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Workflow of the In Situ Combustion EOR Method in Venezuela: Challenges and Opportunities

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ABSTRACT: In situ combustion (ISC) is one of the oldest thermal enhanced oil recovery methods to have been applied in Venezuela to increase the production of highly viscous crude oils, with a first field application in 1959 in the Tia Juana Field-Lake Maracaibo Basin. This method, which is characterized by high energy efficiency, consists of injecting air into the reservoir where exothermic oxidation reactions initiate to increase the mobility of the oil. Compared to other thermal enhanced oil recovery methods such as steam injection, ISC has a lower environmental impact in terms of water and fuel consumption, and emission of gases as the produced gases can be reinjected or stored. Several ISC projects



have been carried out in Venezuela in Tia Juana, Morichal, Miga, and Melones fields. Although the technical results have been satisfactory in terms of viscosity reduction and improved crude oil properties (such as °API), other important aspects of project evaluations have not been convincing due to the following factors: high temperatures in producing wells, acid gases management, generation of complex emulsions, corrosion, and high CAPEX and OPEX costs. Nevertheless, additional research work has been conducted on process optimization, using catalysts and hydrogen donors, to better address these other factors. Due to the great need to increase hydrocarbon production in Venezuela and to the advantages of ISC as an upgrading technique where low-carbon fuels and hydrogen as byproducts are generated, this paper presents a revisit of ISC projects in Venezuela from R&D technical aspects to field applications. It seeks to identify the main insights regarding the success and failure of the evaluated projects and make substantiated recommendations in the case of future applications of this technology.

1. INTRODUCTION

The application of improved oil recovery (IOR) methods and new technologies has been a need in Venezuela to produce the immense highly viscous oil reserves, in both Eastern Venezuela (the FPO) and Maracaibo basins. Figure 1 shows the main IOR methods that have been evaluated in both basins for conventional and unconventional reservoirs, either in the fields or in the laboratory, namely, water injection, thermal processes, miscible gas injection, water-alternating-gas, chemical EOR (CEOR), microorganisms, and hybrid methods, among others.¹

Thermal^{2–6} and thermo-chemical IOR (hybrid) have been the most suitable methods to recover bituminous oils in Venezuela, in zones without significant risk of water production from aquifers.^{1,7}

Air injection or in situ combustion (ISC) is one of the oldest thermal enhanced oil recovery (tEOR) methods evaluated in highly viscous oil reservoirs worldwide,⁸⁻¹³ and in Venezuela it has been considered as a highly potential method for increasing oil production for more than 6 decades,^{14–21,23} the first experience being at the end of the 50s in a deposit of the Lake Maracaibo Basin.^{15,19,22}

ISC is an advantageous technique over steam flooding in terms of water consumption (for steam generation) and

greenhouse gases emissions. This method has been considered as a technology with potential application for highly viscous oils, late stage, or very deep reservoirs.²⁴ Applications in thin bed heavy oil and water bottom reservoirs have been also reported for field experiences in China.²⁴ For the case of carbonate reservoirs, there are few worldwide experiences reported in the literature.^{25,26} ISC in Venezuela has been applied in sandstones and the main criteria for the application of this technology has been reported in the literature by Hincapie (2011)¹⁹ and Amaro (2013).²²

The ISC process is classified as dry or wet.^{22,27,28} Laboratory studies and numerical simulations have shown the advantages of wet combustion over dry combustion from both technical and economic points of view, due to the lower air requirement in wet combustion, which considerably reduces the compression costs

Received: December 27, 2022 Accepted: March 14, 2023 Published: July 25, 2023







Figure 1. IOR methods that have been evaluated in Venezuela either at lab or at field scales: Maracaibo Basin (on the left) and Eastern Venezuela Basin (on the right). Reprinted with permission from Rodriguez,¹ OMAE2021-63529, Copyright ASME 2021.

of the process.²⁷ Toe-to-heel air injection (THAI), combustion override split production horizontal well (COSH), combustionassisted gravity drainage (CAGD), and in situ catalytic upgrading are improved variants of the ISC method.^{24,29–31} In THAI, COSH, and CAGD processes a horizontal well is used to avoid some drawbacks of the conventional ISC process such as mobility reduction, low sweep efficiency, and low injectivity related to gravity override of the injected gases.²⁴

The main stages of the ISC process are ignition, combustion, evaporation, and condensation.³² In the case of highly viscous oils (heavy and extra-heavy oils, and bitumen) and cooler reservoirs, the injection wells need to be heated by other techniques to ignite the reservoir.^{32–36} Figure 2 shows a schematic of temperature and phase distribution during ISC process.²⁴

Recent studies have reported that due to complex multiple chemical reactions and multiphase flow physics, the stability of the displacement front during the ISC processes is not well understood,^{37–39} and it is complex to describe and define. The chemical reactions generated during the ISC process can be divided into three temperature ranges: low-temperature



Figure 2. Schematic of temperature and phase distribution during the ISC process.²⁴ Reprinted with permission from Yao et al., 2018,²⁴ Copyright Journal of Oil, Gas and Petrochemical Sciences, 2018.

oxidation (LTO), middle-temperature oxidation/fuel deposition (MTO), and high-temperature oxidation/combustion (HTO).⁴⁰ LTO enhances the amount of fuel available during HTO and affects the physical properties of the crude oil.^{40–47} In presence of water, aquathermolysis reactions are generated (hydropyrolysis) with production of acid gases, such as CO₂ and H₂S.^{40,48–52} Cracking occurs throughout the temperature range, but generally prevails at high temperatures.⁴⁰ It is also related to the API gravity of the crude oil, but the ISC occurs over the LTO and HTO.

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The application of the ISC depends on variables such as initial fluid saturations,^{26,53,54} local bodies of water/channels formed after steam injection,⁵⁵ heterogeneities,⁵⁶ and clay and asphaltene content,^{57,58} among others. Analytical frontal stability criterion considering several key factors (e.g., viscous forces, heat conduction, matrix permeability changes produced by coke deposition, and gravity) has been presented in the literature by Zhu (2021).³⁷ At the field scale, the main challenges in the application of the technology are related to ignition, high temperature of the wells, oxygen breakthrough, management of acid gases, corrosion, formation of emulsions, lack of injectivity-connectivity, sand production,^{59,60} mobility reduction and low injectivity,²⁴ etc.

Due to the complexity of the reactions involved in the combustion process at the combustion front along with multiple operational problems reported in the application of this technology in Venezuela (high temperatures in the wells, no control of the propagation of the combustion front, production of greenhouse gases, corrosion, etc.),^{19,22} this method is still under optimization and research aimed at the applications at pilot scale and or possible massification in some reservoirs in the Orinoco Oil Belt or the Faja Petrolifera del Orinoco (the FPO).

In this sense, recent research projects reported by the PDVSA Research Center, PDVSA-INTEVEP, and the Universidad Central de Venezuela (UCV), have shown how the ISC process might be optimized using catalysts and hydrogen donors.^{22,57,61,62} The use of catalysts has been proposed by different authors to improve the success rate of ignition and enhance the stability of the combustion front, transition metals and their oxide particles being one of the most studied nanoparticle catalysts^{64,65} because of their good properties to adsorb and activate oxygen/oxygen species and improve the propagation of the combustion front.^{22,39} A detailed review of the use of different metal-based nanoparticles to improve the performance of ISC is also reported by Simao (2022).⁶⁶ In the same way, a review of in situ upgrading technologies has been reported.^{63,67–71} The use of hydrogen donors with catalysts^{57,61–63,72} has been proposed in Venezuela to improve the physicochemical properties of highly viscous crude oils in the FPO to mitigate acid gases at reservoir conditions and as an alternative to reduce consumption of diluents and lower lifting and transportation costs.⁵⁷

This article presents a detailed review of the ISC projects performed in Venezuela and the latest research studies conducted with the purpose of identifying main insights, determining main technical challenges, and assessing economic aspects to be taken into consideration in the implementation of this technology at field scale.⁷²

2. DESCRIPTION OF THE ISC PROJECTS IN VENEZUELA

The application of the ISC in Venezuela has been focused on the Tia Juana, Morichal, Miga, and Melones fields. Table 1 shows the main reservoir properties and the recovery factor obtained after the application of this tEOR method.

