Kinetic Diameter effect on hydrocarbon differential permeability in carbonate reservoirs

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Abstract

With the purpose of improving hydrocarbons production, it is crucial to focus not only on the mechanisms that will allow the production, but also on the reservoir rock main properties (porosity and permeability) from which hydrocarbons are going to be extracted. Since carbonate reservoirs represent the larger proportion of hydrocarbon reservoirs over the world, the flow analysis of reservoir fluids on specimens of this kind of porous rocks was performed, in relation to fluid properties.

The core flood system was applied for hydrocarbons homogeneous mixtures (isooctane / dodecane and isooctane / n-octane) permeabilities analysis, to understand their overall behaviour and eventual changes in mixture composition when crossing carbonate samples. The effluent collected from the mixture's injection was analysed on the Gas Chromatograph equipment, to understand if preference flow of a particular component is observed.

In addition, the results of this study were directly compared with the work of Pinto (2020) who performed similar analysis for a sandstone rock. With this comparison, it was possible to enhance the knowledge concerning the fluid flow of homogeneous oil mixtures in multiple porous media. As a complement, analysis of seismic waves throughout the core sample (dry and saturated) was performed by using an ultrasonic equipment.

Keywords: Carbonate rock; Porosity and Permeability; Core flooding; Kinetic diameter; Hydrocarbons; Seismic Waves

1. Introduction

Despite the growing of renewable energies, crude oil and hydrocarbons in general are still the main traded commodity. Tertiary Recovery or Enhanced oil Recovery (EOR) is a technique, which allows the extraction of up to 60% or more of the oil in the reservoir (depending on the employed EOR technique) thus, understanding its concept is vital. EOR seeks to alter oil properties to make it more willing to extraction, this alteration can occur mechanically, chemically, thermally, and biologically. For instance, it was reported that a reduction in oil viscosity due to the high temperature fluid injection (hot water) accelerates the imbibition recovery rate. High temperature also impacts reservoir rock's wettability turning it more water-wet, which contributes to enhance oil recovery. [1]

EOR has as main target to maximize the amount of oil recovered with the lowest possible cost from the existing fields before moving to the remote areas. [2]

Core flooding, as a branch of EOR, is a laboratory test that replicates reservoir conditions with specific pressure, temperature, and flow rates. By injection,

the fluids go through a rock sample filling up the pores and expelling the fluid that the rock was previously saturated with. It is also important to take into consideration that oil is a very complex mixture of hydrocarbons and, although it is usually treated as a single fluid, even if it is a homogeneous mixture, flowing through a porous rock with very small pores, may induce changes in its composition. This also applies, in different ways, to many of the EOR techniques.

In this research, the most important aspect is to study the behaviour of a mixture of hydrocarbons flowing throughout a carbonate rock. The origin and migration of petroleum is and has been a field of active discussion [e.g. 3, 4]. Fluids not only percolate through rocks but also several interactions between the rock itself and the fluids occur during its flow [3]. It has been accepted for decades that systematic changes in petroleum composition occur during petroleum expulsion from the source rock (primary migration) followed by movement through carrier beds (secondary migration) [3, 4]. One type of interaction is selective adsorption which assumes that light and low-boiling hydrocarbons percolate first while higher boiling ones, flow later. Additionally, asphaltic matter and some high molecular hydrocarbons are removed from the liquid phase [5]. According to Leythaeuser et al. (1983) [6] for C_{15+} alkanes, the lower molecular weight components undergo migration more readily than higher molecular weight components and n-alkanes migrate faster than branched alkanes. Bonilla et al. (1986) [7] performed experiments which supported this theory. Cheng and Huang [8] stated that there is a large adsorption selectivity of hydrocarbon gas molecules (C_1-C_6), in specific a strong preferential adsorption of wet hydrocarbon gases over methane, which confirms a stronger adsorption for the heavier gas molecules (Figure 1).
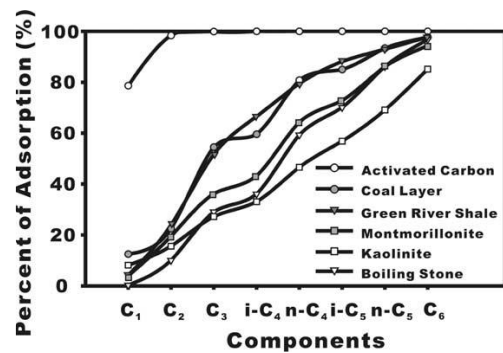

