be formed, that is called "*oil trap*". Otherwise, they may eventually seep to the surface and form oil pools (*Figure 4*), we can find some examples in Venezuela and the Middle East.

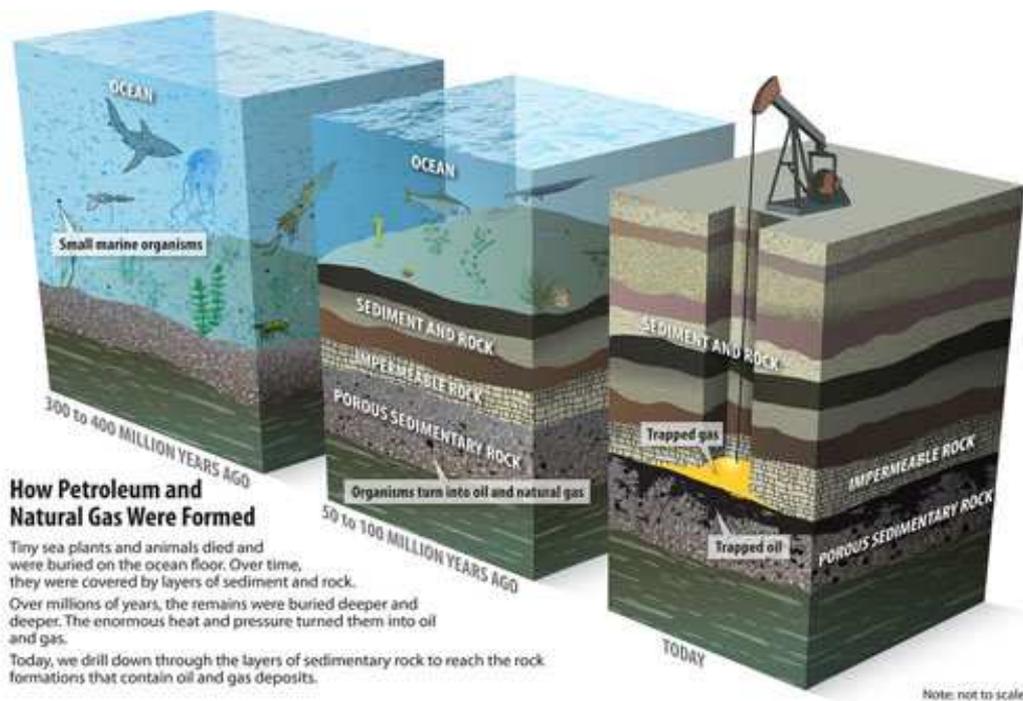


Figure 3 : Petroleum formation[5].

In *Figure 4*, it is showed the route travelled by oil leaving the subseafloor reservoir as it travels through the water column to the surface, and finally falls back to the seafloor where it remains in the sediment[6].

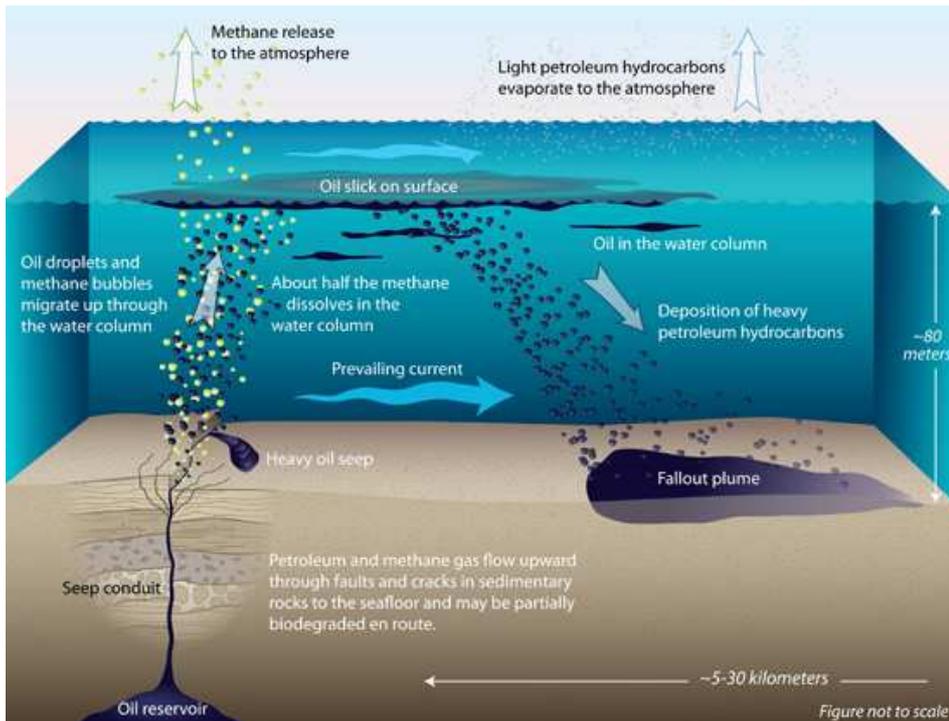


Figure 4 : Naturally seeping oil in the ocean[6].

Analyze the composition of a crude oil requires a **separation process**. The large number and variety of molecules that are part of it, make not possible the characterization of the individual molecular types, so hydrocarbon group type analysis is normally employed[7].

In this type of separations, crude oil is divided in **four families** based on differences in solubility and polarity regrouped into the following acronym **S.A.R.A**, which means Saturated, Aromatic, Resins and Asphaltenes[7],[8].

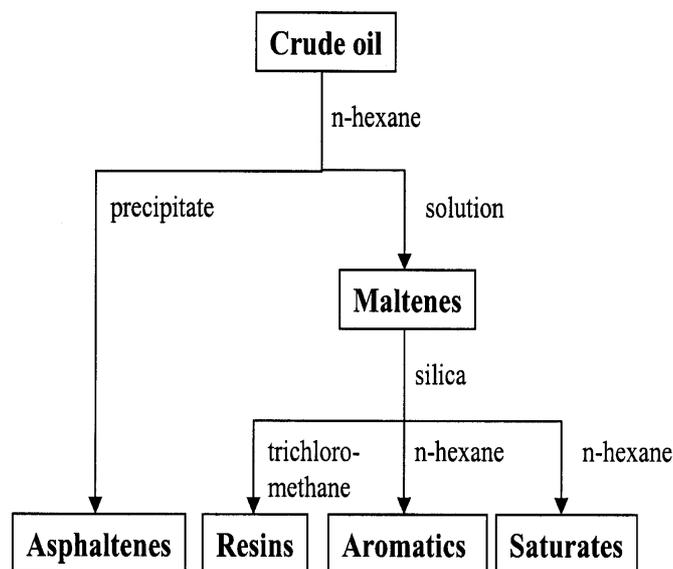


Figure 5 : S.A.R.A. separation scheme[7].