Table 1. Summary of the ISC Projects in Venezuela;Adapted with Permission from Amaro, 2013,22 CopyrightUniversidad Central de Venezuela—PDVSA INTEVEP,2013

project	starting year	depth (ft)	recovery factor (%)	°API	viscosity (cP)
Tia Juana	1959	1585	50	12-16	500
Morichal	1960	4000	60	9-12	400-1850
Miga	1964	4050	25	13-14	280-430
Melones	1977	3000		10-12	50

Despite obtaining good results in terms of oil properties' improvement (viscosity reduction and increase of the API gravity), technical-operational and economic issues (low productivity of the wells, a higher than expected air-injected oil produced ratio, high temperature in the wells, generation of corrosive fluids/acid gases, sand plugging of the wells, failure of compression units, low oil prices, and high costs) led to the suspension of the projects.^{14,19,22} According to the literature, currently there are no active ISC projects at field scale in Venezuela, and efforts have been made on research projects (at laboratory and simulation scales) with a view of understanding the key variables of the process and implementing a pilot test project in the FPO in the future. This section includes a review of the projects performed in the last 2 decades, as follows.

2.1. Simulation Study for Designing an ISC Pilot in the Orinoco Oil Belt.¹⁶ A numerical simulation study for the design of a ISC pilot test, based on combustion tube test results and basic design calculations, was reported in the literature by Anaya (2010).¹⁶ The simulation model was built with the purpose of having a tool that would allow the selection of an optimal number of well locations, operating strategies of the pilot, history matching of the production, and subsequent optimization.

According to Anaya (2010),¹⁶ a kinetic model developed inhouse by PDVSA to simulate the ISC process was incorporated, using thermo-gravimetric and scanning calorimetry experiments (performed in both air and nitrogen atmospheres). The chemical reactions of the kinetic model are summarized in Table 2, and a detailed description of each reaction (e.g., distillation, combustion, and cracking) is reported by the authors.¹⁶

Anaya $(2010)^{16}$ states that based on the reaction model presented in Table 2, it was realized that the first two reactions represent a physical process which could be captured by characterizing the dead oil in terms of pseudo-components LO (light oil fraction), MD (medium oil fraction) and RC (heavy residue), and by modeling the phase behavior using an equation of state. This characterization reduced the number of reactions which would lower the simulation run time of the ISC process at field scale. In this sense, the kinetic model used for the simulation model was limited to the three reactions illustrated in Table 3.

The first stage of the numerical simulation model considered the characterization of the crude oil in the same pseudocomponents used in the kinetic model (LO, MD, and RC components). Subsequently, an adjustment of the main PVT data was carried out using the Peng–Robinson equation of state. Furthermore, a historical comparison was made with this new proposed fluid model, including the characteristic foaming effect of the FPO crude oil (Figure 3). Anaya (2010)¹⁶ reported that the best fit with the field data was obtained with a dispersed-gas foamy oil model with velocity-dependent kinetics of the reaction that converts the low-mobility dispersed gas into high-mobility free gas.

Figure 3 illustrates the impact of the foamy oil effect on the overall field performance. It is reported that the foamy oil behavior helped in matching the gas production and in achieving higher and more realistic bottom hole pressures for the production wells in the evaluated reservoir zone.¹⁶

Additional stages of this simulation work consisted of the history matching of the combustion test with an assisted history matching tool, and the results of which were applied to the full field model.

It is reported that several pilot configurations were considered combining vertical and horizontal wells with the purpose of

Table 2. Reaction Model Original from Perez and PDVSA-INTEVEP;¹⁶ Reprinted with Permission from Anaya et al., 2010,¹⁶ CSUG/SPE-137491-MS, Copyright Society of Petroleum Engineers, 2010^{*a*}

reaction type	reaction equation	temperature range
distillation I	$CO \rightarrow LO + RL$	100–260 °C/212–500 °F
distillation II	$RL \rightarrow MD + RC$	260-360 °C/500-680 °F
combustion I	$MD + O_2 \rightarrow CO_2 + H_2O$	260-360 °C/500-680 °F
cracking-combustion II	$RC + O_2 \rightarrow CK + CO_2 + H_2O$	400-500 °C/752-932 °F
combustion III	$CK + O_2 \rightarrow CO_2 + H_2O$	500+ °C/932+ °F

^aCO: original oil (dead oil). LO: light oil fraction. RL: long residue of oil. MD: medium oil fraction. RC: short residue. CK: coke.

Table 3. Modified Reaction Model for the Numerical Simulation;¹⁶ Reprinted with Permission from Anaya et al., 2010,¹⁶ CSUG/ SPE-137491-MS, Copyright Society of Petroleum Engineers, 2010



Figure 3. Impact of the foamy oil effect on the field performance.¹⁶ Reprinted with permission from Anaya et al., 2010,¹⁶ CSUG/SPE-137491-MS, Copyright Society of Petroleum Engineers, 2010.



Figure 4. Production well completion, ISC Project Bare Field. Reprinted with permission from Perozo et al., 2011,²¹ SPE-144484-MS, Copyright Society of Petroleum Engineers, 2011.

determining the most appropriate well locations for injectors and producers. Subsequently, a sensitivity analysis was carried out considering the injection rates and distance between the producer and injection wells. According to Anaya (2010),¹⁶ the best pattern configuration was selected with the optimum operational parameters.

2.2. ISC for Bare Field in the FPO.^{20,21,23} A pilot test study of the ISC process for the Bare Field was presented by PDVSA INTEVEP in 2011.²¹ This proposal was based on laboratory tests, static model, dynamic reservoir simulation, and design of downhole and surface units. The Bare Field is located in the

Anzoátegui State, approximately 70 km North of the Orinoco River. Specifically, the field is in the Ayacucho Block of the Orinoco Oil Belt.²¹ The ISC pilot test in the FPO-Bare field aimed to increase the recovery factor from 8% (cold production) to 20%.²³

For the ISC Project in the Bare field, it was proposed to use non-conventional drilling techniques and special mechanical well configurations in order to consider the critical reservoir conditions during this thermal process (high temperatures and production of corrosive gases). Vargas (2009)²⁰ reported that different phases were considered at the Bare ISC project looking to: minimize formation damage during drilling operations; maximize pay-zone contact and navigate close to bottom; handle high fluid production and injections rates; monitor well variables in real time; reduce well completion equipment corrosion; prevent sand production; improve cement zonal isolation; and increase the use life of the wells.

According to Perozo (2011),²¹ the configuration of the wells for the ISC project must be appropriate for the high temperatures of the wells and to control the presence of H₂S and CO₂. For the case of the Bare Field, continuous real-time monitoring of pressure and temperature was planned in the injecting well, as well as in the producing well and in the observing well. Figure 4 shows the schematic configuration of the producer horizontal well considered for the Bare Field ISC project.

Perozo $(2011)^{21}$ reported that for the ISC project in the Bare Field, laboratory tests were carried out in combustion tubes in the laboratories of PDVSA-INTEVEP and ONGC India. These analyses were a key aspect in the design and planning of the pilot project. Perozo $(2011)^{21}$ states that following important pertinent data are obtained through these tests: reaction kinetic; creation, maintenance, and propagation of the combustion front; evaluation of the design parameters for the laboratory tests and surface facilities; air requirement; coke accumulation; combustion analysis; maximum temperature; recovery factor; crude enhancement; and combustion gases' analysis. The results of the tests in combustion tubes using the same samples of fluid and sand are shown in Table 4. Figure 5 shows the crude's global balance of the performed tests.

Table 4. Results Obtained in the Combustion Cell by PDVSA-INTEVEP and ONGC Using the Same Sand and Fluid Samples; Reprinted with Permission from Perozo et al., 2011,²¹ SPE-144484-MS, Copyright Society of Petroleum Engineers, 2011

	PDVSA	ONGC IRS (India)
maximum temperature	570 °C (1058 °F)	613 °C (1135 °F)
air requirement	260–400 m ³ air/m ³ rock	170–400 m ³ air/m ³ rock
combustible array	23–34 Kg combust/m ³	15–35 Kg combust/m ³
N ₂ concentration	81%	83%
CO concentration	14-16%	13-15%
CO ₂ concentration	2%	not measured by the instrument
O ₂ concentration	0.5-2.7%	0-2%
H ₂ S concentration ^{<i>a</i>}	0-855 ppm	0-200 ppm
molar ratio	0.7-1	1.8-2.7
^{<i>a</i>} Dry combustion.		