Figure 1- Selective adsorption capacities of different hydrocarbon gases on the studied adsorbents near saturation measured at 1 atm total pressure and 26°C [8]

The study of hydrocarbons flow throughout a core sample was also analysed by Pinto (2020) [9] which work, as mentioned, served as basis for this dissertation.

Pinto (2020) [9] analysed differential permeability in sandstones and carbonates samples. His work consisted of characterizing reservoir and fluid properties, physical and chemical mechanisms behind hydrocarbon recovery methods and a relation between these two concepts. Furthermore, it was analysed how different classes of hydrocarbons homogeneous mixtures moved along these rocks considering different sample conditions and methods.

For sandstone specimen, Pinto (2020) [9] stated that there was a preferential flow of the lower molecular weight component and for the carbonate a preferential flow of linear hydrocarbons.

2. Methodology
2.1 Materials

On this research the samples were obtained from Codaçal carbonate rocks. The specimens were collected in the surroundings of Alcanede and belongs to the Maciço Calcário Estremenho region.

This area corresponds to a limestone massif that covers an area of 900 km² in the center of Portugal, around 150 km to the north of Lisbon. The

productive units of the main ornamental varieties with origin in this thick carbonate sequence are dated of Middle Jurassic more specifically from the Bathonian period [10-12]. Portuguese limestones are mostly made of calcite carbonates (CaCO3) and dolomite (Ca,Mg CO3) [12].

Figure 2 - Geological map of the Maçico Calcário Estremenho region [12]

In this work, a total of twenty-five cores were sampled with a specific mechanical machine which provided cylindrical forms with the tops cut in planes parallel to each other and perpendicular to the core axis. For consistency, all samples were taken in the same direction (either x or y) and discontinuities were avoided, nevertheless some geological variability is expected to be present on the analysed cores which will be around 38mm of diameter and length between 90 and 100 mm.

The reservoir fluids used in this work were brine, distilled water, and four different synthetic oils, to simulate reservoir oils. Isooctane was selected as branched hydrocarbon, octane as the linear hydrocarbon with the same carbon number and hexadecane and dodecane as linear hydrocarbons with growing number of carbons. The synthetic oils isooctane and n-octane were obtained from the brand PanReac AppliChem, and dodecane and hexadecane from the brand CamLab Chemicals.

For the hydrocarbon mixtures, performed to analyse the influence of different kinetic diameters and molecular weights on the fluid flow, isooctane/dodecane and isooctane / n-octane were used. Kinetic diameter is commonly referred as the size of a molecule. [13]

2.2 Methods

As mentioned, the method used to inject fluids on the carbonate core sample was core flooding. It involves pressurized reservoir rocks to mimic reservoir conditions and flowing a fluid through it in the laboratory. Core flooding tests can be performed at varying injection rates, temperatures, and pressure. Here, a constant confining pressure (50 bar), and different injection rates (3 mL/h and 6 mL/h) were applied.

Regarding to rock properties, porosity is calculated according to Eq.1 and Eq.2 and permeability according to Darcy law (Eq.3).

$$\Phi = \frac{BV - GV}{BV} \qquad \text{(Eq.1)}$$

Porosity is here denoted as Φ, GV is the grain volume (volume of solid material) and BV the bulk volume of the sample (usually expressed as a fraction or percent). [14]

$$\Phi_{eff} = \frac{Vol.of\ interconnected\ pores + Vol\ of\ dead-end\ pores}{BV} \qquad \text{(Eq.2)}$$

Effective porosity, denoted as Φ_{eff}, is mathematically defined as the ratio of the volume of interconnected pores and the dead-end ones to the total or bulk volume of the sample. [15-17]

$$K = \frac{Q\mu L}{A\Delta P} \qquad \text{(Eq.3)}$$

Where K[m^2] is the permeability, Q[m^3/s] is the fluid flow rate, μ[N s/m^2] is the viscosity of the flowing fluid, L[m] is the length of the fluid pathway, A[m^2] is the cross-section area and ΔP[N/m^2] is the pressure difference.