Within the family of **saturated**, non polar compounds not containing double bonds are found, consist of waxes and paraffins, these last ones could be cyclic or branched[7],[8]. **Aromatic** fraction is soluble in n-hexane and contains aromatic benzene rings, which can be linked up with naphthenic rings and/or aliphatic side chains[7]. **Resins** include molecules with the highest molecular weights and with the strongest polar behaviour, due to the presence of heteroatoms such as N, O or S. They are soluble in light alkanes, such as n-pentane, n-hexane or n-heptane, but they are insoluble in liquid propane. In this fraction, molecules with a carboxylic function can be found; such molecules are called naphthenic acids. The last group, **asphaltenes**, they are insoluble in light alkanes but they are soluble in toluene or benzene. N, O and S along with organometallic constituents such as Ni, V and Fe can be found in this fraction, giving to it a polar character. Their structure consists of polycyclic aromatic clusters, substituted with varying alkylside chains, and probably is responsible for this high viscosity[7],[9]. Due to polar character of both, Asphaltenes and Resins, they are able to form aggregates so that they are less volatile and that is why they are mainly located in high boiling point fractions.

In this procedure, asphaltenes are precipitated while the others fractions elute with appropriated solvents [10]. Resins can be separated by diluting crude oil with highly polar solvents such as trichloromethane. Saturated could be separated using solvents as n-hexane[8] through silica columns and aromatics with toluene.

Taking into account the above mentioned points, crude oil can be divided in two general groups, light fractions and heavy fractions. In the first ones, (Saturated and Aromatic) hydrocarbon structures are mainly aliphatic, while in the heavy fractions (Resins and Asphaltenes) rather include **naphthenic acids**, aromatic structures with more than six alkylated cycles and molecules containing more than 25 carbon atoms (C₂₅). Heavy crude oil presents specific characteristics such as high viscosity and significant content of heteroatom, which are related with the major presence of resins and asphaltenes[8].

1.3. INTEREST

1.3.1. PROBLEMS IN PETROLEUM EXTRACTION AND REFINING

Crude oil production is connected the most of the time to water production from the deposits. Owing to different processes during the transport of both immiscible fluids, an emulsion of water in oil is produced. They can be separated naturally in a few seconds or by the contrary, in some cases, if no treatment is applied; several weeks are needed to do it[7].

An **emulsion**[11] is a fluid colloidal system in which liquid droplets and/or liquid crystals (dispersed phase) are dispersed in a liquid matrix (continuous phase). Between both phases of an emulsion is found the interface, where different exchanges of compound take place, and its properties control the formation and stabilization of the emulsions.

Emulsions can be named as oil/water (O/W) emulsion, (when the dispersed phase is an organic material and the continuous phase is water or an aqueous solution) or Water/oil (W/O) emulsion (if the dispersed phase is water or an aqueous solution and the continuous phase is an organic liquid, such as oil)[11].

In the interface, molecules tend to be placed to minimize the interfacial energy, so a high interfacial energy stimulates a diminution of interfacial area causing the coalescence, which is the disappearance of the boundary between two particles in contact[11]. Otherwise, the presence of chemical products, called as surfactants, facilitate the interfacial tension reduction in between these two phases and therefore the emulsion formation. These molecules must be placed in the interface and they must have affinity for both of them. Due to the different behaviour between water and oil, the first one is polar and the other is generally apolar, the surfactant has to consist in two parts, one polar (hydrophilic) and the other apolar (hydrophobic) (*Figure 6*).

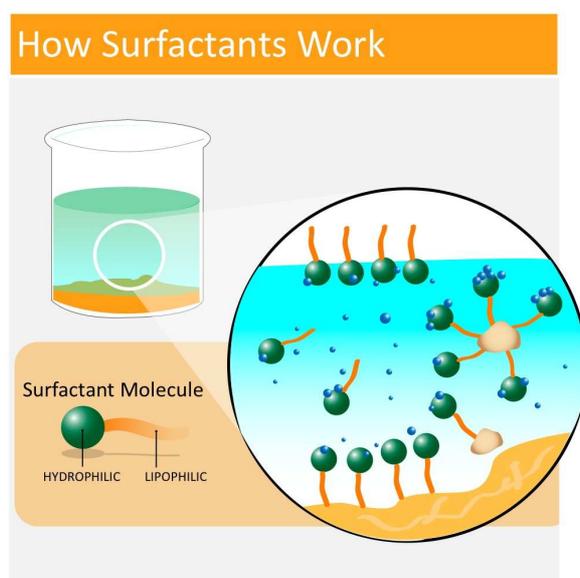


Figure 6 : Action mode of a surfactant[12].

A real problem exists, as these emulsions can affect to the production and the refining step. From the point of view of the production, there is an increase of the production costs owing to the facilities, treatments products or lower yields due to the duration of the processing operations. Furthermore, it is important to satisfy the required specifications for the maximum water content (less than 0,5%)[7] in order to sell the crude oil to the refineries. In fact, separation must be complete between both phases, if this not happens, crude oil can contain a significant amount of water (dispersed as fine droplets). Finally environmental problems must be taken into account, since water, normally used for secondary recovery phase by reinjection into the pool, can be released into nature. The presence of crude oil droplets can difficult the cleaning treatment. Taking into account the refining step, distillation units can be corroded or catalysts can be poisoned in the cracking operation[7],[8].

Petroleum industry must identify chemical compounds responsible for the stability of the W/O emulsions formed and studied the mechanisms of formation and stabilization of them. Possible responsible for the formation and stabilization of the emulsions are the natural surfactants presents in crude oil which are asphaltenes and naphthenic acids but their effects is not clear yet, specially in real systems, since in many studies the compounds are studied alone out of their natural environment. According to the bibliography, comparing both types of emulsions, those caused by asphaltenes are more stable, because asphaltenes form a rigid film between water and oil[13]. Also pH[14] has an important role in stabilizing emulsions; it is up to him that asphaltenes or naphthenic acids are responsible of this stabilization. At low pH, asphaltenes are the responsible of the stabilization because just a small quantity of acids is ionized, by contrast at high pH; naphthenic acids are responsible because they increase the ionized form[15].

Other important problem, which can affect to crude oil production, is the formation of aggregates or deposits of asphaltenes, caused by their polydispersity[16]. The aggregation state of asphaltene macromolecules strongly depends on the experimental conditions (concentration, temperature and solvent)[8]. Asphaltene deposits can be produced either during the transport and the storage of these heavy fractions[8]. Normally, they are accumulated inside the pipes, decreasing the diameter of them and avoiding the transport of crude oil (*Figure 7*)[17].



Figure 7 : Asphaltene deposits inside the pipes[18].