Perozo (2011) stated that the fuel gases expected to be generated during the ISC pilot test do not contain hydrocarbons and have traces of hydrogen and oxygen that are not compatible with many sweetening technologies at the time of the project design, whereby these technologies are limited specially when the H₂S content might have variations during the different phases of the pilot tests. In this regard, the proposed technology for the treatment of H₂S and CO₂ consisted of the thermal oxidation of these gases followed by the neutralization of the oxidation products (SO₂ and CO₂) in a basic medium with calcium carbonate (CaCO₃).



Figure 5. Crude's global balance of tests performed at INTEVEP and ONGC.²¹ Reprinted with permission from Perozo et al., 2011,²¹ SPE-144484-MS, Copyright Society of Petroleum Engineers, 2011.

The methodology reported by Perozo $(2011)^{21}$ for the treatment of H₂S and CO that could be present in the gas stream of the ISC pilot project in the Bare Field comprises the following stages:

- 1. The gas current coming from the gas-liquid separation system enters a furnace at high temperatures (400-600 °C) and is treated through a thermal oxidation process with air in excess, in which H_2S and the CO are transformed to sulfur dioxide (SO₂), sulfur trioxide (SO₃), and CO₂. The efficiency of this process is estimated to be close to 9.9%.
- 2. After the thermal oxidation, the temperature of the gas is reduced by a heat exchanger (Figure 6) until reaching a value of 60 °C.



Figure 6. Diagram for the flue gas treatment. ISC pilot test, Bare Field.²¹ Reprinted with permission from Perozo et al., 2011,²¹ SPE-144484-MS, Copyright Society of Petroleum Engineers, 2011.

- 3. The gas enters a reactor which is bubbled in a $CaCO_3$ solution aiming to neutralize the SO_2 , obtaining as main product calcium sulfate ($CaSO_4$), which is innocuous for the environment. Most of the CO_2 is vented to the atmosphere.
- The reactions that take place in the device presented by Perozo (2011)²¹ are absorption, oxidation, neutralization, regeneration, and precipitation.

On the other hand, Perozo $(2011)^{21}$ reported that for the ISC project in the Bare Field it is essential to implement various strategies for the control and monitoring of critical variables that could affect the success of the project such as the production flow rate, air injection rate, downhole temperature (along the horizontal and vertical sections of the production wells, and the temperature of the injection and observation wells), pressure, and water cuts.

2.3. Evaluation of the Effect of Nanoparticles on ISC Processes.²² The experimental work presented by Amaro $(2013)^{22}$ considers the application of nanoemulsions to improve the ISC process on a Venezuelan bituminous crude oil reservoir. The ISC project combined with a chemical additive (a nanoemulsion containing a catalytic precursor based on a salt of a transitional metal) seeks to improve the rate of combustion in the contact area between the oil and the air.²² The base catalyst was formulated as a reverse nanoemulsion with the catalytic precursor at its saturation point. This was mixed with the crude oil to be subsequently introduced into pre-packed combustion cells with sand and saturated with formation water. The characteristics of the fluids and sand used for the tests can be observed as presented in Tables 5-7. The average porosity and permeability of the combustion cells were 30% and 4.6 D, respectively; initial oil saturations were in the range of 79-92%.

Table 5. Properties of the Original Crude Oil and Mixtures;²² Adapted with Permission from Amaro, 2013,²² Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2013

property	original crude oil	crude oil with the distillate matrix	crude oil with the nanoemulsion
API gravity (°API)	8.84	9.42	10.37
viscosity at reservoir temperature (50 °C) (cP)	49,250	28,740	40,200
saturates' content (% w/w)	10	7	5
aromatics' content (% w/w)	48	36	51
asphaltenes' content (% w/w)	27	47	35
resins' content (% w/w) atomic H/C ratio	15	10	9 1.47

Table 6. Reservoir Water Properties;²² Adapted with Permission from Amaro, 2013,²² Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2013

formation water (synthetic brine)
1400
17,660
180
240
3880
39
5373
796
1700
287
6.92

Five tests were carried out in the combustion cells: three thermals (conventional combustion process) and two catalytic (adding the nanoemulsion).

According to Amaro (2013),²² the catalytic nanoemulsion promoted an improvement in crude oil properties, specifically in both the original viscosity of the crude oil and its API gravity, significantly influencing the mobility of the crude oil. Table 8 shows a significant increase in the API gravity of crude oil in the tests with catalysts (P3 and P4) compared to the tests without catalysts (PC and P2); namely, 15.1 °API for P3 and an abrupt Table 7. Composition of the Selected Reservoir Sand;Adapted with Permission from Amaro, 2013,22CopyrightUniversidad Central de Venezuela–PDVSA INTEVEP, 2013

metal	reservoir sand sample
calcium (Ca), mg/Kg	4664.1
iron (Fe), mg/Kg	5821.7
barium (Ba), mg/Kg	<200
copper (Cu), mg/Kg	<200
molybdenum (Mo), mg/Kg	<200
sodium (Na), mg/Kg	471.9
nickel (Ni), mg/Kg	<200
vanadium (V), mg/Kg	<200
aluminum oxide (Al ₂ O ₃), %	<1
silica (SiO ₂), %	98.2
carbon (C), %	1.05
sulfur (S), %	0.38

increase in P4 with the final flash product of 36.8 °API that behaves like a light crude oil. These laboratory experiments showed the positive effect of the ultra-dispersed catalyst in the form of nanoparticles and encourage a possible application at a field scale.²²

It was observed that as the temperature increases, H/C decreases. When the front temperature was higher (P1 and P2), the quality of the gaseous product decreased (lower H/C). In the presence of a catalyst, the H/C ratio was higher, indicating a product richer in hydrogen. Following were the other important results of the evaluated hybrid method: an increase in the fractions of saturates and aromatics, a decrease in the fractions of resins and asphaltenes, a high generation of light compounds, production of H₂S, and an increase of up to 93% in recovery factor of crude oil. The stability of the combustion process was also observed as evidenced by constant temperature peaks, stabilized front velocities, and constant concentrations of CO, CO_{2} , and N_2 .²²

Amaro $(2013)^{22}$ indicated that the use of the catalytic nanoemulsion in the ISC process led to high recoveries due to an increase in the oil mobility and other possible mechanisms such as vaporization, condensation, solution gas drive, steam drive, miscibility, and thermal and catalytic cracking.

2.4. Evaluation of the Effect of Nanoemulsions and a Hydrogenating Agent to Improve the Physicochemical Properties of the Crude Oil Produced through ISC.⁶² The experimental work presented by Goncalves $(2015)^{62}$ reports the influence of an ultra-dispersive catalyst in the form of nanoemulsion, and of a hydrogenating agent on the physicochemical properties of a crude oil from the FPO through the ISC process. According to Goncalves (2015),⁶² the use of nanoemulsions as an additive establishes a means of transport to the transition metal that promotes the breaking of the carboncarbon bonds of the compounds present in crude oil, allowing the formation of molecules with free radicals that will be stabilized by the hydrogen atoms in the ISC process. On the other hand, the use of the hydrogen donor aims to avoid the formation of high molecular weight compounds, which are generated due to the reactions that are the product of the thermal effect of the combustion process. The reaction mechanism between free radicals and the hydrogen donor is presented in the following reactions⁶²

$$\mathbf{R} - \mathbf{R}^{*} \to \mathbf{R}^{*} - \mathbf{R}^{*} \tag{1}$$

$$R^* + DON - H \rightarrow R - H + DON^*$$
(2)

F

Table 8. Variation of the API Gravity throughout the ISC Tests Performed by Amaro (2013);²² Adapted with Permission from Amaro, 2013,²² Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2013

steps	sample	PC (°API)	P1 (°API)	P2 (°API)	P3 (°API)	P4 (°API)
1	original crude oil	8.84	8.84	8.84	8.84	8.84
2	dehydrated crude (PC)/distilled crude (P1 and P2)/crude with nanoemulsion (P3 and P4)	8.46	9.42	9.42	10.37	10.37
3	drive			9.08	9.84	10.26
4	flash 1	8.09	9.59	9.38	9.71	10.77
5	flash 2	8.35	9.85	9.74	10.37	9.90
6	flash 3		10.57	10.57	11.05	11.03
7	flash 4		10.74	10.79	11.01	10.25
8	flash 5	9.52	11.69	11.69	13.06	12.80
9	flash 6	12.26			15.10	36.86
10	flash 7		13.90	12.13		

According to Goncalves (2015),⁶² eq 2 shows how a hydrocarbon chain can be stabilized by the transfer of hydrogen atoms from the donor, where polymerization to higher molecular weight compounds is avoided. Similarly, Goncalves $(2015)^{62}$ indicates that the quality of the crude produced depends on the quantity and type of the donor. In this sense, the use of additives is intended to obtain a lighter crude oil, with a decrease in viscosity and an increase in its API gravity.