Regarding to the seismic measurements, an ultrasonic equipment was used. This method assumes that ultrasonic seismic pulses are discharged by the pulse generator and converted to mechanical vibration by the transmitting piezoelectric transducer. After traveling through the rock sample, the elastic waves are converted back to an electrical signal by the receiving transducer. [18, 19]

The travel time of the acoustic waves can be measured on a digital oscilloscope so that the velocity values were calculated by dividing the length of core and the pulse transit time (Eq.4):

$$V_p = \frac{L}{\Delta t} \qquad \text{(Eq.4)}$$

Where V$_p$ is the P-waves velocity in m/s, L is the length of the core sample (m) and, Δt is the travel time (s).

3. Results and Discussion

3.1 Rock properties characterization

For the rock properties characterization, porosity was measured with water for every core samples. Overall, the cores presented porosities ranging from 9,27% to 13,52%, which correspond to the common ultimate porosity in carbonate rocks (5-15%) [20]. However, higher values of porosity were expected since more than half of the samples presented porosities lower than 10%. According to Figueiredo et al. [21] and Alves et al. [22], an

evaluation of the pore structure of Codaçal carbonates showed an open porosity value in the range of 11,2 and 12,8%. Low porosity may be associated to less pores, fractured or closed pores caused by compression, among other reasons.

For the rock permeability, measured with brine, two rock samples were used with low and high porosity to establish a connection between porosity and permeability (Table 1). Again, the tests were performed for different flow rates and constant confining pressure. Permeability varies greatly in carbonate reservoirs from values of less than 0,1 mD in tight, crystalline mosaics in mudstones to over 10 D in fracture, cavern, or connected vug systems [20].

Table 1 - Brine permeability for different cores at different conditions

Core Samples	Porosity %	Permeability (mD) with Flow rate - 3 mL/h	Permeability (mD) with Flow rate - 6 mL/h
1	10,35	0,022	0,069
4	13,52	0,128	0,116

Sample 1, with lower porosity, showed a lower permeability for different flow rates when comparing to sample 4 with higher porosity. Therefore, it is possible that exists a correlation between porosity and permeability values, higher porosity may imply a higher permeability.

Regarding to seismic waves analysis, the velocities were calculated for a dry core and for a core saturated with reservoir fluids (water, brine, and oil).
The range of values for the dry core was between 3000-4000 m/s and it was observed that low velocity values were associated to high porosities. The same range of values was obtained for the saturated core, regardless of the saturation fluid however, the velocities were higher for the saturated samples in particular, the ones saturated

with hydrocarbons (Table 2). Here, the samples presented the same behaviour, low velocity values associated to high porosities.

Table 2 - Dry and saturated core samples P-wave velocity

Core samples	Dry core P-wave velocity (m/s)	Water saturated core P-wave velocity (m/s)	Brine saturated core P-wave velocity (m/s)	Hydrocarbon saturated core P-wave velocity (m/s)
1	3681,79	4212,65	4193,06	-
2	3652,18	4193,24	-	4252,11
3	3301,97	3738,60	-	3882,83
4	3307,37	3744,71	4195,37	-
6	3119,52	3388,24	-	3662,75
8	3520,08	4002,92	-	4075,23
9	3725,60	4352,50	-	4416,10
11	3320,73	3640,80	-	4177,88
12	3356,43	3875,02	-	3977,53
13	3356,22	3760,08	-	3957,21
14	3555,84	3793,89	-	4084,23

It was shown through Biot's theory and Gassmann's equation that P-wave velocity increases when a porous media is saturated with a liquid [19]. It is difficult to affirm that the values of velocity are what is expected because carbonate rocks present different conditions, porosity, heterogeneities, pore size and faults therefore, different ranges of velocities according to these characteristics can be obtained.