It cannot forget, problems caused by deposits of calcium naphthenate (*Figure 8*). Their precipitation causes the obstruction of pipes and separation units. This sort of deposits is typical of crude oil with high concentration of naphthenic acids.



Figure 8 : Calcium naphthenate deposits in crude oil processing equipment[19].

Therefore, it is necessary to avoid these abovementioned problems in order to ensure a process as profitable as possible.

1.3.2. NAPHTHENIC ACIDS

As it was explained before, naphthenic acids since they are interfacially active and absorbed at water/oil interfaces to form monolayer or other colloidal structures[20] are responsible for the stabilization of emulsions in crude oils, not only that happens, but also they are toxic to animal and aquatic life (Natural groundwater levels of naphthenic acids in the region lie between $<4\text{mgL}^{-1}$ in near-surface aquifers and $>55\text{mgL}^{-1}$ in basal and limestone aquifers)[21] since they are weakly biodegradable and it is difficult to remove them from the environment, so first of all, it is important to explain what the naphthenic acids are, as they represent a large amount within the total content of acids.

Naphthenic acids are carboxylic acids with a number of carbon atoms varying from six to thirty, whose structure is R-COOH, where R could be fused saturated ring structures such as cyclopentyl or cyclohexyl rings[22], it is also possible to observe other structures[23],[24] such as linear acids where R is an aliphatic hydrocarbon chain or polyaromatic structures characteristic of asphaltenes and the carboxylic acid group is apparently attached to a side chain rather than directly to the ring [25].

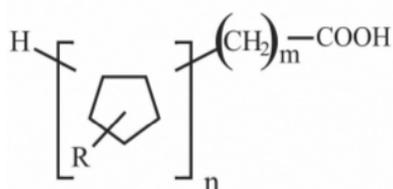


Figure 9 : General structure of naphthenic acids[26].

Naphthenic acids are classified by their structures and the number of carbon atoms in molecules. Both, distribution of carbon number and ring content vary with crude oil source. Its empirical formula is $C_mH_{2m+z}O_2$ where z is the hydrogen deficiency and m is the carbon number[22]. Their molecular weight, which is determined by mass spectrometry, varies over a wide range, to 200 a 700 amu.

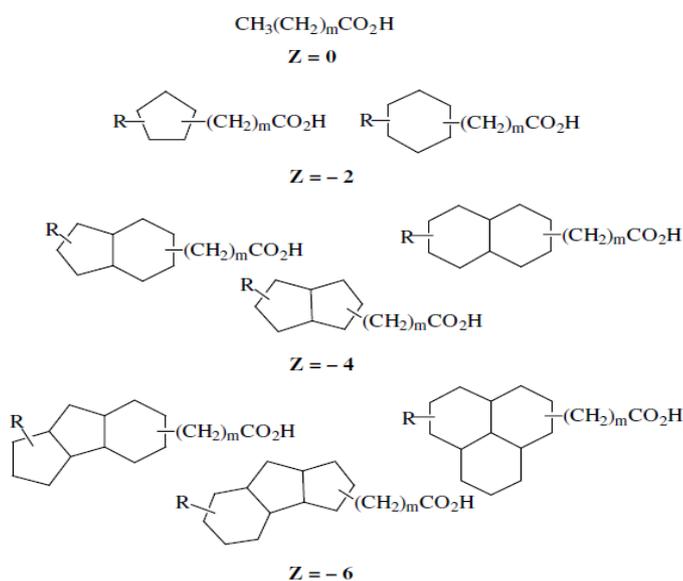


Figure 10 : Structure of homologues Naphthenic Acids[27].

These acids are generated during the hydrocarbons degradation in petroleum reservoirs, it is a kind of bacterial degradation in which bacterial preferentially attack the paraffin chains to form compounds with naphthenic or aromatic rings of shorter chain[26]. Their distribution varies according the different oils; they are predominant in immature, biodegraded and heavy crude oils. Due to their relatively high molecular weight they tend to concentrate towards the heavier cuts during distillation (200-400 °C). Also, they are found in waste water generated in bitumen extraction from crude oil[16].

Their amphipathic structure, they contain a hydrophilic part (COOH) and other hydrophobic (hydrocarbon chain), makes them behave as surfactants, so that, they can remain in the interface W/O, the hydrophilic part will be in contact with the water, while the hydrophobic part will be in contact with the oil, permitting an interfacial tension reduction and emulsion formation. It is therefore essential to analyse the aqueous phase pH, as it plays an important role in the interfacial activity. High pHs produce an interfacial W/O reduction, due to ionization of naphthenic acids and absorption of ionized species onto interface. At this pH, naphthenic acids shift from oil-soluble to water soluble due to dissociation[7]. Interactions in between the acid groups of naphthenic acid and the basic groups of asphaltenes are possible.

Regarding to their properties, the first characteristic thing is their colour. Non distillate naphthenic acids are dark yellow while distillate ones are typically light yellow to amber. They are viscous liquids. Their pH is correlated to solubility, small molecules are dissolved in aqueous phase (pH=5), big molecules are dissolved in oil and homologues in aqueous phase (pH=10)[28],[29]. Taking into account their chemical behaviour, these acids are slightly weaker than low molecular weight carboxylic acids, such as acetic acid and they have acid strengths similar to those of the higher fatty acids. Other properties such as polarity and non volatility increase with their molecular weight[27],[30] but in general, they can be used to describe the overall mixture as shown in Table 1.

Table 1 : General characteristics of NA [27],[30].

| Parameter | General characteristic |
|---------------------------------------|---|
| Color | Pale yellow, dark amber, yellowish brown, black |
| Odor | Primarily imparted by the presence of phenol and sulphur impurities; musty hydrocarbon odor |
| State | Viscous liquid |
| Molecular weight | Generally between 140 and 450 amu |
| Solubility | <50 mg/L at pH 7 in water Completely soluble in organic solvents |
| Density | Between 0.97 and 0.99 g/cm ³ |
| Refractive index | Approximately 1.5 |
| pK _a | Between 5 and 6 |
| Log K _{ow} | Approximately 4 at pH 1 |
| (octanol water partition coefficient) | Approximately 2.4 at pH 7 Approximately 2 at pH 10 |
| Boiling point | Between 250 and 350°C |

Regarding to their applications and knowing that they are possible metabolites of bacterial action, they can be used as indicators of this biodegradation process. Correlation between these acids and biodegradation levels was studied by Meredith et al. [31]. Also, they can be used as geochemistry markers. They can be transformed in cobalt, calcium and manganese salts to be used in several applications such as polymerization and oxidation of drying oils and resins, conservation of solvents or catalysis in organic systems [27]. Heavy metal naphthenates promote solidification of inks and varnishes, and copper and zinc salts work as fungicides in the wood industry [32].