Goncalves $(2015)^{62}$ reported that five experimental tests were carried out: a blank (the reference case) to establish comparisons and two tests for each additive separately. The effluents obtained from the combustion process (liquid, solid, and gaseous) were characterized to know the chemical transformations of the crude oil for which density; viscosity; saturates, aromatics, resins, and asphaltenes (SARA); and gas chromatography analyses were carried out.

The results presented by the author⁶² showed that with the use of additives (nanoemulsion and hydrogen donor), the speed of the combustion front increased (21% for the nanoemulsion and 11% for the hydrogenating agent). On the other hand, when using additives in the process, Goncalves (2015)⁶² indicated that there was a significant improvement in the physicochemical properties of the crude oil produced where a significant increase in API gravity was achieved (8 °API for the hydrogen donor test as an additive, and 5.5. °API with the nanoemulsion additive for flash 5, this being one of the most important cuts due to its proximity to the combustion front). Also, a decrease in viscosity was achieved (Figure 7) which is related to the transformation of asphaltenes into compounds of lower molecular weight (corroborated with the SARA analysis). Furthermore, with the



Figure 7. Variation of the oil viscosity for each test as a function of the cuts of the combustion process at reservoir temperature (T).⁶² Adapted with permission from Goncalves, 2015,⁶² Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2015.

use of hydrogenating agent, the formation of coke was reduced and consequently the generation of gases in the system, specifically carbon dioxide (CO_2) and carbon monoxide (CO).

The analyses performed on the crude oil cuts obtained from the ISC process⁶² showed that there were significant improvements in viscosity (a decrease of 60,900 cP for the blank, 61,700 cP for the nanoemulsion, and 62,300 cP for the hydrogenating agent tests, corresponding to flash 5) and API gravity (an increase of 3.5 °API for the blank, 5.5 °API for the nanoemulsion and 8 °API for the hydrogen donor tests), being the hydrogenating agent, the additive that had the greatest relevance in the mentioned parameters. Such improvements translate into obtaining lighter crude oils that facilitate their mobility in the reservoir.

Figures 8–10 show the temperature profiles for each test, and Tables 9 and 10 list the average speeds of the combustion fronts.



Figure 8. Temperature profiles for the blank test—reference case.⁶² Adapted with permission from Goncalves, 2015,⁶² Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2015.

Table 9 shows the average speeds of the combustion front in the stable period by the method of the maximum temperatures reached. For a separation between the thermocouples of 5 cm, this is the point where the highest value of the temperature is obtained, corresponding to the passage of combustion front. With the use of additives, the average speed of the combustion front is higher than the reference case, reaching speeds that oscillate between 14.9 and 16 cm/h, which correspond to an increase of 11 and 21%.

On the other hand, Table 10 shows that with the use of additives in the ISC process, the air requirement decreases. This shows that the use of ultra-dispersed catalysts and hydrogen donors in highly viscous crude oils might allow optimization of



Figure 9. Temperature profiles for nanoemulsion testing.⁶² Adapted with permission from Goncalves, 2015,⁶² Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2015.



Figure 10. Temperature profiles for hydrogen donor testing.⁶² Adapted with permission from Goncalves, 2015,⁶² Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2015.

Table 9. Speed of the Combustion Front as a Function of the Maximum Temperatures Reached;⁶² Adapted with Permission from Goncalves, 2015,⁶² Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2015

test	stable zone by thermocouples	maximum temperatures method (VTM ± 0.1 cm/h)	air requirement (m ³ standard air/m ³ packed sand)
reference	Т3, Т4, Т5	13.2	315
nanoemulsion	Т5, Тб	16.0	263
hydrogen donor	Т2, Т3, Т4	14.9	282

Table 10. Speed of the Combustion Front as a Function of the Maximum Temperature Reached and Air Requirement;⁶² Adapted with Permission from Goncalves, 2015,⁶² Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2015

test	stable zone by thermocouples	increased velocity with respect to the reference test (VTM \pm 0.1 cm/h)	decrease in air requirement (%)
reference	T3, T4, T5		
nanoemulsion	Т5, Тб	21	19.7
hydrogen donor	Т2, Т3, Т4	11	11.1

the air injection. The lowest air requirement was for the nanoemulsion case, attributed to the fact that this parameter was determined from the relationship between the amount of air injected and the front speed, where an increase in speed leads to a lower air requirement.⁶²

Regarding the temperature profiles, it can be seen in Table 9 that the stable zone for the reference case is maintained from the thermocouples 3-5 as reflected in Figure 8, where the temperatures remain stable. Then, for the nanoemulsion test, the stability is observed from thermocouples 5-6 (Figure 9) and for the donor test from thermocouples 2-4 (Figure 10). According to Goncalves (2015),⁶² the stability of the combustion front depends mainly on the amount of deposited fuel (coke) and on the air injection rate, which when reacting, produces an increase in temperature.⁶² The average temperature in the stable zone for the blank reference test was kept at 500 °C, while for the nanoemulsion test it was kept at 560 °C, and finally 540 °C for the hydrogen donor.⁶²

2.5. Comparative Study of Ignition Methods for the Enhanced Thermal Recovery Process of ISC–Bare Field.³² One of the key stages for the success of the ISC process is the ignition, which occurs when the heat emitted becomes sufficient to originate the different chemical reactions and improve the physicochemical characteristics of the crude oil. Ignition and generation of a stable combustion front depend on the type of crude oil and characteristics of the reservoir (pressure, temperature, geological properties, etc.).

An experimental study on the ignition stage and the feasibility of its application under different methods in the Bare Field of the FPO was reported. According to Quijada (2015),³² the ignition can be generated spontaneously through the injection of air into the reservoir for a prolonged period or in an induced manner, where an external agent is introduced into the reservoir to serve as a bridge in the emission of heat required to initiate the combustion.

This work consisted of a thermogravimetric analysis to identify the temperature range of the pseudo-reactions that occurred in the ISC process. It was done with tests in tubes packed with sand and saturated with formation water and crude oil from the Bare Field (9 °API and 49,250 cP; prospective area for an ISC pilot test), where the ignition method with which the process is started was modified through electric heating, injection of a hot fluid, and introduction of a pyrophoric agent. In order to simulate a section of the reservoir, the combustion cells were packed and saturated with formation water and crude oil to achieve a permeability of around 4 darcy and a crude oil saturation of 80%. Results of the thermal analysis carried out by Quijada $(2015)^{32}$ are presented in Table 11, indicating the events produced during the analysis.

Among the results obtained, what stands out is that the greater the energy delivered to generate the ignition, the more efficient the process is. In this sense, the electric heating method proved to be more feasible when applied under the given reservoir conditions. Figure 11 shows the temperature profile achieved

Table 11. Summary of Events that Occurred during the Thermogravimetric Analysis.³² Adapted with Permission from Quijada, 2015,³² Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2015

reference	temperature (°C)
evaporation of light compounds	31-240
LTO reactions	240-380
MT-HTO reactions	380-500
HTO reactions	+500
	reference evaporation of light compounds LTO reactions MT-HTO reactions HTO reactions



Figure 11. Temperature profile achieved by the electric ignition method.³² Adapted with permission from Quijada, 2015,³² Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2015.

with the electric ignition method, recorded by each of the thermocouples throughout the cell.³²

Quijada (2015)³² indicates that one of the advantages of the electric heating method is that by having a controlled heating ramp, ignition temperatures can be reached above the minimum temperature, thus avoiding excessive oxidation at low temperatures (LTO), reducing the formation of more viscous products, and giving greater weight to HTO reactions, which form more gaseous products capable of increasing the displacement of the oil.