Wang, et al. (1991) [18] stated that, P-wave velocity increases due to a decrease in compressibility. The difference between P-wave velocities of water and hydrocarbons saturated cores is very little, however, in theory cores saturated with water should have presented higher velocity comparing to hydrocarbon saturated cores since water is less compressible than oil, even though the obtained results show very similar P-wave propagation velocities.

3.2 Hydrocarbon Recovery

Hydrocarbon's flow was the main interest of this research. Its absolute and mixtures permeabilities were analysed as well as the changes in composition when percolating the rock porous media. Therefore, the core samples were saturated and injected with isooctane, n-octane, dodecane and hexadecane. Regarding to the oil mixtures, isooctane/dodecane and isooctane/n-octane were used. For all the tests, the same condition of constant confining pressure (50 bar) and different injections rates (3 mL/h and 6 mL/h) were applied.

Also, different cores with different porosities were chosen to analyse its influence in the absolute permeability results. As expected, considering a Darcy flow, hydrocarbon's permeabilities presented similar results as brine (Table 3). In addition, lower porosity samples obtained lower permeability and, subsequently, high porosity samples obtained higher permeability results. This effect happens for all hydrocarbons and, for hydrocarbons with analogous rock characteristic, permeability is very similar which means that, besides the molecular weight, density, viscosity, polarizability and molecule linearity, permeability values are not too different, for the developed tests.

To analyse this phenomenon, a graph was made (Figure 3) to directly compare the values of rock porosity and hydrocarbons permeabilities and it is possible to notice three clusters of values. The first one includes the values of permeabilities lower than 10% porosity, second one permeabilities with porosities between 10-12% and lastly permeabilities with porosity values higher than 12%. According to the graph, the high coefficient of determination (0,9313), proves that in fact exists a relation between these properties.

Table 3 - Hydrocarbon porosity and absolute permeability

Core Samples	Rock porosity %	Hydrocarbon Porosity %	Absolute Permeability mD	Saturation Fluid
2	9,75	10,11	0,053	Isooctane
3	12,92	14,02	0,138	Isooctane
6	13,19	14,98	0,200	Hexadecane
8	10,78	11,36	0,065	Dodecane
9	9,34	9,76	0,022	Isooctane
11	9,61	10,73	0,036	Isooctane
12	12,62	14,38	0,174	Isooctane
13	10,59	11,93	0,077	n-Octane
14	10,76	11,57	0,075	Hexadecane

$y = 0,0406x - 0,3559$
$R^2 = 0,9313$
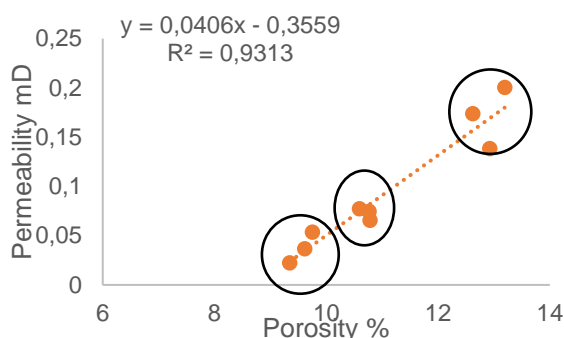
Figure 3 - Rock porosity Vs Hydrocarbons permeabilities

For oil mixtures, different hydrocarbons proportions were analysed as well as the influence of porosity for the isooctane/dodecane mixture.

Table 4 - Rock and hydrocarbon Porosity, Absolute permeability for isooctane/dodecane and Isooctane / n-Octane

	70% Isooctane / 30% Dodecane	70% Isooctane / 30% Dodecane	70% Isooctane / 30% n-Octane	50% Isooctane / 50% n-Octane	30% Isooctane / 70% n-Octane
Rock Sample #	18	5	10	7	22
Rock Porosity %	12,31	10,38	10,38	10,15	10,75
Hydrocarbon Porosity %	15,46	12,12	10,74	10,72	11,98
Absolute Permeability mD	0,0163	0,025	0,033	0,053	0,078

According to the results, it is possible to see that for isooctane/dodecane mixture, sample #5 with

lower porosity obtained a lower permeability result when comparing to sample #18 which presented a higher porosity. Therefore, porosity influence is constantly present regardless of the saturation fluid.

