Hydrodynamic in Nanopores: Applications for Recovery of Unconventional Resources or for Energy Storage

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1.Theme Description

World oil demand is growing steadily. Today it reaches about 100 million b/d[1]. Conventional oil reserves are about 1/3 of the non-conventional ones[2] such as: heavy oil, tight oil, shale gas, methane hydrates etc. These resources are deployed on extensive areas and need of specific technologies to be extracted. Hence nowadays, they are very expensive compared to the conventional ones.[3],[4]Several Enhanced Oil Recovery Technologies exist (Thermal, Gas and Chemical) but they don't exceed 40% of recovery. Hence, to increase this percentage isnecessary to better understand the transport of oil and gas into nanopores rocks.Indeed, due to dimension of pores and the rock heterogeneity the flow description with conventionalmathematical modelareno longer suitable[5].In the following sections the flow in nanopores rocks, the mathematical tools, simulations and experimental studies are described.

2.Transport in Material with Complex Pore Geometries

The flow through the nanopores rocks takes place within

channels less than 100 nm[6] and can't be described by conventional models. Unlike conventional reservoirs, theunconventional ones, indeed, have worse features of porous bed. The porosityis between 2-6%, the permeability can change quickly from 0.001 μD up to 1 mDand the system is oil wet rock (the contact angle between fluid and rock is more than 90°C).[7] Referringfor example to tight oil, the pore diameter is between 30-200 nm including micro-macro and meso-pores. The reservoir is formed by several zones such as oil+mobile water and gas+oil+immobile water as shown in Figure 1. The oil productionreaches low flow rates in 9-12 months. Therefore, as described in the following sections several techniques have been studied to enhance oil recovery.[8]