Table 2: Industrial uses for naphthenic acids [27], [31],[32].

| Naphthenic acid metal salt | Industrial applications |
|----------------------------|---|
| Na salt | Emulsifying agent for agricultural insecticides Additive for cutting oils emulsion breaker in oil industry |
| Ca naphthenate | Additive for lubricating oil |
| Fe and Mn naphthenates | Fuel additives for improved combustion and reduced corrosion |
| Pb and Ba salts | Catalysts for oil-based paints |
| Cu and Zn naphthenate | Wood preservatives |
| Co naphthenate | Curing agent in rubbers and resins Adhesion promoter of steel cord to rubber |
| Mn, Pb, Co, and Ca soaps | Oxidative catalysts |

1.3.3. ACIDITY IN THE CRUDE OILS

All crude oils contain acids present as additives or as degradation products, e.g. Naphthenic acids, but the amount of them differs among crudes, since some of them are more acidic than others, i.e. crudes of high gravity and large asphaltene content usually have more acids than paraffinic crudes[33].

This acidity has a particular impact on crude oil utilization and management of its waste. Measure of this acidity, which is normally due to acids or salts with $pKs \geq 9$ [34], is carried out through the total acid number (TAN) using potentiometric titration in non aqueous solvents or in mixtures of solvents, and can provide acid/basic behaviour of different crudes. The acid number is also used as a guide in the quality control of lubricating oil formulations and as a measure of lubricant degradation.

As well as it is possible to determine acidity in oils, also potentiometric titration allows determining the acidic content in water in contact with crude oils. It is believed that compound transfer exists in between crude oils and water during the emulsion formation. Acids can migrate to aqueous phase giving the acidic behaviour to it. By potentiometric titration, it could be possible to confirm this transference as well as to quantify the acidity.

TAN is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample in a specified solvent to a specified end point [34]. TAN measurement points out corrosion possibility but it is not enough from a quantitative point of view, since a variety of oxidation products contribute to the acid number and the organic acids vary widely in corrosion properties, so that, there are slightly corrosive crude oils with high TAN and vice versa. This shows that corrosion depends on nature and presence of a determined group of acids, whose concentration is not just explained by TAN [22], [31]. No general correlation is known between acid number and the corrosive tendency of oils toward metals.

Classification according to TAN value is possible (crude oils can vary in TAN from <0.1 , to as high as 8 mg/g KOH). Acid crude oils have a TAN $>0.5 \text{ mg/g KOH}$ and opportunity crude oils have more elevated values of TAN, i.e. 2 mg/g KOH . Crude oils with TAN $<0.5 \text{ mg/g KOH}$ represents less risk in refining processes[31].

Other technique, which permits to identify carboxylic acids and then the organic acidity in crude oil samples, is Fourier transform infrared spectroscopy (FT-IR). It has increased its utilization as analytical tool in different fields such as agricultural industry, food, petroleum industry, etc., over the last 30 years. The main reasons are its low time-consumption, simplicity or non-consumption of the samples. Its disadvantage is the insensitivity to minor components[35]. Qualitative studies can be performed, because around 1700 cm^{-1} a peak appears corresponds to the stretching of the C=O group. Recently, quantification of acidic content is also possible[36].

2. OBJECTIVES

The main objective of this work is performed around the study of the acidity in several crude oils, the identification and quantification of different acids that contribute to this acidity in oil and contact water samples by potentiometric titration and Fourier transform infrared spectroscopy (FTIR).

A second objective will be focused on the study of compounds that stabilize emulsions formed between oil and water from production step by liquid chromatography coupled to high resolution mass spectrometry (MS / MS), allowing a better description of compounds transference between W/O interfaces and according to the different physicochemical conditions (temperature, pH of the aqueous phase, salinity, etc.).

3. EXPERIMENTAL PART

3.1. PERFORMED TECHNIQUES

As it was introduced in the first part of the work, potentiometric titration and FT- IR are the most suitable techniques to determine and quantify Nas in crude oil samples, although their high complexity normally represents a great challenge in terms of analytical characterization. Low concentrations and the complex matrix make even more difficult their analysis.

3.1.1. POTENTIOMETRIC TITRATION

Electroanalytical methods are a kind of techniques in analytical chemistry which are based on the measurement of a basic electrical magnitude, such as current intensity, potential, resistance (or conductance) in electrochemical cell containing the analyte. These methods can be divided in two large groups, interfacial methods and methods that take place within the solution, being the first ones the most commonly used. Interfacial methods study phenomena which happen in the interface between the electrode surface and the thin layer of solution adjacent to these surfaces. At the same time, it can be divided in two categories, static and dynamic methods. Potentiometric measures are employed in static methods, which provide different advantages such as selectivity and rapidity, and measure the potential developed by a cell consisting of an indicator electrode and a reference one. This potential, E_{cell} , must be measured under static conditions, i.e. under negligible current flow to avoid changes in the concentration of the component being measured[37].

The technique, which is going to be used in this work, belongs to static interfacial methods. The required equipment is simple and economic. **Reference electrode** (half-cell potential constant, known and insensitive to the composition of work solution), **indicator electrode** (in theory, this electrode measures the activity of a single component of the solution, but in practice, the indicator electrode is calibrated to respond to concentration rather than activity and is usually not specific for a single analyte) and **measure device** are just necessary. A potentiometric titration is a technique in which potential is measured across the analyte, normally an electrolyte solution, enabling to determine the end point of the titration. No indicator is used. The potentiometric endpoint is widely applicable and provides more accurate data than the corresponding method using indicators. It is very helpful to titrate coloured and turbid solutions[37], [38], [39].

3.1.2. FOURIER TRANSFORM INFRARED SPECTROSCOPY

Infrared spectroscopy is a versatile tool employed in qualitative and quantitative determination of different molecular species, such as organic and biochemical species. Its applications are related to the three infrared spectral regions, near IR ($4000 - 14000 \text{ cm}^{-1}$), mid IR ($4000 - 1000 \text{ cm}^{-1}$) and far IR ($400 - 10 \text{ cm}^{-1}$). The most used region is the mid infrared.

Different ways to prepare the samples are employed, since sample manipulation requires a long time and is the most difficult part of the analysis. Also, it is important to take into account the solvent used, as it can absorb in the IR and can interfere in the analysis. Water and alcohols are not normally used, because they strongly absorb in the IR and also attack the cell windows, which are metal halides (NaCl or KBr, which are transparent to IR).

Compound identification consists of two stages:

1° Determination of functional groups most likely, such as C=O, C=C, C-H, etc. by examining the group frequency region ($3600 - 1200 \text{ cm}^{-1}$).

2° Comparison of unknown spectrum with spectra of pure compounds which contain all the functional groups found in the first step. Fingerprint region ($1200 - 600 \text{ cm}^{-1}$) is very useful, since small structural and constitutional differences in a molecule cause significant changes in the aspect and distribution of peaks in this region. Two spectra of different compounds which have large similarity in fingerprint region, suggest identity in between the two compounds.

