EXECUTIVE SUMMARY OF THE THESIS

Nanoemulsions as chEOR fluids: from laboratory tests to coreflooding simulations

TESI MAGISTRALE IN ENERGY ENGINEERING – INGEGNERIA ENERGETICA

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1. Introduction

Crude oil still represents one of the principal sources of energy worldwide. According to the British Petroleum Statistical Review of World Energy, it leads the energy market together with other fossil fuels, covering 85% of the total energy mix in 2020. Considering an upcoming relevant increase in the total energy required worldwide associated with population growth and global economy development, it is possible to state that oil will continue to play an important role sustaining the energy demand in the future, also in the context of the growing interest for renewables. Three stages can be distinguished throughout the operation period of an oilfield: primary recovery, based on the production of oil by natural drive mechanisms; secondary recovery, during which pressure maintenance is pursued with the injection of a fluid (typically water or an immiscible gas), and tertiary or enhanced oil recovery (*EOR*). The latter relies on the injection of something different than water or immiscible gas to further improve oil recovery. It includes several techniques, each characterized by a distinct mechanism of action. Nanoemulsions belong to the class of chemical flooding methods, defined by their action on mobility, rock wettability and interfacial tension.

2. Nanoemulsions overview

Nanoemulsions (*NE*) are kinetically stable colloidal systems formed by two or more immiscible liquids, arranged in at least one continuous phase (outer phase), and one inner phase dispersed in droplets of submicrometer size. The mixture of the two liquids is stabilized and forms a unique emulsified phase when mechanical energy is applied to the system in the presence of surfactants. The preparation of an emulsion requires a sufficient mixing energy to spread one phase in the other one, increasing the surface area of the dispersed phase. Several procedures can be applied for emulsion formation. These can be classified mainly as high or low energy methods.
All of the preparation methods require the presence of emulsifiers, usually surfactants (SURFace ACTive AgeNTS). These are

amphiphilic molecules formed by a hydrophilic and a hydrophobic part. Due to their intrinsic structure, they are able to place at the interface between the phases reducing the energy required to spread one phase in the other and the liquid interfacial tension (*IFT*). Nanoemulsions characteristics and stability depend upon the preparation pathway. A major advantage associated with this technology is that they are not subject to gravity-driven separation processes because of the small droplets size.

2.1. Mechanisms of action

Several experiments demonstrate the effectiveness of nanoemulsions in enhanced oil recovery processes. The displacement promoted by this technology in porous media is based on various mechanisms, that are similar to those of standard emulsions: reduction of interfacial tension between water and oil, wettability alteration of rocks, emulsification of trapped oil and mobility ratio improvement. In addition to these mechanisms, the kinetic stability and improved rheological properties shown by nanoemulsions positively influence the oil recovery factor. An important element that makes the difference with respect to a standard emulsion is the high surface to volume ratio of the dispersed phase, that maximizes the interaction with the fluids. This aspect is key in the oil viscosity reduction process obtained through the mixing of the low viscosity nanoemulsion solvent and the viscid oil in place (*solvent effect*).
It is important to recall that Nanoemulsion can show diverse rheological behaviors (Newtonian fluid, non-Newtonian fluid and viscoelastic fluid), that need to be taken into account during the analysis of their action in porous media.

Nanoemulsions currently represent an innovative research topic, investigated almost exclusively with laboratory experiments. Literature on nanoemulsion based *EOR* is not very rich, with the nearly complete absence of simulation works on the topic [1]. The present work tackles simulation of nanoemulsion *EOR* processes, providing a first approach to their modeling which can be possibly improved by future studies.

3. Experimental campaign

To analyze the potential effectiveness of this technology, several flooding tests have been carried out in Eni laboratories. Two of these are considered in this work: the first one involves a slim tube filled with crushed Berea and saturated oil, the second one is performed on a reservoir oil plug.