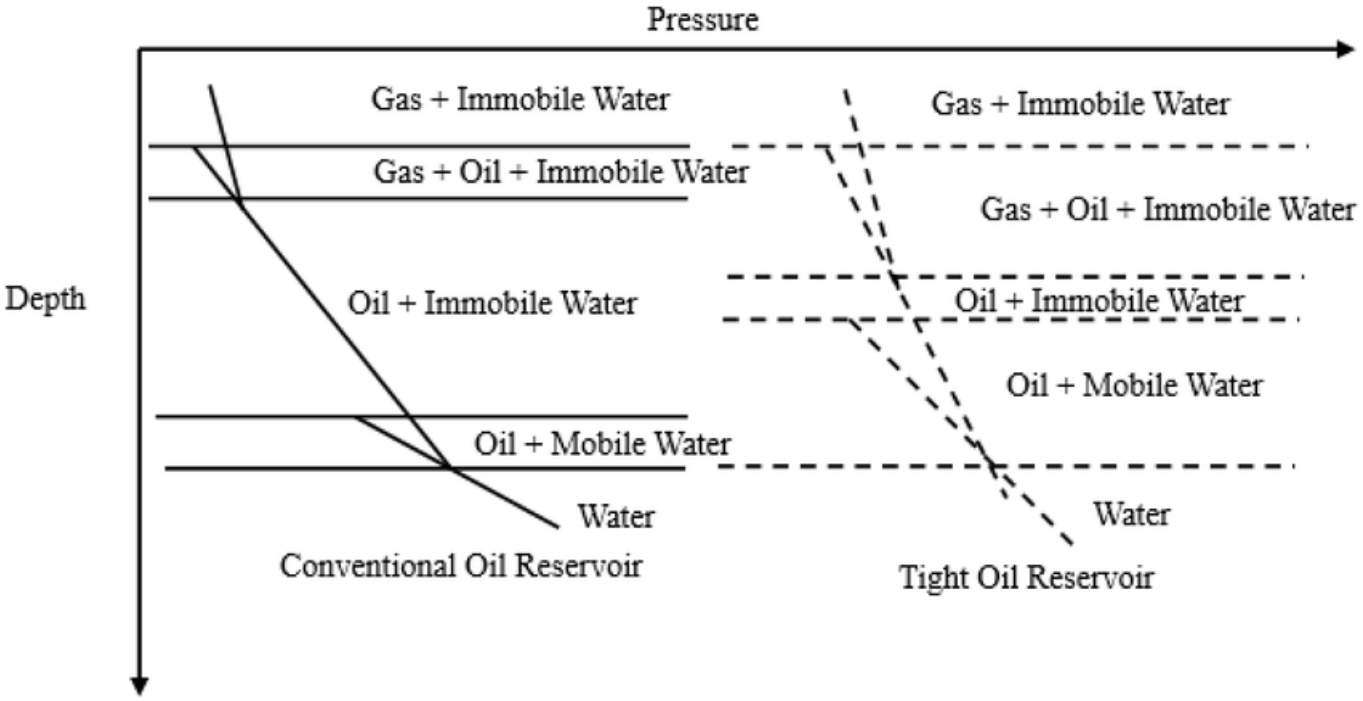

Figure 1 -Conventional Reservoir Vs Tight Oil.[9]

Flow Regimes

The flow depends on Knudsen number5 and due to pore diameter, it isn't continuum. Therefore, it can't be described by Darcy law, but slip, transitionand free-molecule flow need to be

considered. Boltzmann equation can be solved to describe the flow (Figure 2), but to reduce computational costs it is solved only for simple problems. Hence, several mathematical models are used such as Molecular Dynamics (MD), Direct Simulation Monte Carlo, Burnett equation and reduced order Boltzmann equation (LBM and Grads)[10]. Hou et al.[11]has proposed to combine the positive aspects of LBM and MD methods. In this way, MD is suitable to describe the fluid flow near the surfacesofporous media while LBM allows to describe the rest of the flux,saving time by means of simplified kinetics models.

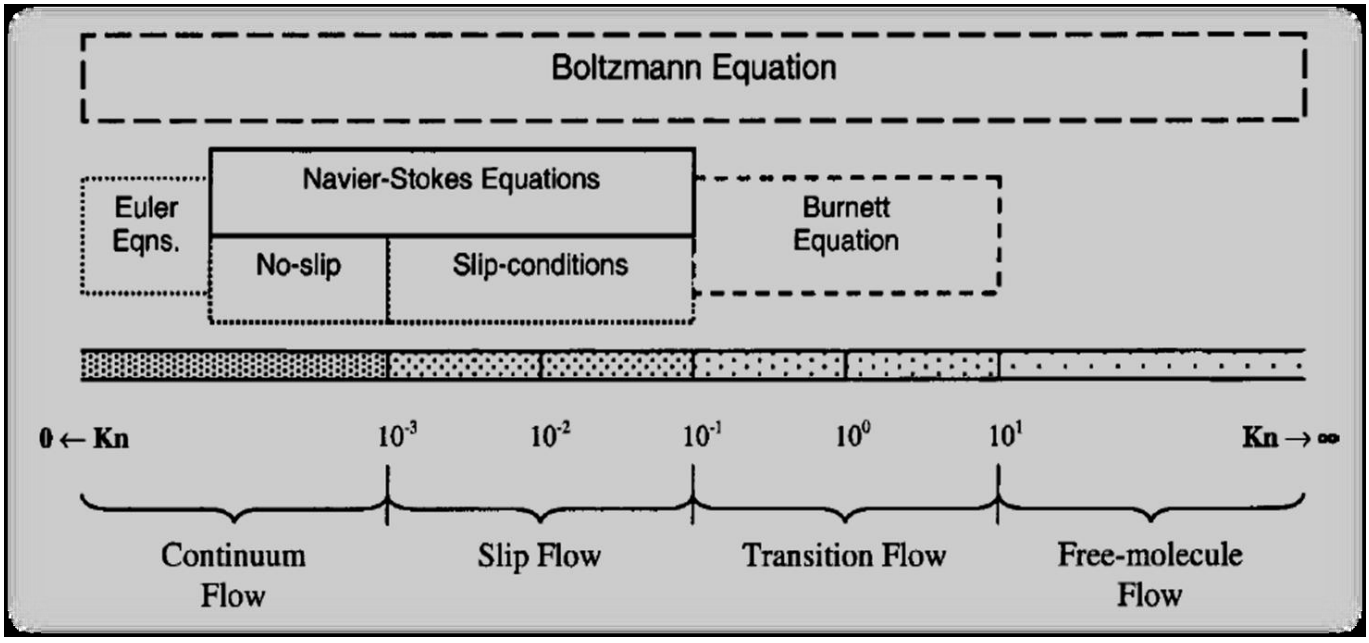

Figure 2 -Flow Regimes depending on Knudsen number[12]