For the isooctane/n-octane mixture, three samples were used (#7, #10 and #22) with different hydrocarbon proportions. As the quantity of n-octane increased over the essays, it was noticed an increase in the permeability of the mixtures as well. The increase of flow and permeability is often related to the increase of the percentage of lighter components. Pinto (2020) [9] identified that for isooctane/dodecane mixtures since it was analysed multiple proportions. Regarding to Isooctane / n-Octane, the main property that distinguish them is their structures (Figure 4) since isooctane is an isomer of n-Octane. Isooctane is a branched hydrocarbon and n-Octane has a linear structure, which means that isooctane presents a higher kinetic diameter when compared to n-Octane. Given this, it is more likely for the increase of permeability on this mixture to be related to the kinetic diameter influence, which enables the flow of lower kinetic diameter hydrocarbons in comparison with higher ones.
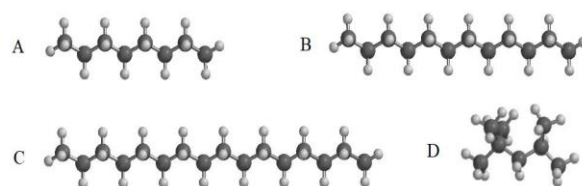

Figure 4 - Side view of n-octane (A), n-dodecane (B), n-hexadecane (C) and Isooctane (D). [9]

3.3 Differential Permeability Analysis

This chapter is focused on the analysis of oil mixtures behaviour when percolating a rock sample, mainly the changes in proportions of the mixture's components. For that, the effluent collected from the previous cores, with isooctane / dodecane and isooctane / n-Octane mixtures, was used and analysed in the Gas chromatograph.

The following figures present the flow of the isooctane/dodecane mixture being the points referred to the percentage of each compound in the effluent provided by the Gas Chromatograph.
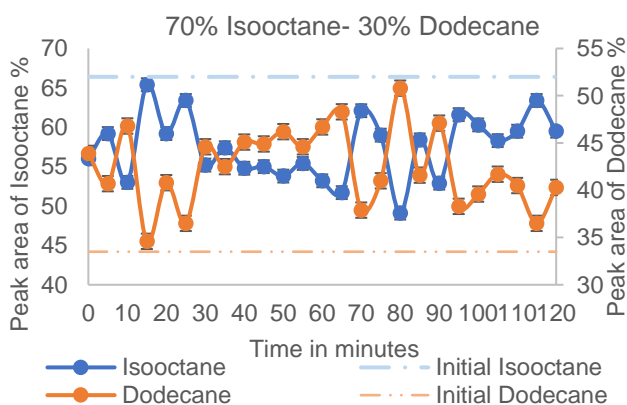
Figure 5 - Differential Permeability of 66,4% Isooctane / 33,6% Dodecane mixture – Core 5
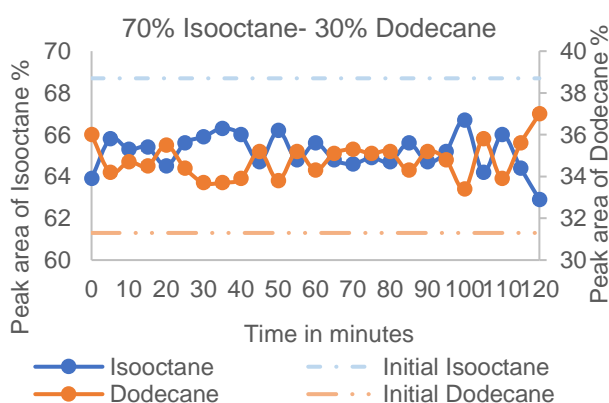

Figure 6 - Differential Permeability of 68,7% Isooctane / 31,3% Dodecane mixture – Core 18