3.1. Plug application

The first experiment to be analyzed was carried out in 2017 by Del Gaudio et al [2] with the aim of evaluating the injectivity of the nanoemulsion selected and optimize the efficiency of their formulation in terms of oil recovery. In this application, the dry core, a Berea sandstone plug characterized by a porosity φ = 22.56% and a permeability k = 360 mD, is first fully saturated with brine and is then flooded with oil until initial water saturation conditions (S_{wi} = 27.2%). At the end of a four weeks ageing period in reservoir oil, the core is placed in an oven to resemble the reservoir temperature of 77°C.
Once the plug has been prepared, the standard fluid injection sequence has been followed to carry out the experiment in tertiary mode:

1. Brine injection (~80 PV; 0.7 ml/min);
2. Nanoemulsion slug injection (0.3 PV; 0.7 ml/min);
3. Chase water injection (0.7 ml/min).

As flooding proceeds, pressure drop across the sample is recorded and effluents are collected in test tubes to determine the quantity of oil recovered. An additional oil recovery (~21%) has been achieved by nanoemulsion (as compared against the water flooding). This effect becomes clear after 81 PV when the recovery factor (*RF*) experiences a steep growth and the pressure (*BHP*) rises up to 2.1 bars, as shown in Figure 3.1.

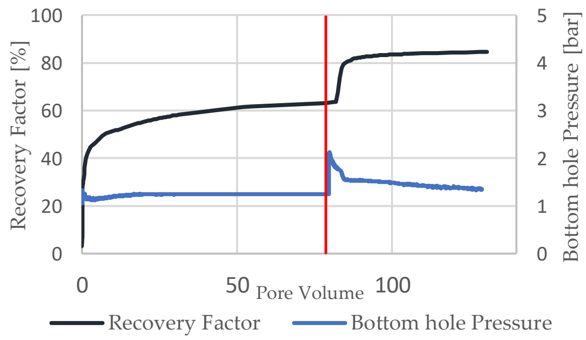


Figure 3.1: Plug experimental results for *RF* and *BHP*.

3.2. Slim tube application

The goal of this experiment was to verify the composition of the eluted phases with respect to the injected formulations and the contribution of the displacement of the nanoemulsion slug to yield

the highest oil recoveries. In addition, thanks to its length (2 m), a slim tube setting enables one to analyze the behavior of nanoemulsion at long distances from the point of injection. The petrophysical characteristics of the sample are φ = 41% and k = 2900 mD.
Slim tube preparation starts with N_2 injection, to dry Berea sand, then brine saturation is attained twice, first at ambient and then at reservoir temperature. The last steps are brine displacement by mean of oil injection until initial water saturation conditions (S_{wi} = 38%) and 40 days ageing in the oven at 90°C.
The applied injection procedure is similar to the one explained in Section 3.1:

1. Water injection (~5.5 PV, 0.5 ml/min);
2. Nanoemulsion slug injection (0.3 PV, 0.5 ml/min);
3. Chase water injection (0.5 ml/min).

Oil recovery due to the injection of a nanoemulsion slug is about 16% as displayed in Figure 3.2.

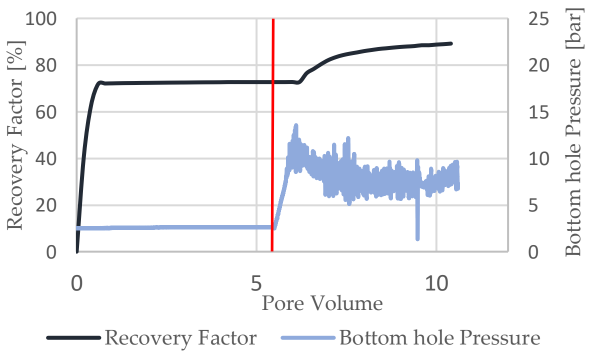


Figure 3.2: Slim tube experimental results for *RF* and *BHP*.