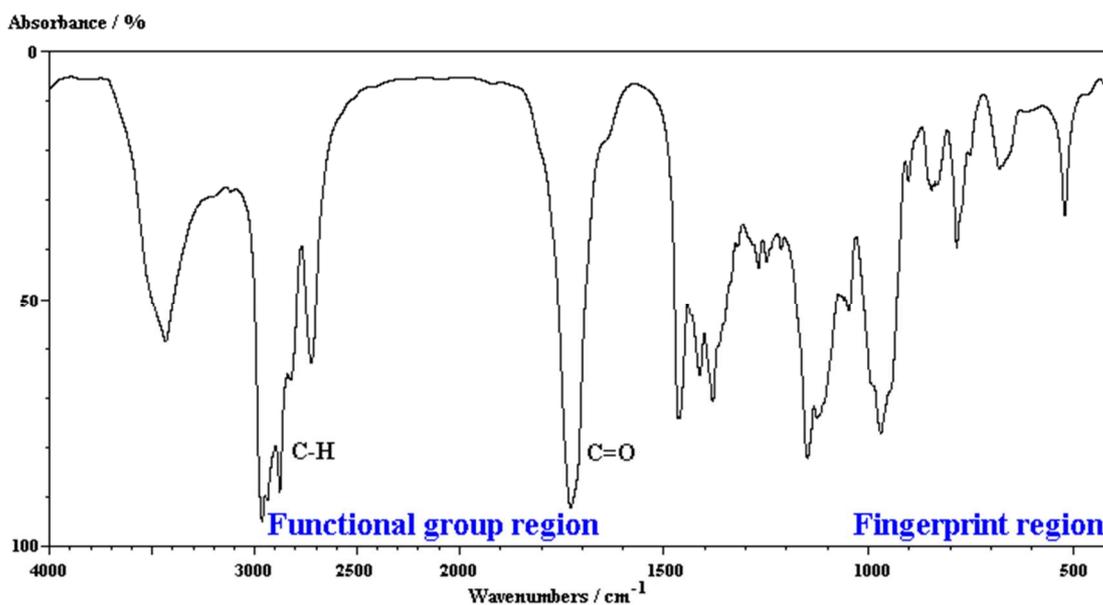


Figure 11 : Infrared spectrum[40].

As can be seen in *Figure 11*, fingerprint region tends to be more complex and much harder to assign, but this complexity provides singularity, necessary to identification.

Calibration curves empirically determined are necessary for quantitative analysis, but some disadvantages, such as failure of Beer's law or spectra complexity, can hamper it. All organic and inorganic molecular species, except homonuclear molecules, absorb in the infrared, therefore infrared spectroscopy offers the possibility of determine an enormous number of compounds[38].

Filter photometer is the device used for IR absorption. These instruments have the advantage of portability. Infrared instruments using a monochromator for wavelength selection are constructed using double-beam optics instead of single-beam optics due to the instability of sources and detectors for IR. Resolutions of $1\text{--}3\text{ cm}^{-1}$ are typical for most instruments.

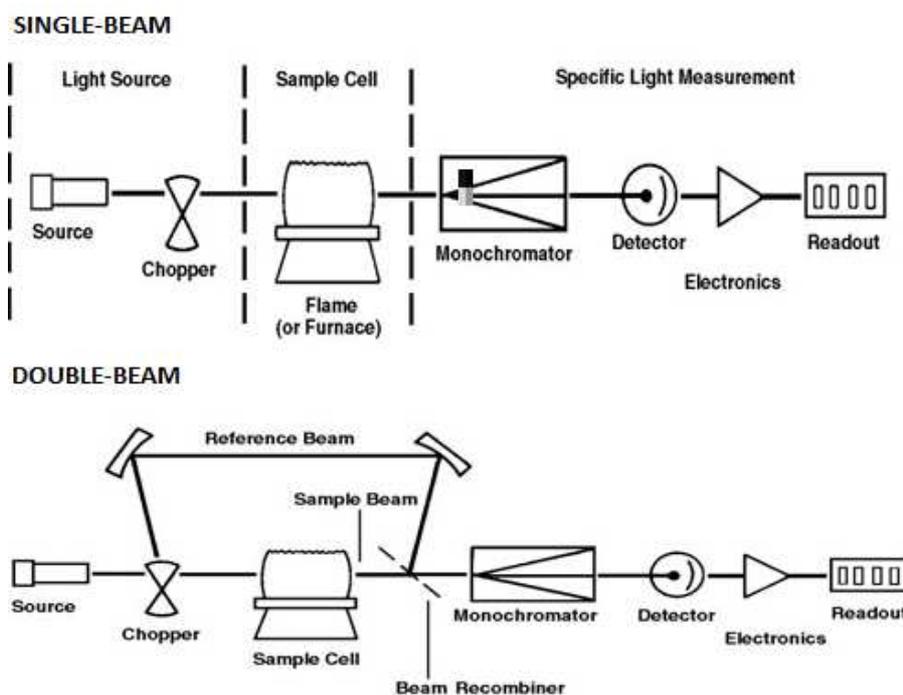


Figure 12: Comparison between single-beam and double-beam spectrophotometer[41].

In a Fourier transform infrared spectrometer, or FT-IR, the monochromator is replaced by an interferometer shown in Figure 13.

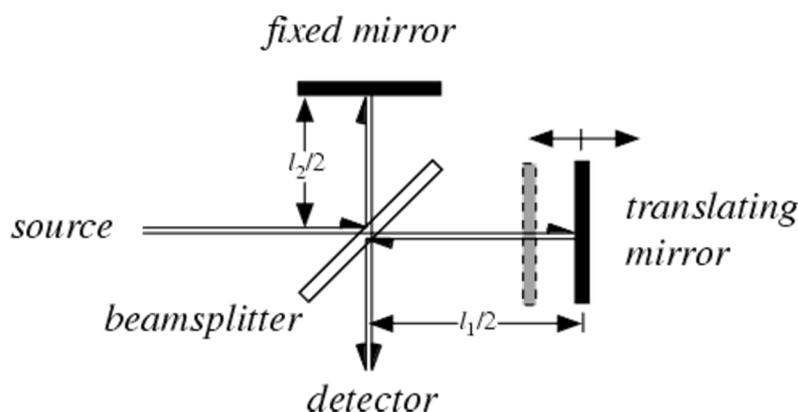


Figure 13: Michelson interferometer[42].

An interferometer, instead of filtering or dispersing the electromagnetic radiation, simultaneously allows radiation source of all wavelengths to reach the detector. The signal at the detector shows intensity as a function of the moving mirror's position, expressed in units of distance or time. The result is called an interferogram. The time domain spectrum is converted mathematically, by a process called Fourier transform, to the normal spectrum (also called as frequency domain spectrum) of intensity as a function of the radiation's energy.