For both samples an initial preference of dodecane flow is observed. After that there were multiple oscillations of preferential flow however, there was an overall preference of isooctane until the end of the experiment. It is also important to mention that core 5 with lower porosity retained a higher quantity of isooctane when compared to core 18 with higher porosity. Isooctane is a branched hydrocarbon when compared to dodecane which is a straight chain alkane [23]. In addition, isooctane presents a higher kinetic diameter of 6,2 Å (Figure 7b) while dodecane has 4,6 Å [24] (Figure 7a). When imagining a pore structure, it is possible that a preference of dodecane flow happens since not only presents a lower kinetic diameter but also a linear structure.
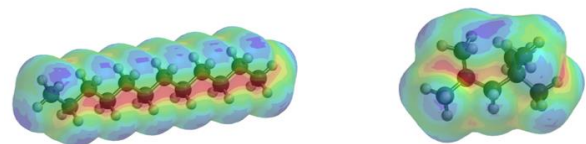

Figure 7 - a) Dodecane structure; b) Isooctane structure

Since it was not possible to analyse the pore structure it is not viable to affirm that a low porosity means that the size of the pores is smaller. Still, it is a possibility that with a higher kinetic diameter and a lower porosity it is more likely for the hydrocarbons to be kept from crossing the rock sample, enabling the hydrocarbons with lower kinetic diameter and linear structure to cross the rock specimen. In conclusion, a higher porosity implies a lower differential permeability which means that there is a more balanced flow of hydrocarbons throughout the rock sample.

Table 5 is presents the mass balance for both core samples with isooctane/dodecane homogeneous mixture which reaffirms what was mentioned before.

Table 5 - Isooctane / Dodecane - Mass balance

Core Samples	Rock Porosity %	Introduced Mass %		Collected Mass %	
		Isooctane	Dodecane	Isooctane	Dodecane
5	10,38	66,4	33,6	59,5	40,3
18	12,31	68,7	31,3	62,9	37,1

The following figures present the flow of the isooctane/n-octane mixture being the points referred to the percentage of each compound in the effluent provided by the gas chromatograph.

Figure 10 - Differential Permeability of 47,8% Isooctane / 52,2% n-Octane mixture – Core 7
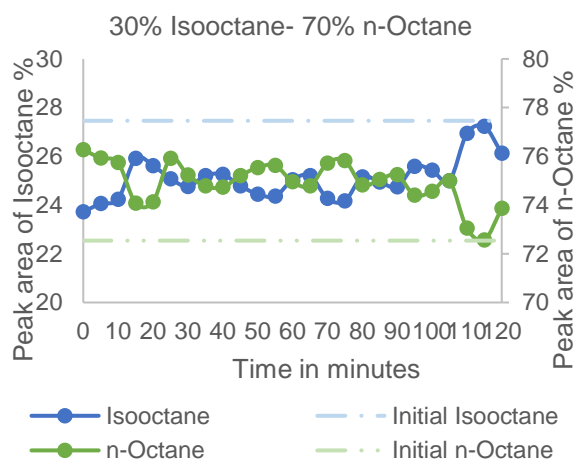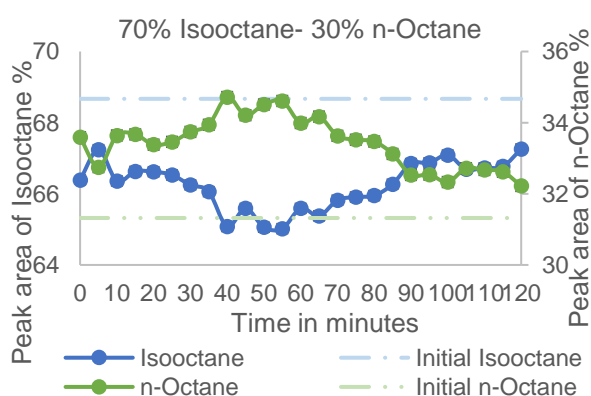

Figure 8 - Differential Permeability of 27,5% Isooctane / 72,5% n-Octane mixture – Core 22