4. Simulation workflow

The simulation tool selected to model the nanoemulsion experimental activity is STARS (Steam, Thermal and Advanced processes Reservoir Simulator) by CMG. Cartesian grids with uniform petrophysical properties have been used to simulate both systems. The grids are parted into 100 blocks along the I-direction, with no divisions in J- and K-directions. Two point wells, injector and producer (along I-direction) have been created at [1 1 1] and [100 1 1] nodes of each grid respectively.
The sand-pack system flooding studies have been simulated in three phases: (1) water flooding, (2) nanoemulsion flooding and (3) chase water flooding. To model nanoemulsion behavior solvent and surfactant contributions have been taken into account, since they are considered to represent the main mechanisms of action of this technology. The dilution of oil and ensuing viscosity reduction operated by the solvent migration towards the oil in place, has been modeled through the action of a partition coefficient. This parameter is indeed defined as the ratio of the concentrations of a given compound in two immiscible solvents at equilibrium. Surfactants effect is implemented in the model through the integration of an additional set of relative permeability curves (generated according to Corey model). These take into account a modification of rock wettability towards a more water wet condition with respect to the one used in the waterflooding simulation. Interpolation of relative permeability curve available sets is then performed by associating in-between high and ultralow *IFT* conditions with relative permeability datasets. The interpolation is settled as a function of surfactant (defined in this case as *key component*) composition in a specified phase. Adsorption of this additive onto rocks is modeled by Langmuir adsorption isotherms.
Boundary conditions are defined via wells operating constraints: constant injection rate on the left boundary and constant bottom hole pressure at the right boundary. The key elements employed in the simulations are listed in Table 4.1.

Model parameters	Plug application	Slim tube application
Grid cells	100x1x1	100x1x1
Grid length	9.72 cm	200 cm
Porosity	22.56%	41%
Permeability	360 mD	2900 mD
Reservoir temperature	77°C	90°C
Oil viscosity	64 cP	0.7335 cP
Solvent concentration in NE formulation	8%	8%
Brine injected	~ 81 PV	~ 5.5 PV
NE injected	0.3 PV	0.3 PV
Injection rate	0.7 ml/min	0.5 ml/min

Table 4.1: Key elements employed in the simulations.

A coreflooding History Matching (*HM*) procedure has been carried out using CMG-CMOST simulator, where 400 model runs are performed with various combinations of uncertain model parameters values. The model obtained with the set of data corresponding to the least deviation

from experimental results is retained as the best one, for the purpose of our analysis.
Results obtained from the simulation compared to experimental data are shown in Figure 4.1 and Figure 4.2 for the plug and slim tube application, respectively.

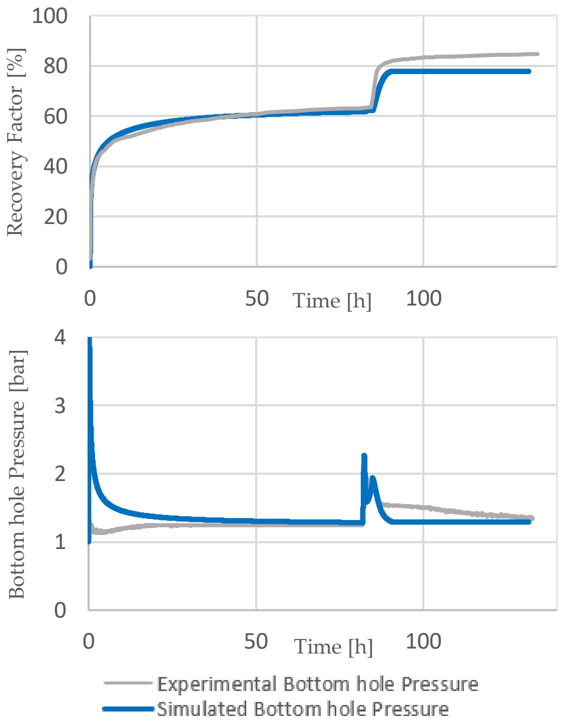


Figure 4.1: *RF* and *BHP* in plug application.