2.6. Evaluation of the Effect of a Solid Additive for the Mitigation of Acid Gases in Improved Recovery through ISC.⁷³ The main objective of the work presented by Mora $(2015)^{73}$ was to investigate the influence of a solid additive composed of a transition metal for the mitigation of acid gases $(H_2S \text{ and } CO_2)$ resulting from the application of an ISC process at laboratory scale, using an extra-heavy crude from the FPO. This study was part of a research and development project for the implementation of a field pilot in a Venezuelan extra-heavy oil reservoir.

Three combustion tests were carried out: one control test for comparison purposes, and two additional tests with additive, in which the solid additive is mixed with the sand. The effluents from the cell (gas, liquid, and solid) were analyzed using the following techniques: chromatographic and calorimetric analysis for the emitted gases, SARA analysis, percentage of sulfur and water for oil cuts and finally diffraction X-ray, and total sulfur analyses for the sand samples.

Within the results obtained by Mora (2015),⁷³ it can be noted that the H₂S adsorption process is strongly related to the increase in temperature (Figure 12).

It is reported that a reduction of 88.33% in the content of H_2S and an increase of 3.7% in the concentration of CO_2 in the



Figure 12. Temperature profiles and H_2S concentrations because of the thermal effect.⁷³ Adapted with permission from Mora, 2015,⁷³ Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2015.

analyzed effluents were observed after using the solid additive. Similarly, a 2.56% decrease in the sulfur content in the produced crude oil was reported, as well as the formation of metallic sulfide in the matrix rock (an increase between 0.14 and 0.38% for the tests with a solid additive compared to the reference case).

2.7. Evaluation of the Effect of Mineralogy on the Mechanism of Ignition with Steam and Generation of Acid Gases in the ISC Process in the FPO.⁷⁴ One of the first experimental studies on the effect of the mineralogy on the ISC process using recombined crude oil and reservoir rock samples from the FPO and its comparison with inert sand was presented by Hernández (2003).⁷⁵ Results of this study indicated that the oil recovery factors of the experiments by using reservoir sand and inert sand samples were similar, with 90% for both cases under ideal laboratory conditions. Nevertheless, Hernández (2003)⁷⁵ indicated that the results obtained with the reservoir

sand samples showed an increase in the temperature of the combustion front and a decrease in the advance speed of the front; in the same way, it was pointed out that the high viscosity of the crude oil generated operational problems when starting the heating for ignition; a final fraction of the recovered crude oil showed an improvement of the oil properties, related to an increase in its API gravity and a reduction in viscosity.⁷⁵

Another experimental work was subsequently presented by Torres and Flores (2017).⁷⁴ This research work consisted of evaluating the effect of mineralogy on the ISC for La FPO, for which five experimental tests were carried out in tubular cells with samples of cores, water, and oil from a reservoir of the FPO, using electric heating (three lab tests) and steam injection (two lab tests) as the ignition methods. The characteristics of the crude oil and the rock from the FPO considered in this study are listed in Tables 12–14.

Table 12. Characterization of the Extra-Heavy Oil from the FPO Used for the ISC Tests Performed by Torres and Flores (2017);⁷⁴ Adapted with Permission from Torres and Flores, 2017,⁷⁴ Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2017

property	value
API gravity	7.9
viscosity at reservoir $T = 52^{\circ}C$ (cP)	20,053
molecular weight (g/mol)	490
micro carbon residue (% w/w)	16.6
H/C ratio	1.38
metal vanadium (mg/L)	395
metal nickel (mg/L)	97
metal iron (mg/L)	24
sulfur (% w/w)	3.69
saturated content (% w/w)	13
aromatic content (% w/w)	50
resin content (% w/w)	28
asphaltene content (% w/w)	7
asphaltene content (% w/w) IP-143	14.96
density at 25 °C (g/cc)	1.0091
density at 52 °C (g/cc)	0.9916

Table 13. Mineralogical Characterization of the Reservoir Rock (Samples 1 and 2) Used for the ISC Tests of Torres and Flores (2017);⁷⁴ Adapted with Permission from Torres and Flores, 2017,⁷⁴ Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2017

	value		
component	sample 1	sample 2	
quartz (SiO ₂), % w/w	89	86	
clay, % w/w	6	10	
calcite, % w/w	4	1	
feldspar_K, % w/w	1	2	
pyrite, % w/w		1	

Table 14. Mineralogical Content of Clay;⁷⁴ Adapted with Permission from Torres and Flores, 2017,⁷⁴ Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2017

clay mineral	content (% w/w)
kaolinite	97
illite	3

The results of the Torres and Flores' work⁷⁴ were compared with studies previously performed at PDVSA-INTEVEP using gravel. The results obtained showed concentrations of hydrogen sulfide (H_2S) significantly higher than those obtained using drilling cuttings (gravel), with values higher than 5000 ppm, which was attributed to a higher clay content in the core. Additionally, the feasibility of using steam injection as an ignition method for the ISC in the reservoir under study was confirmed.

Figure 13 shows an example of the results of hydrogen sulfide (H_2S) in the flue gas for the PC test, observing values of up to



Figure 13. Hydrogen sulfide (H_2S) concentration versus time, test PC-2.⁷⁴ Adapted with permission from Torres and Flores, 2017,⁷⁴ Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2017.

5000 ppm H_2S . According to Torres and Flores (2017),⁷⁴ the generation of H_2S depends on the sulfur content in the original crude oil (for this case, 3.69% w/w of sulfur), in the synthetic brine and in the reservoir sand.

Additional results showed that the H/C ratio obtained from the combustion tests were higher than the H/C of the original crude oil (see Table 15), which suggests the occurrence of LTO

Table 15. Parameters from Combustion Tests Performed by Torres and Flores (2017);⁷⁴ Adapted with Permission from Torres and Flores, 2017,⁷⁴ Copyright Universidad Central de Venezuela–PDVSA INTEVEP, 2017

parameter	test PC-1	test PC-2	test PC-5
hydrogen/carbon ratio (H/C)	1.60	1.75	1.73
oxygen/fuel ratio (OFR), m³/kg	2.32	2.46	2.42
air/fuel ratio (AFR),m³/kg	11.03	11.70	12.09
air excess, %	0.025	0.030	0
total fuel requirement (FR), kg/m ³	35.87	33.46	32.05
air requirement (AR), m ³ /m ³	396	391	387

reactions.⁷⁴ Regarding the air requirements of the tests carried out, these were between 356 and 396 m^3/m^3 , typical results for heavy crude oils.⁷⁴

3. DISCUSSION

The ISC process has been one of the first tEOR methods applied in Venezuela, where despite having a history of more than 6 decades of studies in highly viscous crude oil reservoirs in the country, it is still a research subject due to the significant technical and operational complexity of the process. The no convincing results of the process at field scale have led to efforts for a better understanding of the critical variables in the process at the laboratory scale and numerical simulation studies, with a view of implementing a pilot field project in the FPO. Based on the results of research work in Section 2, it has been observed that due to the high viscosities of crude oil samples (high asphaltene content) the ignition step is one of the main ISC issues. Thus, the application of an external agent to start combustion is necessary, being electric heating and steam injection the methods that have shown the best results at the laboratory scale. Other issues regarding the characteristics/ composition of fluids and rock are related to the generation of acidic gases (i.e., carbon dioxide and hydrogen sulfide) that are of big concern from health, safety, and operational and flow assurance (corrosion, emulsions, scales, etc.) points of view.

One of the encouraging experimental results discussed in Section 2 is related to the use of chemical additives (catalysts and hydrogen donors) that have shown to render improvement of combustion front velocities (higher than reference cases without additives) and decrease of air injection requirements. Being one of the biggest challenges, the selection of the most appropriate additive (catalyst and hydrogen donor) is a prominent factor from both technical and economic points of view. The implementation of these techniques at field conditions is also a challenge, mostly for the control of the temperature and the combustion front in the reservoir.

Each one of the previous aspects, together with the in situ upgrading characteristics of the ISC process and other critical parameters that must be considered for the implementation of the pilot project in the field will be discussed in the next section, along with some descriptions on technical, operational, and economic aspects.