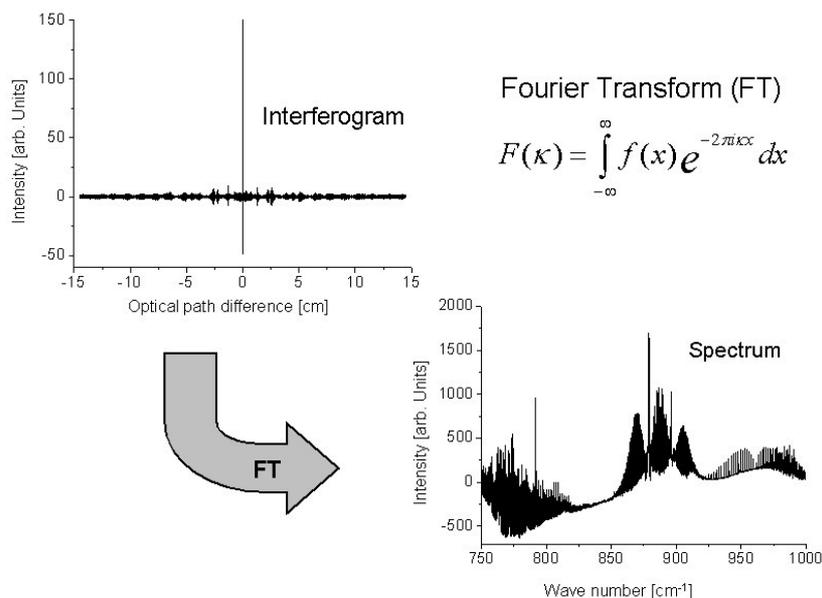


Figure 14: Transformation between interferogram and spectrum by FT [43].

Because an FT-IR includes only a single optical path, it is necessary to collect a separate spectrum to compensate for the absorbance of atmospheric CO₂ and H₂O vapor. This is done collecting a background spectrum without the sample and storing the result in the instrument's computer memory. The background spectrum is removed from the sample's spectrum by ratiating the two signals. In comparison to other dispersive IR instruments, an FT-IR provides two advantages. First one, which is termed Jacquinot's advantage, results from the higher throughput of source radiation. The result is an improved signal-to-noise ratio. The second advantage, which is called Fellgett's advantage, reflects a savings in the time needed to obtain a spectrum [39].

Infrared radiation is passed through the sample, when excitation frequency of a bond (or group of bonds) matches with any frequencies of the infrared beam, absorption is produced. Some of the radiation is absorbed by it and some is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Absorption peaks correspond to the frequencies of vibrations between the bonds of the atoms making up the material.

3.1.3. LYOPHILIZATION

Lyophilisation allows water removal of the sample by sublimation; first of all, the sample is frozen and after is introduced in a vacuum chamber (removing oxygen and avoiding oxidation of compounds) to remove the water. This technique removes solid state water by its transformation onto vapour phase avoiding the liquid phase (it should work below the triple point of water, 0.01°C and 4.5 mmHg) [44].

This technique is mainly used in alimentary industry for food conservation, pharmaceutical industry for medicaments conservation or in medicine. Lyophilisation is hard and time consuming being compared to other traditional drying methods, but sample preserves its molecular structure after the process and its properties after rehydration, because heat is not used to dry. Water content after lyophilisation is below 0.5 % [45].

In the procedure are necessary two basic operations:

1. **Freezing:**

Depending on the solutes into solution, temperature and time of freezing will vary. Variation in freezing velocity affects the ice crystal size and thus the pore size in the dry product. It is expected, therefore, that it influences the drying speed and product characteristics, especially on rehydration. It is intended that frozen product already has a solid structure without gaps, where liquid could be concentrated, to promote that all drying occurs by sublimation instead of evaporation.

2. **Sublimation or primary drying:**

Primary dehydration corresponds to sublimation of frozen water from the sample, whose speed is proportional to the difference between the partial pressures of water vapor of ice at sublimation front and on the capacitor. This pressure difference depends directly on the temperature difference between the product still frozen and lyophilizer condenser. Usual pressures used for this process are 13 to 267 Pa. Humidity is reduced to less than 5% [46].

3.2. MATERIALS

3.2.1. REAGENTS

Naphthenic acids technical, tetrachloroethylene anhydrous (C_2Cl_4 , $\geq 99\%$), Toluene (C_7H_8 , puriss $\geq 99.5\%$, GC), 2-propanol ($(CH_2)_2CHOH$, puriss p.a ACS $\geq 99.8\%$, GC) were acquired in Sigma Aldrich. Tetrabutylammonium hydroxide solution (isopropanol/methanol) (10:1 V/V) for titration in non-aqueous medium ($(C_4H_9)_4NOH$, volumetric 0.1M) was acquired in Fluka. Ultrapure Milli-Q water was obtained from a Milli-Q system.

3.2.2. SAMPLES

Petroleum samples were supplied by TOTAL Petrochemicals. Different crude oils from several parts of the world were analysed.



Figure 15: Some of the samples used during the analysis.

3.3. PROCEDURE

3.3.1. TAN

These measurements normally require considerable crude oil quantities and cannot be performed on small samples or when the crude oil contains large quantities of water[47].

The method performed (ASTM D664) is a potentiometric titration and TAN is reported in terms of KOH mg necessary to neutralize the amount of acids contained in a gram of oil [34]. It was measured by Titrator Metrohm (Basic Titrino 794) and TiAmo was the software employed.



Figure 16: Titrator Metrohm (Basic Titrino 794) and petroleum sample.

The electrode employed was a glass electrode (ball shape) with LiCl (sat) in ethanol as internal electrolyte. The measuring unit is pH and the measuring range is 0-14.



Figure 17: Glass electrode.

TAN values are considered to be a measure of all acidic components, not only NAs[48], i.e. TAN provides acid-basic behaviour of a crude oil.

The protocol is the following:

- Prepare 1 L of **Solution A (Toluene/2-propanol/Water)** necessary to dissolve petroleum samples, measuring 500 ml of Toluene, 497.5 ml of 2-propanol and 2.5 ml of water.
- Measure the blank (only if it is needed)
- Rinse the electrode with Toluene, 2-propanol and water.
- Weigh 1 g of petroleum sample and dissolve it in 100 ml of Solution A.
- Measure
- Rinse the electrode with Toluene, 2-propanol and water.

The method used to carry out the TAN was TAN tbaH and as titrant is going to be used TBAH in 2-propanol/methanol 0.1 M. The blank should be measured whenever Solution A is prepared, and this new value must be introduced in the device. Each sample must be titrated at least two times; the value will be the average between them. Each two measurements, a fixed volume of titrant (0.4ml) must be ejected. For calculations, it is necessary to introduce the reagent titer (0.1M) and the mass of oil (three decimals).