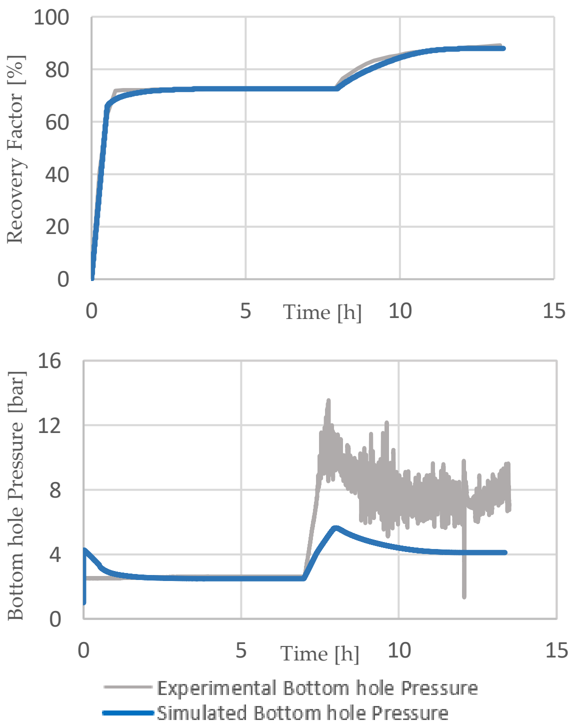


Figure 4.2: *RF* and *BHP* in slim tube application.

5. Global Sensitivity Analysis

The importance of Sensitivity Analysis (*SA*) stems from the observation that a model typically comprises input parameters whose values are affected by uncertainty. Among the different available *SA* techniques, a moment-based Global Sensitivity Analysis (*GSA*) approach introduced by Dell'Oca et. al [3] has been applied to the numerical slim tube flooding model. This enables us to quantify the relative contribution of uncertain model parameters to the *RF* and *BHP* probability density functions, as described by main statistical moments.
The first step required during this type of analysis is to examine all the parameters embedded in the model and select those which could be chiefly affected by uncertainty. All parameters have been considered as independent random variables, each characterized by a uniform probability density function (pdf). A variability range has been associated with each parameter according to data found in the literature.
Due to the consistent computational time required by the CMG software to complete one run of the full numerical model, the construction of a simplified surrogate model is required. Among the different techniques available to build a surrogate model, this work concentrates on the use of the Polynomial Chaos Expansion (*PCE*) based on two diverse methods: Sparse Grids (*SG*) and Quasi Monte Carlo (*QMC*). Several surrogate models for each quantity of interest, i.e. Recovery Factor (*RF*) and Bottom hole Pressure (*BHP*), at different timesteps have been constructed and their suitability has been assesses through a Mean Absolute Error (*MAE*) metric.
The surrogates which reproduced in the best way the full model simulation results have been selected and used to produced 1000000 random realizations of the model, employed for the computation of the AMA sensitivity indices introduced by Dell'Oca et al. [3]. These quantities, computed for mean ($AMAE_{x_i}$), variance ($AMAV_{x_i}$), skewness ($AMA\gamma_{x_i}$) and kurtosis ($AMAk_{x_i}$) , analyze the expected distance between a given statistical moment of a target variable conditional to values of a model parameter and its unconditional counterpart. Results are shown in Figure 5.1 and Figure 5.2.

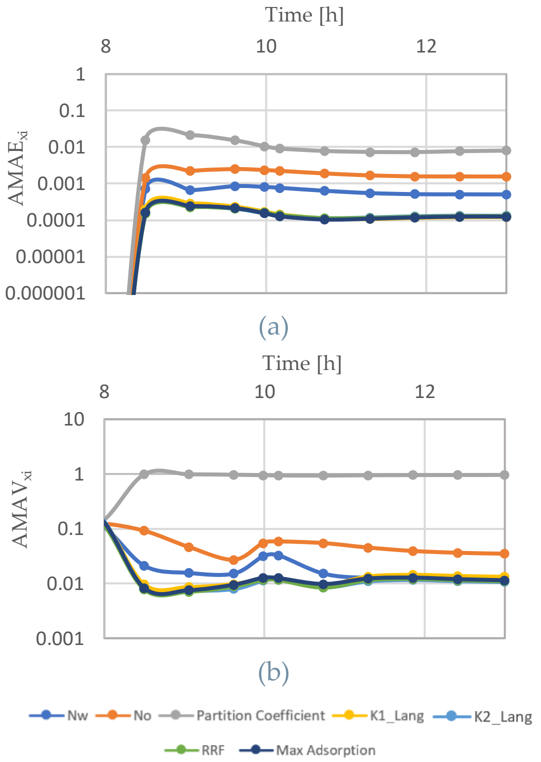
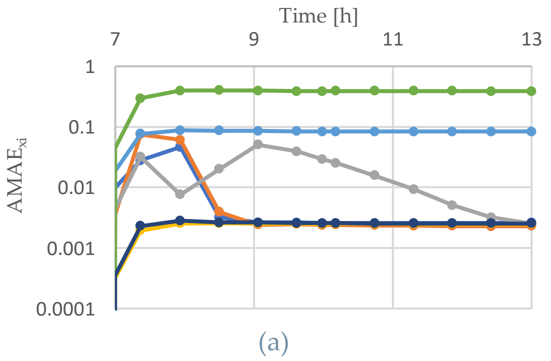