Computational Analysis

On computational level the porous medium can be simulated in different ways. For example, **Unfractured Porous Media** can be described by means of[13]:***One-Dimensional Models,*** where pore spaces are considered like a series of capillary tubes in which the radius can be the same for all or not. The model can take into account the tortuosity, but itcan’t describe the

interconnectivity of the pores.***Continuum Models***,where the domainis considered as a distribution of identical spheres. The model can represent anunconsolidated or consolidated porous medium depending on the overlap of the interconnections.***Random Hydraulic Conductivity Models***,in which domainis divided into rectangles with a random hydraulic conductivity.While, referring to **Fractured Porous Media** the principlemodels are14:***Models of a Single Fracture,***where the simplest model is represented by two parallel flat plates. It can be solved analytically, but it isn't suitable to describe the internal morphology of the fracture; indeed, it doesn'ttake into account the roughness of the fracture. ***Models of Fracture Networks,***in whichfractured rocks are described as a network of interconnected elements. In this way is possible to describe the flow in the fractures by means of 2D and 3D models. ***Models of Fractured Porous Media***are suitable for describing flow in matrices with high permeability. These models include double porosity andpermeability models (see for example the model used byFragoso Amaya[14]). In the former the matrix acts as medium storage, while in the latter both matrix and fractures networks contribute to transport and fluid flow.

3. Methods to Improve the Recovery of Chemical Transformation Processes

There are several techniques that allow to improve oil recovery and can be classified into **primary, secondary** and **tertiary recovery**[15],[16]. The former consists of the extraction of oil via natural rise or pumps. It let to recover only 5-15% of hydrocarbons. Secondary recovery, instead, consists of the injection of water/gas in the reservoirs. It let to reach 30% of recovery while Tertiary recoverytries to make the ground more suitable to the extraction of oil. Currently these technologies don't exceed 40%.[17]Oil recovery from reservoirs, indeed, depends on different factors such as the **Mobility Ratio (M)** and **Capillary Number (N_c)**[18].The first

represents the oil capacity to move through the pores. If M >1, more fluid needs to be injected to obtain an optimal oil saturation into the pore. While M <1, means that mobility ratio is favourable. This can achieve by reducing viscosity of oil (i.e. with thermal techniques) or by increasing viscosity of displacing fluid (i.e. with chemical techniques). The capillary number, instead, measures the relative weight of viscous forces against interfacial tension. In the following section the main techniques to improve oil recovery are described.

Thermal Enhanced Oil Recovery (TEOR)

This technique is applied to heavy crude oil with[19]: API Gravity between 10-20°, reservoirs depth less than 3000 ft, permeability of 500 mDand sand thickness between 30-50 ft. It includes **Steam Injection**and **In-situ combustion**. The firstconsists of the injection of hot steam into the reservoirreducingviscosity of heavy oil and increases the pressure[20]. Steam can be injected periodically (***Cyclic steam Injection***)[21] or by means of two horizontal wells (***Steam assisted gravity drainage, SAGD***), where the oil is drained into the lower well by means of gravity[22]. In situ combustionconsists of the injection of dry air or wet air into the reservoir. The combustion of part of the heavy oil (5-10% of the crude oil)[23] generates a combustionfront that flows along the reservoir. This front is sustaining by means of the coke present in the reservoir or in the case of wet air by means of steam produced.[24],[25]

Gas Enhanced Oil Recovery (GEOR)

This technology includes **Miscible Gas Injection**and **Immiscible Gas Injection**. In the former CO_2 or $N_2$are used to increase oil

recovery. As shown in Figure 3 a) the carbon dioxide is injected at 1200 psi and density 5 lb/gal, it mixes with oil trapped into pores forming a concentrated mixture that goes back to the surface. Then, $CO_2$is removed from the mixture, recompressed and injected again in the reservoir [26].