3.1. Technical-Operational Challenges. *3.1.1. In Situ Upgrading.* Venezuela has focused on making efforts in the last 2 decades to optimize the ISC processes using solid and liquid catalysts. Similarly, the use of catalysts has been envisaged to produce clean fuels (hydrogen and low-carbon fossil fuels) that allow compliance with strict international environmental standards, in addition to providing an alternative to fossil fuels.^{76–80}

ISC with chemical additives (catalysts and/or hydrogen donors) offers advantages to produce hydrocarbons with high hydrogen content, to reduce costs of lifting and transporting highly viscous crude oil from the reservoir to the refining centers,⁶¹ and decrease expenses of diluents in the FPO. In the FPO projects, naphtha-type diluents are typically used,⁸¹ which considerably increases production costs.

3.1.2. High Temperatures in the ISC Process. High temperatures in the wells have been reported as an operational problem in ISC projects in the Venezuelan highly viscous oil reservoirs.^{19,22} The use of chemical additives and/or catalysts (i.e., copper stearate), despite accelerating crude oil oxidation by shifting both the LTO and HTO to lower temperatures³⁹ at the laboratory scale, does not solve the issue of high temperatures. This issue could induce sand movement (high temperatures impact cementing materials $^{82-86}$), as well as mechanical failure of tubing and casing. For these reasons, well failure due to thermal stress is considered a key challenge in the ISC operations.⁶⁰ High temperatures in the wells also affect downhole equipment and increase the risks of air injection system explosion^{59,60,83} and corrosion, representing a big challenge from a safety and technical-economic point of view. Monitoring flow line temperatures and casing pressure along with running temperature logs in injector wells⁶⁰ is critical to maintaining an efficient ISC process. Recent studies have shown the acceleration of research and development of materials together with technology for high-temperature conditions in the

oil and gas, as well as geothermal fields, ^{50,82–85,87,88} which would make it possible to develop materials and techniques better adapted to this type of complex environments.

3.1.3. Initial Water Saturation. Another important aspect to consider for the implementation of the ISC method in the FPO is the variation of water saturation, which can vary between 7 and 100% due to the presence of aquifers and/or flushed zones. It is important to mention that thermal methods in areas with high water risks (adverse mobility ratio), both in the Eastern Venezuela and Lake Maracaibo basins, have not been technically and economically feasible.^{7,89–92} In these reservoirs, methods such as chemical injection or water injection have been envisaged.^{1,7,81}

In the same way, it is reported that water-saturated channels formed in the later stage of steam injection contribute to and aid the propagation speed enhancement of combustion front.⁵⁵ Similarly, it has been reported that as the combustion front propagates in the water-saturated channel, a fast decrease in temperature is observed along with an unstable propagation of the process, with marked reduction of O₂ availability. On the other hand, Zhao et al., 2022^{55} reported that oversized water-saturated channels would lead to a worse combustion process with a much lower COx concentration and O₂ availability or even lead to the extinction of the process.

3.1.4. Effect of Heterogeneities. Laboratory studies and field applications have shown that ISC is sensitive to reservoir heterogeneities.^{19,56} The effect of reservoir heterogeneities must be considered in the selected area of the ISC pilot test in Venezuela. Figure 14 shows an example of a rock sample from the FPO, showing massive sands and reservoir rock with vertical heterogeneities.^{81,89,90}

An experimental study of ISC through one-dimensional combustion tubes, considering fractures oriented perpendicular



Figure 14. Reservoir samples from La FPO: massive unconsolidated oil sands with vertical heterogeneities.⁸¹ Reprinted with permission from Rodriguez, 2016,⁸¹ Copyright Université Sorbonne Paris Cité, 2016.

and parallel to the air injection direction, performed at the same experimental conditions, was reported in the literature.⁵⁶ It is reported that the fractured formation was visualized by X-ray tomography and the results indicated that both fracture types affected the stable propagation of the combustion front and the oxygen utilization rate was detected to be lower for the case of parallel fractures.⁵⁶

Air injection channeling due to reservoir heterogeneities has a direct impact on the costs of the process. As an example, in the ISC Miga Field project in Venezuela,¹⁹ the air injected-oil produced ratio (AOR) was much higher than the estimated value in the original study, which translated into high costs and making the project not economically feasible.¹⁹

3.1.5. Asphaltenes and Clays. The FPO crude oils are characterized by a high content of asphaltenes,^{81,93} whose stability might be affected by the temperature variation during the ISC process. Figure 15 shows a microscopic image of a crude



Figure 15. Qualitative description of an extra-heavy dead oil sample from the FPO: image from microscopy.⁸¹ Reprinted with permission from Rodriguez, 2016,⁸¹ Copyright Université Sorbonne Paris Cité, 2016.

oil sample from the FPO where a system composed of oil (continuous phase), water, and asphaltenes can be described. Figure 16 shows the formation of an emulsion and solids due to temperature and composition changes by diluent.

Authors have reported the impact of the presence of asphaltenes and clays in the ISC process.^{58,61} Typical clays in the FPO are reported to be kaolinite, illite, and smectite.⁷

The effect of asphaltenes and clay content (catalytic impact of clays) based on laboratory studies through one-dimensional



Figure 16. Precipitation of solids in an oil-in-water emulsion after changes of composition (addition of diluent) and temperature.⁸¹ Reprinted with permission from Rodriguez, 2016,⁸¹ Copyright Université Sorbonne Paris Cité, 2016.

combustion tube experiments and different crude oil samples has been reported in the literature by Ismail and Hascakir (2020).⁵⁸ Compositional variations in the SARA fractions were determined by the authors using the Fourier transform infrared technique. Alternatively, the surface of asphaltenes was visualized using scanning electron microscopy and the energydispersive spectroscopy techniques.⁵⁸ Results of this study indicated that the amount of asphaltenes in the produced crude oil decreased due to fuel formation reactions. Ismail and Hascakir (2020)⁵⁸ also reported that under laboratory study conditions, cribriform structures or numerous porous features were formed on asphaltene surfaces in the presence of clays, increasing the surface area of asphaltenes (deformation on the asphaltene's surface).

3.1.6. Modeling of the ISC. The modeling of reaction mechanisms in the ISC process^{16,94–98} is one of the most complex tasks that could have an impact on the evaluation of the technology. The results reported by Amaro $(2013)^{22}$ and Goncalves $(2015)^{62}$ indicate that the addition of additives, nanoemulsions (based on surfactant and nanoparticles of a transition metal), or hydrogen donors improve the stability of the combustion front and the properties of the crude oil. In this regard, kinetic models and numerical simulations are required to reproduce the complex chemical reactions that occur in the process. As also reported in Section 2, ISC modeling in the FPO should consider the foamy oil effect on the overall field performance.¹⁶

Anderson and Kovscek (2022)³⁸ reported that one of the continuous challenges in an ISC process is to determine the most representative chemical reaction model, and in this regard, they propose a workflow optimization to calibrate different ISC reaction models to experimental data for the combustion of two different oil samples. The authors state that both stoichiometry and kinetic parameters for a given model can vary between oil samples.³⁸ Additional reported observations are that a larger number of parameters and reactions of pseudo-components do not necessarily improve the reaction model; however, a higher number of pseudo-components for intermediate coking stages affect the accuracy of results³⁸ with an impact on computation time.

Anbari et al., 2023⁹⁷ presented a field performance and numerical simulation study on the THAI process in a heavy oil reservoir with bottom water. The work focused on the operational aspects of the THAI process. This work for the first time, presents a field-scale THAI model that was validated against data from the Kerrobert THAI project.

Regarding the simulation of the ISC process with the presence of catalysts, Lopeman et al., 2023⁹⁸ recently presented a method for the modeling of the THAI-CAPRI method using a commercial numerical simulator, based on an in situ hydrogen production reaction scheme where the models were run under three conditions: dry, pre-steam, and constant steam. According to the authors, the evaluated models were validated and matched against experimental data taken from the literature with machine learning. Results reported by Lopeman et al., 2023⁹⁸ showed a more accurate oil upgrading behavior of in situ heavy oil.