Figure 5.1: Time evolution of the global sensitivity indices (a) $AMAE_{x_i}$ (b) $AMAV_{x_i}$ of RF.

Statistical moments of recovery factor are very sensitive to partition coefficient during the whole flooding. This is consistent with the hypothesis underlying model implementation, according to which solvent migration towards the oil in place drives the oil recovery process. Another contribution that becomes evident when evaluating changes from unconditional to conditional mean value (Figure 5.1 (a)) is the one given by the exponents of the relative permeability relations. This suggests that wettability alteration process plays a role in oil mobilization although its impact is lower than the previously cited one.



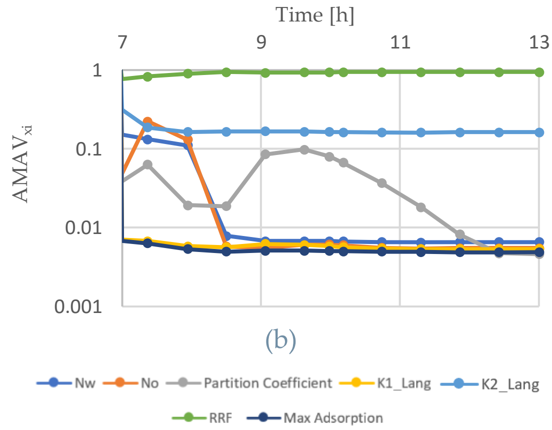


Figure 5.2: Time evolution of the global sensitivity indices (a) $AMAE_{x_i}$ (b) $AMAV_{x_i}$ of BHP.

It is possible to notice from Figure 5.2 that the parameter governing *BHP* pdf is *RRF*. This appears reasonable if we keep into account that this variable describes the reduction of permeability caused by adsorption of surfactants onto rocks. This is linked also to the second variable in order of importance: K_2 appearing in Langmuir isotherm. The trend shown by the two parameters is very similar except for the very first timestep.

6. Upscaling to sector model

Starting from the encouraging results obtained at the laboratory scale, reservoir simulations at the field scale are performed to assess the benefits of this innovative technique. The Beta field, located in North Africa, has been selected. Simulations are performed, with the use of the STARS software. The sector model construction starts with the definition of a 3-D grid made of 12 layers, each 0.5 m thick.

N. cells	20x16x12
Length (i dimension)	2000 m
Height (j dimension)	1600 m
Depth (k dimension)	6 m

Table 6.1: Sector grid dimensions.

To reproduce the thermodynamic and fluid dynamic characteristics of the reservoir, the grid is located at a depth of 3370 m, above the *OWC* (3406 m). The petrophysical properties of the sector are assumed to be homogeneous on each layer but a vertical heterogeneity (z direction) is considered.
To describe live oil behavior, a Black Oil model has been implemented specifying values of R_s, B_o, B_g at variable pressure.
Prior to a 28 years forecast analysis starting in 2022, the current field status in terms of *BHP* and *WC* is

reproduced thanks to the inclusion of one injection well and 3 producers in the model. Four different production forecast scenarios associated to diverse nanoemulsion injection strategies have been elaborated:

1. 0.3 PV of NE injected as a single slug;
2. 0.3 PV of NE split into two separate injected slugs;
3. 0.1 PV of NE injected as a single slug;
4. 0.5 PV of NE injected as a single slug.