Figure 9 - Differential Permeability of 68,7% Isooctane / 31,3% n-Octane mixture – Core 10
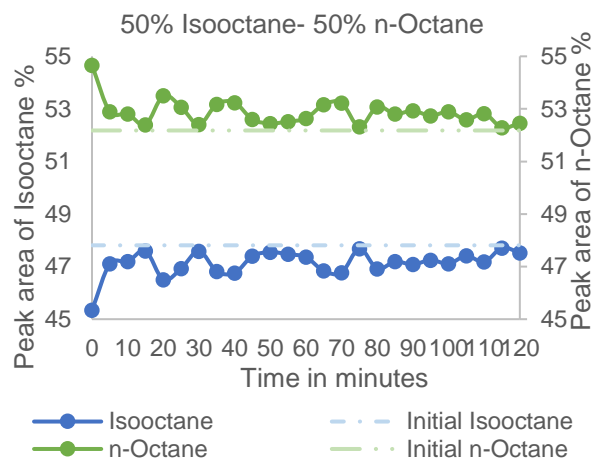
For all the cores with different mixture compositions, the flow was alternated and an initial preference for n-octane was observed. As mentioned before, isooctane molecules present a kinetic diameter of 6,2 Å (Figure 11b) while n-octane has 4,5 Å (Figure 11a) [24]. With this, and having core samples with similar characteristics (porosity, dimension, etc), it is possible to notice that the kinetic diameter had an influence on the flow of these mixtures since there was always a preference for n-octane on the first drop. Also, for the 50-50 proportion, n-octane presented always higher percentage.
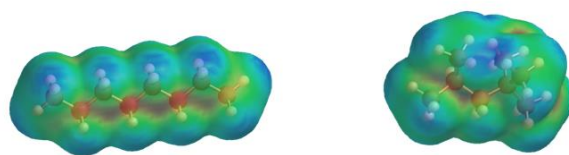

Figure 11 - a) n-Octane structure; b) Isooctane structure

For Isooctane / n-Octane mixtures, a mass balance was also performed (Table 6), which reaffirms the preferred flow for n-Octane in all essays.

Table 6 - Isooctane / n-Octane - Mass balance

	Rock Porosity %	Introduced Mass %		Collected Mass %	
		Isooctane	n-Octane	Isooctane	n-Octane
10	10,38	68,7	31,3	67,3	32,2
7	10,15	47,8	52,2	47,5	52,5
22	10,75	27,5	72,5	26,1	73,9

3.4 Comparison of Results: Carbonate rock Vs Sandstone rock

As mentioned multiple times, an important aspect of this thesis is the comparison of results with the sandstones sample analysed by Pinto (2020) [9]. It is important to mention that the sandstone specimen was disagregatted.

Pinto (2020) [9] obtained porosity results in the range of 30-40% for water, brine and hydrocarbons. It was already expected that the porosity would be higher not only because the rock was disagregatted but also because this specimen often presents macro pores. Regarding to absolute permeability, higher results were expected due to the relation that was noticed on the past graph (Figure 3) and also because of the existence of macro pores. In addition, as the molecular weight of hydrocarbons increase, a permeability reduction occurs but for carbonates, the opposite happens as it was already seen.

According to Jiménez-Cruz [24], isooctane presents a higher kinetic diameter of 6,2 Å while dodecane has 4,6 Å and n-octane 4,5 Å. Ahmed et al. [25], stated that like other n- alkanes, n-hexadecane presents a diameter of 4,6 Å. The order of magnitude from the lowest kinetic diameter is n-octane, n-hexadecane, dodecane and isooctane. When associating these values to permeability results, a high influence of kinetic diameter can be observed because with an increase of kinetic diameter, for branched hydrocarbons (isooctane) the permeabilities decrease and, for a decreased kinetic diameter an increase permeability occurs.

While this phenomenon occurs for carbonates, the opposite occurs for sandstones thus, sandstones pore network is probably composed by macro pores while carbonates pore network is smaller being kinetic diameter's influence more relevant.