The CO_2 flooding is also a promising technique for tight oil reservoirs. Indeed, waterflooding could form a film on the pore surface decreasing the recovery. In figure 3 b) is shown the common techniques used in tight oil. The wells move vertical until tight formation and then parallel to reservoir. The gas in injected to fractur the rocks allowing to oil to move into wells.[27]

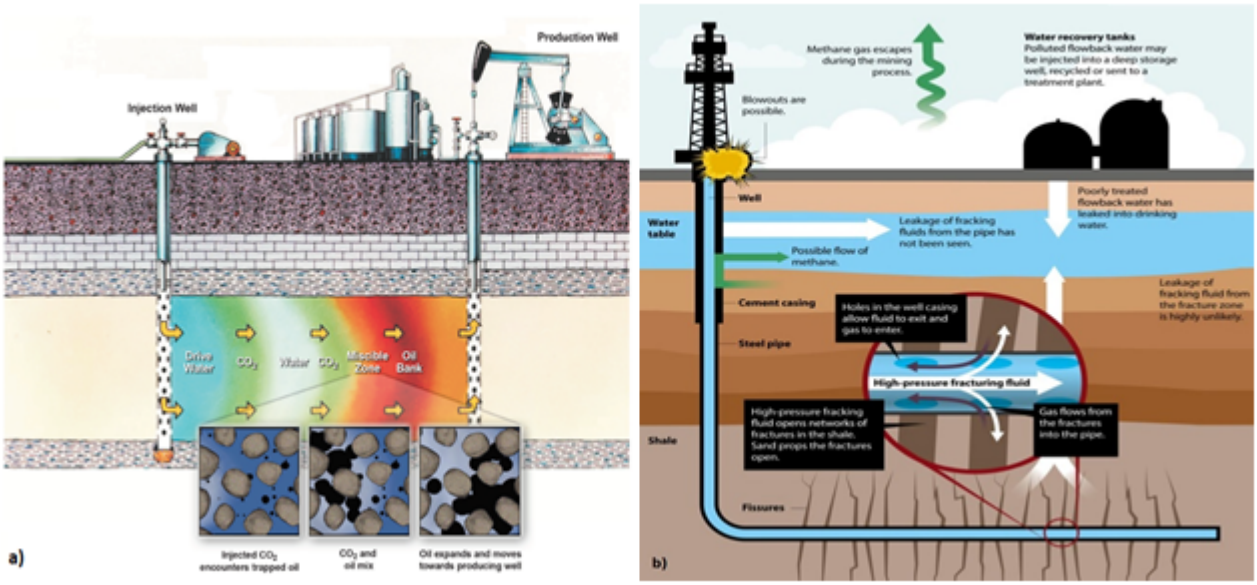

Figure 3– a) Waterflooding and Carbon Dioxide injection; [26] b)Fracking in tight oil.[28]

The **Immiscible Gas Injection**consists of the injection of gas under Minimum Miscibility Pressure (MMP). This technique is suitable for light oil rather than heavy oil.[18]

Chemical Enhanced Oil Recovery (CEOR)

In the case of heterogeneous reservoir CEOR is better than GEOR. This technique, indeed, reducesthe interfacial tension, wettability and mobility.[29]It includes**Polymer Flooding, Surfactant Flooding and Alkaline Flooding**.The formeris used to minimize bypass effects due to capillary forces and to increase water viscosity. Usually, the polymers injected in the reservoir are about the 30% (minimum) of the reservoir pore volume. They can be divided into two categories biopolymer and synthetic polymer[30]. Surfactant, instead, reduces interfacial tension between oil and water and alters wettability, butpart of these substancesis adsorbed onto the rock surface.[31]Alkaline flooding is very efficient in reservoirs with high acid content. Indeed, the alkaline reacts with the acid form a surfactant solution that allows to reduce interfacial tension, emulsification and alters wettability.[32]Combinations of the previous solutions such as **Surfactant Polymer Flooding**and **Alkaline Surfactant Polymer Flooding** are often used.

Nanoparticles to Enhance Oil Recovery

Nanoparticles are having great attention as emerging technologies to be employedin oil & gas field. These materials, indeed, could be used as sensors to be injected into the wells to understand the property of reservoir (pH, hydrocarbon saturation etc.) or as "smart-fluid" for increasing oil recovery altering wettability (more water-wet), improving mobility ratio and reducing interfacial tension[33]."Smart fluid" can be divided into three groups: metal oxide (Al_2O_3, CuO, Fe_2O_3/Fe_3O_4 etc.),organic (i.e. carbon nanotubes) and inorganic (i.e. silica).[34]In Figure 4 is represented the structure of nanoparticles used to evaluate the oil recovery of Berea sandstone sample having 17.45 API, air and liquid permeability of 184 mD and 60 mD respectively and a porosity of 20%. The better response is given by a

mixture of aluminium oxide and silica oxide at a concentration of 0.05 wt. due to reduction of interfacial tension.[35]