Moreover, a base case ("do nothing case") has been defined to compare nanoemulsions performance with waterflooding ones.

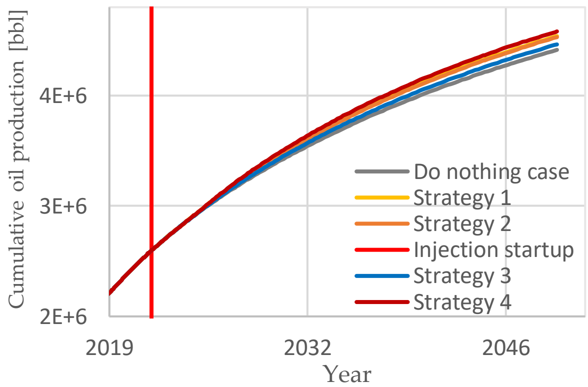


Figure 6.1: Forecast results.

Injection strategy	Cumulative oil production @ 2050 [bbl]
Base case	$4.41 \cdot 10^6$
Strategy 1	+ 130000
Strategy 2	+ 120000
Strategy 3	+50000
Strategy 4	+170000

Table 6.2: Forecast results.

An economic evaluation to assess the effective feasibility of the *EOR* application process has been conducted for three of the four scenarios with respect to the base waterflooding case.

Index	Strategy 1	Strategy 3	Strategy 4
ΔNPV [M$]	- 123.3	- 40.7	- 177.0
ΔCWP [$/bbl]	1211.6	908.8	1355.9
ΔCWP@WACC [$/bbl]	915415.9	764508.1	1005181

Table 6.3: Economic indicators results.

The values of economic indicators suggest that the project is not economically feasible at the moment, and the benefit coming from the additional production obtain from *EOR* application is not sufficient to overcome the related costs.

7. Conclusions

Nanoemulsion technology has been investigated in collaboration with Eni, as potential applicable *EOR* technique. It represents a promising way to recover oil remaining in place after primary and secondary field production processes. Results coming from the laboratory tests, confirm the enhanced action of nanomulsion for oil mobilization in both plug and slim tube applications. In each case an additional recovery (~21% and ~16% respectively) has been reached in agreement with conventional *EOR* processes.

A major achievement of the present work is the successful construction of the entire simulation workflow used to reproduce the laboratory experiments. This aspect represents a substantial innovation in nanoemulsion *EOR* studies, offering a concrete starting point for future improvements. The elaborated model and the associated History Matching procedure have allowed to identify the "solvent effect" as the main driving force to mobilize oil in place. In addition to this, also *IFT* lowering, and wettability alteration have been recognized as significative, even if their impact is considerably smaller compared to the solvent one. Such considerations have been validated through the *GSA* analysis. The good response of the model at laboratory scale has encouraged the upscaling at field scale. Different forecast scenarios have been performed over 28 years considering a variable amount of nanoemulsion employed and different injection strategies. An enhancement in production linked this technology of roughly 170000 bbl has been highlighted in the best scenario. However, from a preliminary economic analysis, the analyzed *EOR* technique results unaffordable, due to its costly components and advanced preparation methods.

References

[1] Kumar, N., Pal, N., Mandal, A., 2021. Nanoemulsion flooding for enhanced oil recovery: theoretical concepts, numerical simulation and history match. J. Petrol. Sci. Eng. 202, 108579.

[2] Braccalenti, E., Del Gaudio, L., Belloni, A., Albonico, P., Radaelli, E., Bartosek, M., 2017. Enhancing oil recovery with nanoemulsion flooding. In: Offshore Mediterranean Conference. OMC-2017-819.

[3] Dell'Oca, A., Riva, M., and Guadagnini, A., 2017. Moment-based metrics for global sensitivity analysis of hydrological systems, Hydrol. Earth Syst. Sci., 21, 6219–6234.