Naphthenic acids have a transition to 400mV. If we see a transition to 50mV are often strong acids added during refining.

TAN is calculated by the next expression.

$$TAN = \frac{(V_{eq} - V_{blank}) \cdot C_{KOH} M_{KOH}}{m_{petroleum}}$$

V_{eq} = Volume (L) of titrant in the acid-basic equivalence point.

V_{blank} = Volume (L) of titrant in the acid-basic equivalence point for the solvent without sample.

C_{KOH} = Concentration KOH (Mol/L)

M_{KOH} = Molar mass of KOH (mg/mol)

m = mass of petroleum (g)

3.3.2. LYOPHILIZATION

Although, it is possible to use potentiometric titration in order to analyse the acidity content in water samples after contact with petroleum, in this work a new approach is going to be tested, including a first step of lyophilisation and a second step of analyse with FT-IR.



Figure 18: Lyophilizer used during the analysis.

First, it will be tested real samples of unknown concentration, because it is assumed that the highest content of naphthenic acids should be found into them, since these samples are the water in contact with the oil. Samples were supplied by the laboratory of Chemistry of UPPA; they were responsible for obtaining the water in contact with the oil.

For the lyophilisation, samples were frozen overnight to ensure a good freezing, after that, they were coated with perforated parafilm to facilitate the evaporation of water and they were introduced into the lyophilizer. The work conditions were selected ($P=3.5 \cdot 10^{-1}$ mbar and $T= -49.3$ °C). It was necessary three days to evaporate all the water of the samples. After lyophilisation, yellowish particles were observed inside the tubes.

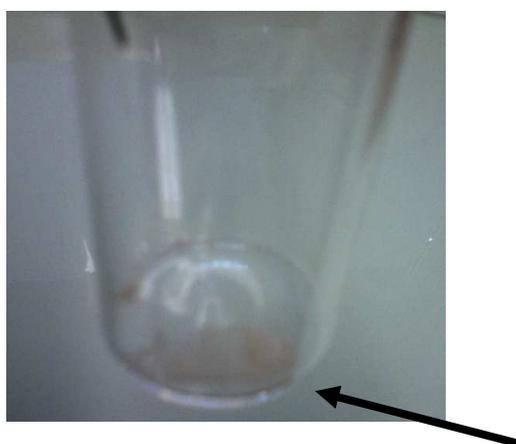


Figure 19: Residues found after lyophilisation.

3.3.3. FT-IR

Fourier transform infrared spectroscopy will be used first in a qualitative way, to check if real samples, after lyophilisation, contain naphthenic acids, i.e. an identification method. In case that these acids were found in samples, it would be necessary to find out the concentration of them, since sample concentrations are unknown, to do that, a calibration curve with NAs in tetrachloroethylene is carried out.

The protocol is the following:

- Measure the blank
- Measure the samples

The device is Alpha series T Bruker and Opus 6.5 was the software employed. A 0.2mm CaF₂ cell is used to do the measurements. Transmittance was the mode of measure. After each measurement, the cell must be rinsed with solvent.

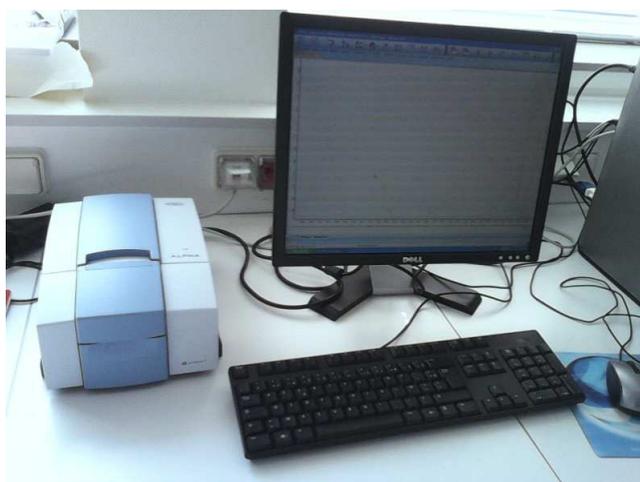


Figure 20: FT-IR device Alpha series T Bruker.

Table 3: Parameters employed in the FT-IR:

| | |
|----------------------|----------------------------|
| Resolution | 4 cm ⁻¹ |
| Sample scan time | 16 scan |
| Background scan time | 16 scan |
| Save data from | 4000-1000 cm ⁻¹ |

Naphthenic acids have the carboxylic function (COOH), which appears around 1700 cm⁻¹ in IR spectra.

3.4. RESULTS AND DISCUSSION

3.4.1. TAN

A classification of acid-basic behaviour of different crude oils in function of the TAN values is possible to establish. Eight petroleum (OIL 1, OIL 2, OIL 3, OIL 4, OIL 5, OIL 6, OIL 7 and OIL 8) were analysed but data of four of them just were obtained. The data obtained from the automatic potentiometric titration are as follows.

Table 4: Tan values of different petroleum.

| SAMPLE | TAN pot/ mgKOH/g |
|--------|------------------|
| OIL 1 | 1.37 |
| OIL 4 | 2.85 |
| OIL 5 | 0.15 |
| OIL 6 | 1.33 |

The other crude oils, such as OIL 2, OIL 3, OIL 7 and OIL 8 have negative values of TAN. It has not sense, since it expresses mg of KOH. It probably happens due to the low content of acids in samples which is under device sensitivity. According to the value obtained, crude oil can be classified as follow.

Table 5: Classification according TAN values.

| SAMPLE | TAN pot/ mgKOH/g | BEHAVIOUR |
|--------|------------------|---------------------------------|
| OIL 1 | 1.37 | ACID CRUDE OIL |
| OIL 4 | 2.85 | OPORTUNITY CRUDE OIL |
| OIL 5 | 0.15 | PRESENTS NO RISK FOR PROCESSING |
| OIL 6 | 1.33 | ACID CRUDE OIL |

An attempt to carry out the same potentiometric titration in order to quantify the amount of acidity in contact water was unsuccessful, because the observation of the equivalence point after several tests varying titrant concentration was impossible, since a small amount of titrant increases a lot the solution pH.