Among them emerging nanoparticlesare represented by carbon nanotubes(CNT). These compounds fall in fullerene category, have good resistance to corrosion. They can be arranged in single or multiple wall made of graphene and the surface is hydrophobic with high slip length.6,[34]For other applications of nanoparticles in oil and gas industry such as corrosion inhibition, methane release from gas hydrate, etc. it can be consulted Fakoya et al.[36]

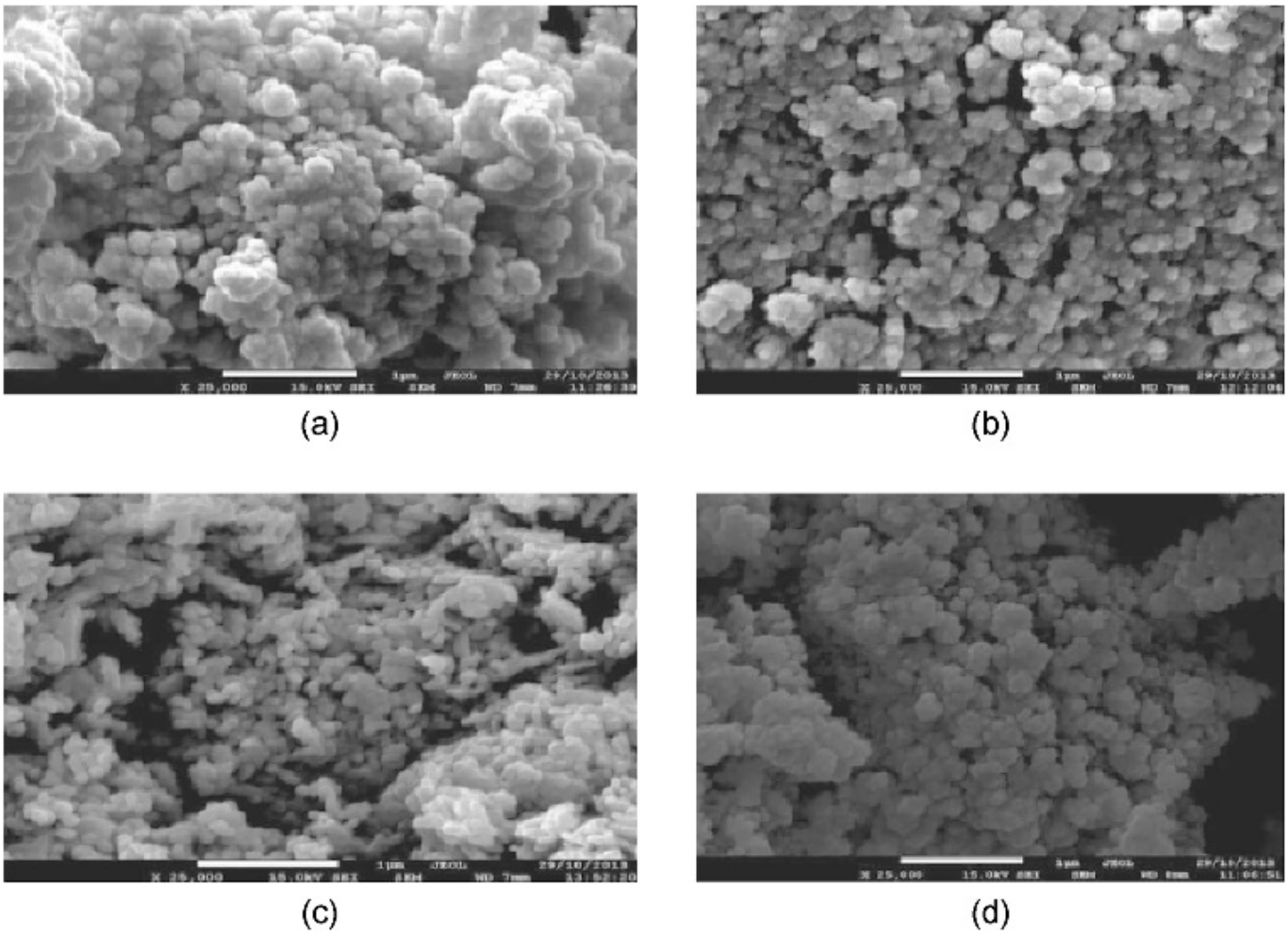

Figure 4– Smart fluid application on Berea sandstone sample: (a) titanium oxide, (b) aluminium oxide, (c) nickel oxide and (d) silica.[37]