3.1.7. Sand Production. Sand production^{19,99–165} and low productivity is one of the biggest drawbacks in field ISC projects in Venezuela (Miga and Melones fields).¹⁹ Sand production is attributed to high temperatures that affect the matrix cement and mineralogical composition, as well as flux velocities that promote the migration of particles to the production wells. Figure 17 shows a microscopic image of grains of a rock sample



Figure 17. Microscopic image of a rock sample from the FPO.⁸¹ Adapted with permission from Rodriguez, 2016,⁸¹ Copyright Université Sorbonne Paris Cité, 2016.

(unconsolidated sandstone) from the FPO where the degree of rock consolidation can be observed, in which the grains are united thanks to the high viscosity of the crude oil.

A study to evaluate the response to mechanical stress produced by high temperatures in the ISC process for Chichimene Field in Colombia has been reported based on geomechanical, mineralogical, and morphological studies with the purpose of determining the following parameters: Young's modulus, Poisson relationships, internal friction angle, mineralogical and morphological compositions, porosity, permeability, and rock grain density. $^{\rm 59}$

For the case of the FPO, additional geomechanical studies^{106–108} should be carried out taking into consideration the possible effects of subsidence such as those observed in the Maracaibo Basin where a direct relationship was detected between the thermal recovery process (steam injection in this case) and subsidence.^{99,101,102} Figure 18 shows the relationship between production and subsidence after the application of a thermal recovery process in the Maracaibo Lake Basin. The subsidence in conjunction with the injection of steam allowed recovery in the order of 25%.¹⁰² It is important to mention that the oil viscosities of the FPO.

3.1.8. Scale/Incrustations. Garcia $(2016)^{59}$ reports that scaling/incrustations is an operational challenge in the ISC process, which could be linked to factors: (1) compatibility between the injection and the formation waters when a wet combustion process is carried out; (2) sedimentation due to variation of the composition of the fluid with pressure and temperature, and as a consequence, of the limiting solubility of certain minerals causing their precipitation in the form of scales; and (3) release of combustion gases (CO₂) that might alter pH of solution and generate carbonate precipitates with potentially adverse impact on the productivity of the wells.

In the case of the Orinoco Oil Belt or the FPO, compositional variations of static and dynamic waters^{109–112} might generate calcium carbonate precipitates/scales⁸¹ and consequently cause complexity in the phase production process. Chemical additives



Figure 18. Subsidence effect on oil production, Maracaibo Oil Basin.¹⁰² Reprinted with permission from Layrisse, 1999,¹⁰² SPE-53464-MS, Copyright Society of Petroleum Engineers, 1999.

to control H_2S production also might generate scales (i.e., sulfide scales) and cause formation damage and/or obstruction of tubing and surface facilities.^{113–116}

3.1.9. Formation of Emulsions and Separation of Produced Fluids. Fluid production should be constantly monitored to detect compositional changes related to the ISC process at field conditions.^{86,117} The separation of produced fluids (water, oil, gas, and sand) in highly viscous oil reservoirs in the FPO is a frequent operational challenge, both in cold production and after the application of EOR processes, such as ISC tEOR. The generation of emulsions¹¹⁸⁻¹²⁶ is commonly observed

The generation of emulsions^{118–126} is commonly observed during the application of EOR methods¹¹⁹ as shown in Figure 16. Figure 19 shows an example of a microscopic image of a



Figure 19. Water-in-oil emulsion of a Venezuelan dead extra-heavy oil sample.¹¹⁸ Reprinted with permission from Rodriguez, 2016,¹¹⁸ SPE-179624-MS, Copyright Society of Petroleum Engineers, 2016.

stable water-in-oil emulsion of a dead oil sample (cold production) with 6% wt of water from the FPO.¹¹⁸ Operational problems associated with the formation of emulsions have also been reported for projects in Colombia (Figure 20)¹¹⁷ and in the USA.⁶⁰



Figure 20. Evaluation of the pH effects on oil emulsions at different water–oil ratios from microfluidic experiments: Chichimene Field-Colombia In Situ Combustion Pilot.¹¹⁷ Reprinted with permission from Manrique et al., 2022,¹¹⁷ SPE-209390-MS, Copyright Society of Petroleum Engineers, 2022.

A Colombian study of water-in-oil (W/O) emulsions during an ISC project for three different crudes has been reported by Álvarez-Martínez (2021).¹²⁶ This study considered the characterization of emulsions through their gravimetric behavior, droplet size distribution, rheology, and viscosity. After the study of critical variables of emulsion generation (shear rate, water content, oxidation level, and the addition of silica nanoparticles), it was determined that the inclusion of silica nanoparticles (1000 mg/L) had a slightly positive impact in the emulsion formation process due to an increase in the rate of evaporation of the water in the emulsion, a reduction in the viscosity of the emulsion, and a reduction in the size of the droplets.

Conversely, in the case of a field project in Louisiana-USA (Bellevue Field), chemical treatments to break emulsions based on a mixture of polyglycerol fumarate ester, heavy aromatic naphtha, and electrical heaters have been successfully applied.⁶⁰

3.1.10. Oxygen Breakthrough. The oxygen (O_2) breakthrough in producing wells is one of the most critical problems in ISC operations, ^{59,60,97,127–129} which could affect the areal sweep efficiency, the proper functioning of the artificial lift methods, and combustion performance at field conditions. O₂ breakthrough can be attributed to incomplete combustion, ⁵⁹ heterogeneities, and channeling in areas of the reservoir with high permeability, ^{59,129} location of the injector and producer wells in the reservoir, etc.

Methods to control O_2 breakthrough consist of monitoring the temperature, composition of the produced fluids and fluid saturations at reservoir conditions, and analysis of injectivity and connectivity to identify heterogeneities and flow patterns. This allows for the optimization of the design and configuration of the pilot wells (nitrogen connectivity tests).^{59,117} It is reported that optimization of the distance between the injection and horizontal production wells together with optimization of the air injection rates are the key parameters in reducing the risks of O_2 breakthrough.^{97,128} The air injection rate is an important parameter to provide the heat necessary for thermal cracking reactions (i.e., deposited coke). Exceeding air injection could affect the general performance of the ISC technology, as high gas production is difficult to handle at surface conditions (high temperatures in wells, impact on artificial lift systems, etc.).

3.1.11. H_2S Production. The application of thermal EOR methods promotes the generation of H_2S due to the transformation of sulfide at high temperatures (aquathermolysis) and/or the rock—fluid interaction (oil and clay content effects). Scavengers have traditionally been applied in the oil industry to remove H_2S (i.e., amines and triazines).^{130–136} Due to their high ability to reduce sulfide concentration, monoethanolamine (MEA)- and monomethylamine (MMA)-based triazines are regularly used to remove H_2S during hydrocarbon processes.¹³⁶

In Venezuela, one of the traditionally applied methods for H_2S mitigation consists of the injection of liquid scavengers and corrosion inhibitors into flow lines. González $(2004)^{135}$ reported that the injection of scavengers can generate the deposition of amorphous yellowish polymeric solids as byproducts in multiphase fluid lines, producing a reduction in the internal diameter of pipes and affecting transmission systems (Figure 21). The effect of H_2S scavengers on the formation of scales and/or impact in production facilities has likewise been reported by Wylde et al., 2020_i^{132} Taylor et al.; 2021_i^{133} Manrique et al., 2022_i^{117} and Rafferty et al., 2022_i^{137}

Due to the multiple issues observed with the application of H_2S scavengers related to the correct dosage of these chemicals and the formation of emulsions, scales, and fouling at surface conditions (downstream refining process) related to reaction products, efforts have been made by PDVSA-INTEVEP to control H_2S underground at reservoir conditions using additives/catalysts.¹³⁶ However, so far, it is on a research scale activity.

3.1.12. CO_2 Sequestration and Utilization. Likewise, efforts should be made to sequester and manage the produced CO_2 .¹³⁸⁻¹⁶³ Perez et al., 2010¹³⁸ proposed a mineral carbonation approach for the ISC pilot project in the FPO, based on caustic byproducts (liquor and red mud) from alumina



Fuente: PDVSA-Anaco, febrero de 2004.