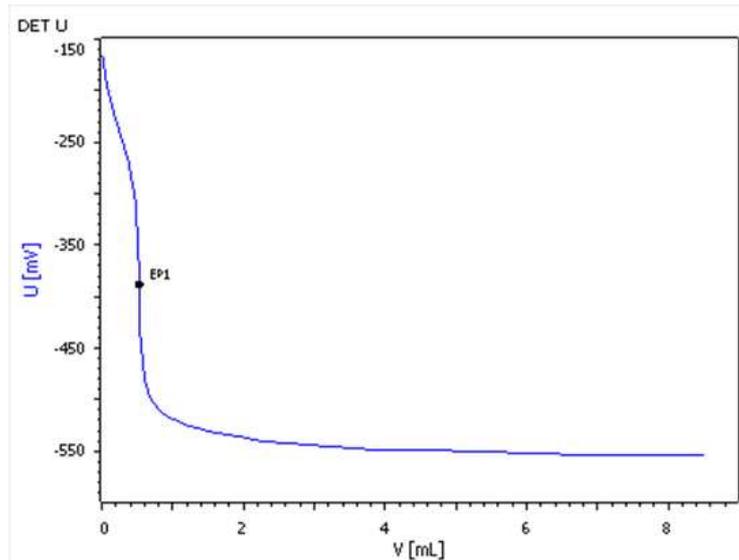


Figure 21: Example of a titration curve performed by the device.

3.4.2. LYOPHOLIZATION AND FT-IR

The FT-IR detection limit is reported to be 10 mg L^{-1} and its linear dynamic range approximately 10 to 300 mg L^{-1} (0.001% - 0.03% w/w)[48].

A calibration curve was prepared by weighing different amounts of NA and subsequently dissolving them in 10 ml of tetrachlorethylene. The prepared concentrations were: 0.176%, 0.156%, 0.054%, and 0.033% w/w. To avoid possible loss of acids by adhesion to the walls of the containers, all solutions were prepared directly in the 10 ml container. Samples from the lyophilizer were collected with 10 ml of tetrachloroethylene to analyse in the FT-IR.

In *Figure 22* is shown the IR spectrum with the calibration curve and the real samples. Around 1700 cm^{-1} carboxylic function (COOH) appears and carbon hydrogen bond (C-H) is found around $2800\text{-}3000 \text{ cm}^{-1}$.

Comparing both spectra, neither the OIL 1 nor the OIL 3 do exhibit any peak related to the acidic function (COOH), so it means that samples do not contain NAs and therefore it cannot assure that transfer of compounds exists. It is clear that some acid compounds pass through the interface between W/O since pH solutions are acids, with pHs around 5 -6.

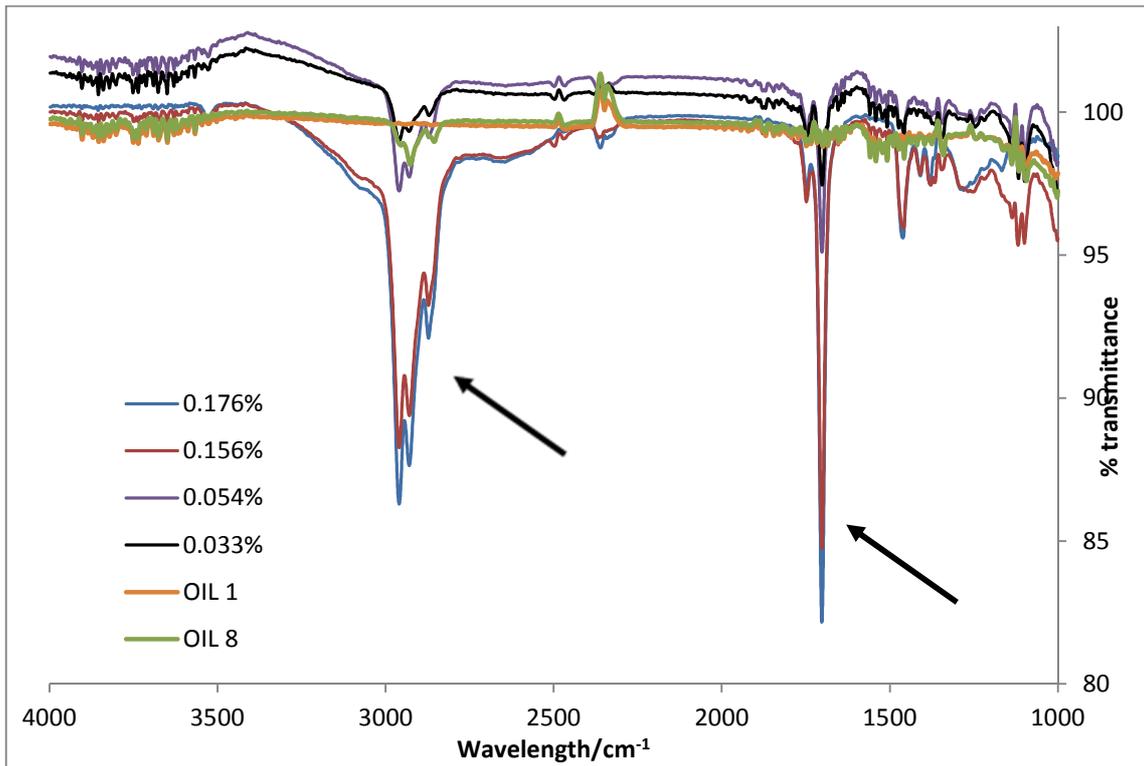


Figure 22: IR Spectrum of calibrations and real samples.

4. CONCLUSIONS

It has been shown that potentiometric titration has allowed determining the total acid content in petroleum samples, allowing a classification of them by the TAN value.

On the other hand, it has not been possible to perform the same procedure in contact water. This study is going to be continued in more details, but first, it is necessary to optimize and develop all the process. Neither it was possible to corroborate the acid transfer in W/O interface, which will attempt to further study by mass spectroscopic techniques.

5. FUTURE STUDIES

Due to failure achieving the objectives in the experimental section, in relation to contact water, new attempts in order to quantify the acidity and to explain whether the compound transference happens, will be tried.

Regarding to the potentiometric TAN evaluated in petroleum samples, it will be compared with IR TAN, which will be performed following the official procedure provided for TOTAL, to see if any differences exist in between both techniques. It will be also necessary to evaluate the strength of different bases, in order to find several which allow obtaining other equivalence points in crude oil titration. In further studies, it will be interesting to correlate this equivalence points with the function which causes them. In case of potentiometric TAN in water samples, it will be necessary to test weaker bases in order to a better observation of the equivalence point.

Finally, it will emphasize the study of compound transference, because according to bibliography, this transfer occurs. Some hypotheses can be considered, as increasing pH of water in contact with oil, to produce investment in the formed emulsions (water as continuous phase) and to stimulate more passage of acids into the water. But perhaps, the most useful attempt will be the combination of any analysis with mass spectrometry.

Since it is necessary to establish if transfer of compounds exists, an adequate technique to do that is liquid chromatography coupled with MS or MS/MS, using ESI (detects strongly polar or ionic species, it is best suited to studying the acidic or basic components in petroleum samples)[47] as ionizer. UPLC against HPLC offers higher resolving power and increased reproducibility, allowing to obtain narrow elution profiles[49].

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