4. Simulation Studies and Experimental Works

In literature there are several simulation studies some of them are summarized in this section.Moraes de Almeida et al.[38]described the fluid flow of water and light crude oil on silica nanoporesby means of Molecular Dynamics. The nanopores were simulated with two hydrophilic terminations (silanol and siloxane rich) and three different scenarioswere considered: water/oil infiltration on empty nanopores and water infiltration on oil filled nanopores and vice versa. For empty nanoporesboth water and oil infiltrated quickly (0.5 ns for oil and 1 ns for water) and the interfacial tension was reduced of about 35% for oil/siloxane terminations. For the other cases water infiltration on water/oil filled wasensuredat10 and 5000 atm respectively while oil infiltration on water filled occurs at 600 atm. Ross et al.[39]studied friction coefficient for the fluid flow of water inside flat graphitic slabs (5 x 5 nm) and inside/outside carbon nano-tubes (5 nm length) varying the characteristics length of the two configurations.Molecular Dynamics model was used considering no-slip conditions at solid-fluid interfaces. In this way was possible to calculate the slip length. Tests showed that friction coefficients depended on the curvature of porous surfaces. In particular, they were higher in presence of convex surfaces and lower for concave ones.Lee et al.[40]treated hydrocarbon recovery from shale gas. They simulated kerogen structure by means of several models (disordered, ordered and composite) based onmolecular and statistical simulation.The recovery depends on interfacial tension and is thermally activated. Particularly the energy barrier is strong for immiscible fluids such as water while it is less for miscible ones such as CO_2 and C_3H_8. Despite carbon dioxide, propane is recovered together with the methane extracted.

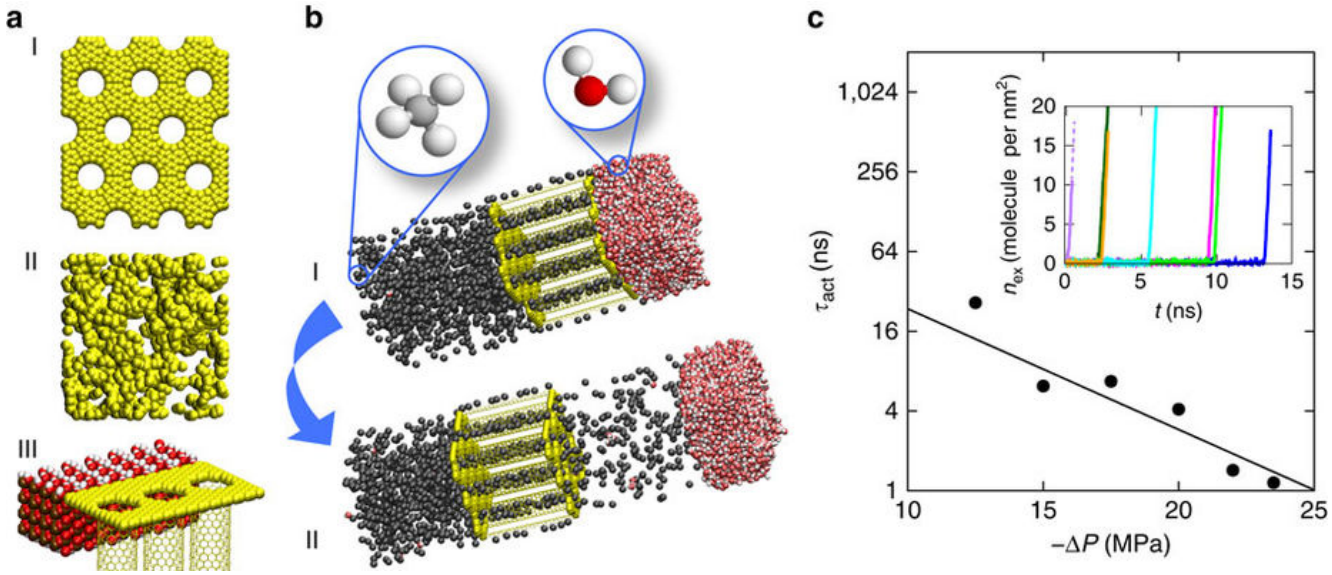

Figure 5– Model simulations and Results in presence of Water: a) I,II and III represent three different structures considered in the simulations; b) I and II outline the starting and end points of the simulation where the methane is trapped inside a CNT membrane with a triangular shape (yellow). The left side is set at constant pressure by methane while the right side is maintained at low pressure by water; c) It is shown the amount of methane extracted from the pores as function of time.[41]