Table 7 - Overall sandstone permeability [9]

Hydrocarbons	Permeability (mD)	% Isooctane / % Dodecane	Permeability (mD)	% Isooctane / % Hexadecane	Permeability (mD)
Isooctane	8143.7			88.2 / 11.8	7924.4
		69.6 / 30.4	5776,7		
Octane	7885.2			70.5 / 29.5	4284.0
		47.9 / 52.1	5554.5	49.0 / 51.0	4221.0
Dodecane	2737.4				
				30.3 / 69.7	3868.4
		31.4 / 68.6	4472.7		
Hexadecane	2300.9			10.9 / 89.1	2501.8
Water	220.3	Brine	488.6		

Regarding to the oil mixtures permeability analysis, Pinto (2020) [9] also used isooctane/dodecane mixture. Here it was noticed an increase in permeability with the increment of isooctane percentage. This effect happens for the sandstones because isooctane in comparison with dodecane has lower molecular weight thus, its flow is enabled, even though isooctane has a higher kinetic diameter when compared to dodecane.

For carbonates, the mixture is isooctane and n-Octane and as mentioned, Isooctane being a branched hydrocarbon creates more difficulty flowing through carbonates porous since they are smaller (when compared to sandstones), enabling the flow of n-Octane, linear hydrocarbon. Therefore, permeability increases when n-Octane increases.

Summarizing, permeability increases with the increase of lower molecular weight compounds or

when the kinetic diameter of the compound with higher percentage is lower. However, the effect of the kinetic diameter is more evident when dealing with smaller pore sizes. For the changes in composition of sandstones and carbonates oil mixtures (isooctane/dodecane), it was noticed an alternated flow for both specimens and an overall higher percentage of isooctane along the essay.
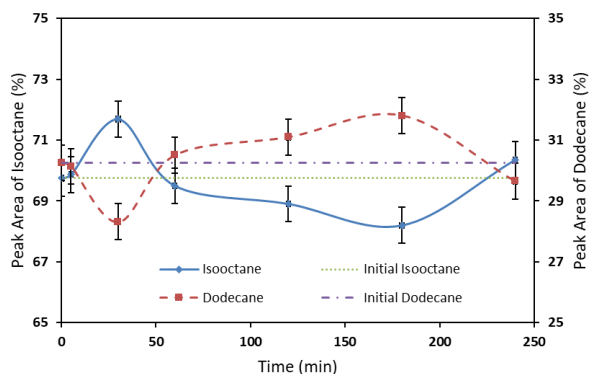

Figure 12 - Differential permeability for 69.7% Isooctane / 30.3% Dodecane mixture for Sandstone sample [9]

However, for sandstone sample it was noticed a higher percentage of isooctane at the end of the test when compared to the carbonate sample, which was expected. Since the sandstone was considered to be composed by macro pores, it allows a higher quantity of hydrocarbons to flow with higher kinetic diameters.

Table 8 - Mass balance at Isooctane / Dodecane mixtures

	Introduced Mass (%)		Collected Mass (%)	
	Isooctane	Dodecane	Isooctane	Dodecane
Sandstone	69,7	30,3	69,5	30,5
Carbonate	68,7	31,3	62,9	37,1

On the other hand, carbonate samples are composed by smaller pores when compared to sandstones which could have an influence in branched hydrocarbons (isooctane) flow. Thus, carbonate samples may enable a preferential flow of linear hydrocarbons (dodecane).

4. Conclusion

After analysing the carbonate rock from the Maçico Calcário Estremenho region, it was concluded that there was preference of fluid flow for lower kinetic diameters hydrocarbons. Even though the mixtures used were homogeneous, its flow was not, meaning that it did not occur as a bulk movement.

Also, lower porosity samples were more likely to retain higher kinetic diameter hydrocarbons and branched structure, allowing hydrocarbons with lower kinetic diameter and linear structure to flow through the rock sample.

In conclusion, it is possible to say that for rock specimens with a larger pore structure (sandstones), the kinetic diameter effect is almost negligible. On this type of specimen, lower molecular weight compounds have a preferential flow regardless of the kinetic diameter. Thus, kinetic diameter has more influence on carbonate samples when compared to sandstones samples.

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