Alfarge et al.[42] simulated oil recovery from Bakken formation injected three different miscible gases such asCO_2, lean and rich gas. The well was stimulated by means of 5 hydraulic fractures spacing of about 200 ft. The test showed at first high production but then a rapid decline due to reduction of pressure nearby the production well.Three different scenarios were simulated changing the number of cycles from two to ten, the duration of injection from two months to six and the duration of soaking from one month to three.The use of CO_2 increased molar diffusivity, while rich gases needed a major soaking period despite lean gases that requiredmore volume to be injected. Prajapati et al.[43]simulated the flow through shale reservoirs. They

considered a binary mixture of CH_4-CO_2 flowing through a kerogen matrix by means of four models: Wilke, Wilke-Bonsaquet, Maxwell-Stefan and Dusty Gas Model. This led to a system of nonlinear equations solved by means of COMSOL Multiphysics. It was demonstrated that Knudsen diffusion and binary molecular diffusion had to be considered, indeed the flux is 10 times higher in Wilke, Maxwell-Stefan rather than Wilke-Bonsaquet, Maxwell-Stefan and Dusty Gas Model.Regarding to **pilot tests**, in 2010 there were about 1500 EOR (i.e. Carabobo[44], Grosmont[45]etc.) of which 78% refers to sandstone, 18% to Carbonate and 4% to turbidite and offshore fields. Among EOR technologies thermal and chemical projects are widespread in sandstone while gas and water recovery in the rest.[46]One of the most interesting project concerns **Bakken formation** one of the biggest oil and gas reservoir in the USA. It is estimated that this geological formation could yields until 40 billion barrels[47], but only 10% is nowadays recovered due to low permeability (0.0018-0.0036 mD).[48] Therefore from 2008 to 2014 seven pilot tests are performed to improve oil recovery: 2 in Montana and 5 in North Dakota. Several techniques are used: cyclical injection with CO2 and water, flooding with water and enriched natural gas and vertical injection with CO_2. Despite ultra-low permeability emerges that injectivity doesn't be an issue for either gas or water. However, increasing in oil recovery is low. Therefore, new tests need to be performed to understand fractured networks, flow in nanopores rocks and collect more data. This can be achieved by means of cores from vertical and later section subsequently analysed in laboratories. (for more information about pilot tests see[49]).

5.Energy Subsurface Storage

The most mature and widely used technology is the **Underground Gas Storage (UGS)**. Nowadays, indeed, there are 630 underground gas storages[50]. The gas is injected, from the pipeline to the ground such as depleted oil reservoirs when the demand is

low and is used when the demand grows. The storages don't have 100% efficiency because part of the gas called "cushion gas" remains in the subsurface to maintain pressurized the reservoir.[51] A promising technology is the **Carbon Capture Storage (CCS)**of CO_2 where the gas injected in the subsurface can work as a displacing fluid (see Section Gas Enhanced Oil Recovery) or can be stored. Generally, it is injected at a depth of about 800 m where CO_2 is in a liquid or supercritical state. It can be stored by a "cap rock" such as clay rock that is impermeable to CO_2 or by capillary forces that block the CO_2 in pores.[52]

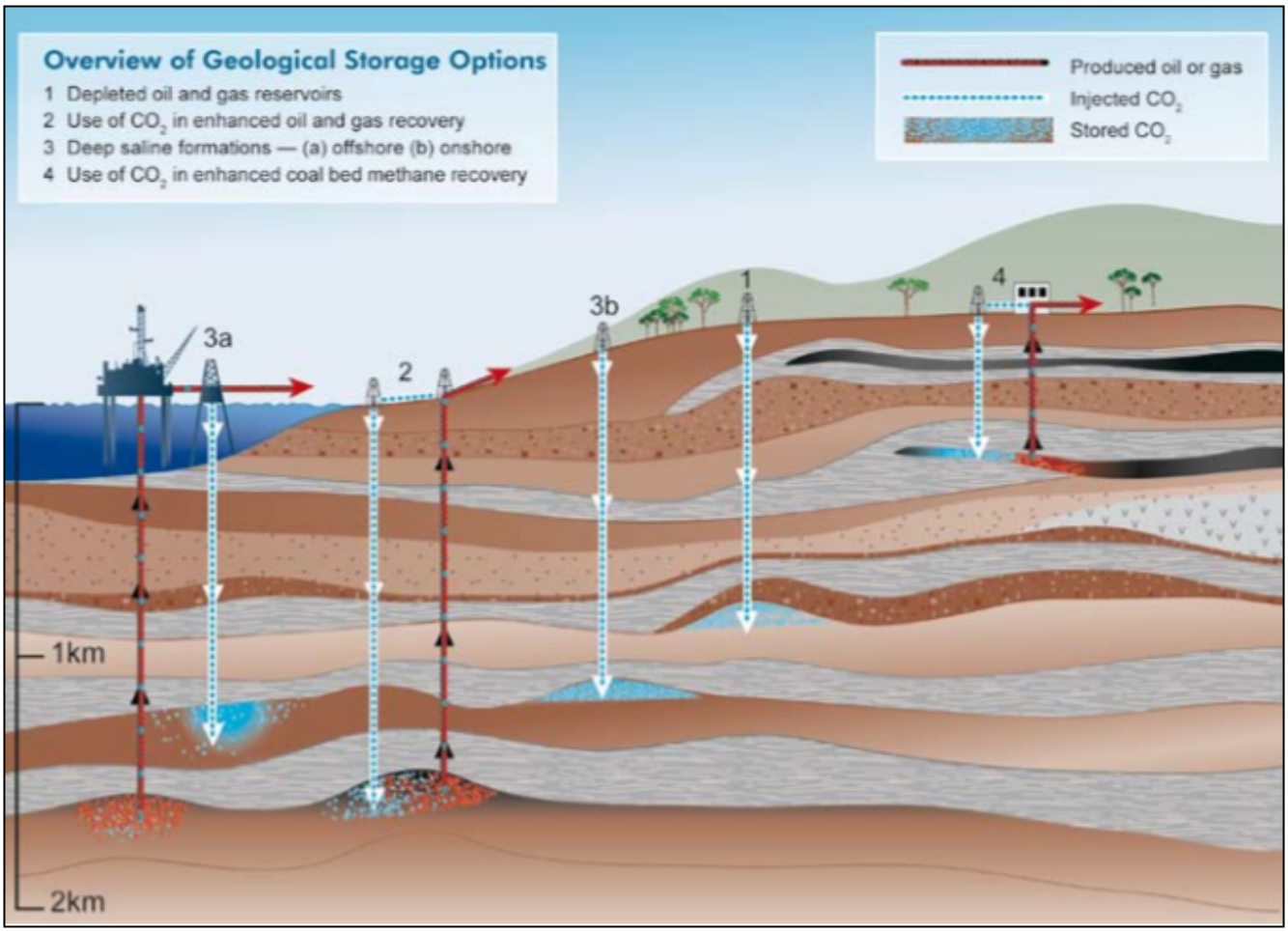

Figure 6 – Applications of Carbon Capture Storages.[52]

6. Conclusions

Nowadays technologies to Enhanced Oil Recovery of unconventional hydrocarbons and Energy Storages exist. The most widespread are TEOR (ThermalEnhanced Technology) and Underground Gas Storage but they don’t achieve high efficiency.

Several mathematical models are used to describe the flow in porous rocks. However, porous media have a chaotic configuration and the equation of transport can be resolved analytically only in few cases. Furthermore, the models are based on simplified hypothesis that allow to describe a specific phenomenon. Therefore, is necessaryto continue investigating the hydrodynamics in nanopores rocks by means of pilot tests (i.e. Carabobo, Grosmont, Bakken etc.) In this way is possible to improve technologies and models that allow to describe the phenomena exhaustively.Among emerging technologies, nanoparticles (i.e. silica, CNT etc.) can be a pivotal role in increasing oil recovery. However, these compounds are tested only on laboratory scales and are very expensive. Therefore, is necessary to reduce the cost of production by having better performances with lower concentration

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