Figure 21. Solids found in the multiphase flow line of a well in the Anaco District - Venezuela.¹³⁵ Reprinted with permission from Gonzalez, 2004,¹³⁵ Copyright Universidad Central de Venezuela—PDVSA, 2004.

production. Additionally, EOR projects could be focused on other deposits where previous studies have indicated the technical feasibility of application, but because they did not have enough source of CO_2 they were not applied (e.g., reservoirs in the North Monagas area).^{149–151} CO_2 could also be injected into aquifers, in this sense feasibility studies have been carried out in deposits of the gas area of Anaco -Venezuela.^{160,161}

Regarding the selection of candidate aquifers for storage, this study should be based on geological analyses, static and dynamic reservoir parameters, laboratory studies (geomechanics, caprock integrity), and socio-cultural and economic factors.¹⁶² A characterization study of aquifers in the FPO for use as water disposal reports that there are shallow aquifers that are not considered to be confined, this is the case of La Mesa Formation. Rodriguez (2018)¹⁶² indicated that the use of this aquifer for fluid injection might have an environmental impact on agriculture, human consumption activities (some aquifers are used for human consumption after treatment), and the fauna present in the rivers.

3.1.13. Corrosion. The corrosion of underground and surface equipment due to high temperatures, the presence of acidic gas $(CO_2 \text{ and } H_2S)$ dissolved in water and other products of oxidation reactions^{87,164–170} has been one of the greatest drawbacks of the application of the ISC process in Venezuela.^{19,22} It is reported that based on field experiences in the USA, chemical treatments to reduce the rate of corrosion have been based on a mixture (blend) of acetic acid, imidazoline, and quaternary ammonium.⁶⁰

3.1.14. Air Compression. Air compression systems represent a critical point in the success of an ISC project and represent one of the largest operating expenses (OPEX) of the process.⁶⁰ One of the main issues reported in one of the ISC projects of the FPO Fields (Melones Field) was a failure in the compression units and high temperatures in the injection well causing operational problems that resulted in the suspension of the pilot project.¹⁹

3.2. Economic Challenges. Economic evaluations to assess the feasibility and development strategies of the Bare Field ISC project in the FPO and future ISC projects in Venezuela should consider electricity costs for compressors, surface and treatment equipment, maintenance, chemical treatments, and overhead. Capital costs in the FPO are related to drilling and completion of new wells, surface facilities, and equipment.

Sharma (2021)⁶⁰ reported a distribution of cost estimates per barrel of oil produced between 2014 and 2019 for Bellevue ISC operation (Figure 22). Production costs for the evaluated period

were generally higher than production costs reported for other thermal EOR operations.



Figure 22. Average cost for producing a barrel of oil in the period of 2014 to 2019 for the Bellevue ISC operation in the USA.⁶⁰ Reprinted with permission from Sharma et al., 2021,⁶⁰ Copyright Fuel, 2021.

4. CONCLUSIONS

The extent of success in ISC applications has depended on the degree of implementation of experimentally supported information, the advancement of material integrity technologies, the monitoring and follow-up of critical project variables, and the economic aspects. Furthermore, and from a different perspective, the application of the ISC (field) process in Venezuela represents multiple advantages for in situ crude oil upgrading and reduction of cost related to lifting and transportation. The positive effect has been observed on the mitigation of acidic gases (CO_2 and H_2S) at reservoir conditions as well as on the increase in the H/C ratio, which represents an alternative to produce hydrocarbons having lower carbon content with low environmental impact. Being a combination of nanoparticle catalysts and hydrogen donors, this hybrid ISC is one of the most encouraging schemes, based on laboratory trials. The study and evaluation for optimizing the critical variables of the process (e.g., ignition, combustion front, oxygen breakthrough, kinetic models, high temperature in the wellbore, corrosion, emulsions, etc.) and the management of undesirable gases, together with technical-economic studies, will be the decisive factors for the application of the ISC EOR method in Venezuela.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank Petróleos de Venezuela S.A. (PDVSA), Khalifa University of Science and Technology, and Universiti Teknologi PETRONAS for their support. Authors would like to acknowledge the Research Center of PDVSA, PDVSA-INTEVEP, and the Universidad Central de Venezuela (UCV) for their scientific advances and contributions for the application and optimization of the ISC process in Venezuela.

NOMENCLATURE

ISC in situ combustion

tEOR thermal enhanced oil recovery

THAI toe-to-heel air injection

COSH combustion override split production horizontal well CAGD combustion-assisted gravity drainage

 CO_2 carbon dioxide

CO carbon monoxide

 N_2 nitrogen

H₂S hydrogen sulfide

REFERENCES

(1) Rodriguez, F. Review of Chemical EOR Projects in Venezuela: From Light to Extra-Heavy Oil Reservoirs. *ASME/International Conference on Ocean, Offshore and Artic Engineering; OMAE2021*-63529, 2021.

(2) Hoye, T.; Kass, I.; Allers, J. Improved Reservoir Characterization and Its Impact on Locating Thermal Development Wells in the Petrocedeño EOR Pilot Area; World Heavy Oil Congr., 2009. WHOC09-160.

(3) Devaux, V.; De Pellegars, O.; Hubans, C.; Mus, E.; Yuh, S. Preparation of a 4D Seismic Acquisition Program for Steam Chambers Monitoring on Petrocedeno Field in The Venezuelan Orinoco Belt; World Heavy Oil Congr., 2009. WHOC09-163.

(4) Vega, G.; Barrios, H. Steam Injection Experiences in Heavy and Extra-Heavy Oil Fields, Venezuela. SPE Heavy Oil Conf. Exhib; SPE-150283-MS, 2011.

(5) Pena, D.; Patino, D. Development of a Completion Model for the Monitoring of EOR in Wells with Heavy and Extra Heavy Crude in the Largest Deposit in Latin America. *SPE Middle East Oil and Gas Show and Conference; SPE-194830-MS,* 2019.

(6) Gasbarri, S.; Diaz, A.; Guzman, M. Evaluation of Electric Heating on Recovery Factors in Extra Heavy Oil Reservoirs. *SPE Heavy Oil Conf. Exhib.*; *SPE-149779-MS*, 2011.

(7) Rodriguez, F. IOR/EOR Methods Adapted to High Water Production Zones of Heavy and Extra-Heavy Oil Reservoirs in La Faja Petrolifera Del Orinoco-Venezuela: State of the Art. *ASME/International Conference on Ocean, Offshore and Artic Engineering; OMAE2021*-63525, 2021.

(8) Turta, A.; Chattopadhyay, S.; Bhattacharya, R.; Condrachi, A.; Hanson, W. Current Status of Commercial In Situ Combustion Projects Worldwide. J. Can. Pet. Technol. **2007**, *46*, 1–7.

(9) Yang, X.; Gates, I. D. Combustion Kinetics of Athabasca Bitumen from 1D Combustion Tube Experiments. *Nat. Resour. Res.* 2009, *18*, 193–211.

(10) Barzin, Y.; Moore, R.; Mehta, S.; Mallory, D.; Ursenbach, M.; Tabasinejad, F. Role of Vapor Phase in Oxidation/Combustion Kinetics of High-Pressure Air Injection (HPAI). SPE Annu. Tech. Conf. Exhib.; SPE-135641-MS, 2010.

(11) Alvarado, V.; Manrique, E. Enhanced Oil Recovery: An Update Review. *Energies* **2010**, *3*, 1529–1575.

(12) Liu, Z. x.; Liang, Y.; Wang, Q.; Guo, Y. j.; Gao, M.; Wang, Z. b.; Liu, W. l. Status and Progress of Worldwide EOR Field Applications. *J. Pet. Sci. Eng.* **2020**, *193*, 107449. (13) Yang, M.; Harding, T. G.; Chen, Z. Numerical investigation of the mechanisms in co-injection of steam and enriched air process using combustion tube tests. *Fuel* **2019**, *242*, 638–648.

(14) Terwilliger, P.; Clay, R.; Wilson, L.; Gonzalez-Gerth, E. Fireflood of the P2-3 Sand Reservoir in The Miga Field of Eastern Venezuela. *J. Pet. Technol.* **1975**, *27*, 9–14.

(15) Herrera, A. The M6 Steam Drive Project Design and Implementation. In The Oil Sands of Canada-Venezuela. *Spec. Vol. Can. Inst. Min. Metall.* **1977**, *7*, 551–560.

(16) Anaya, I.; La Cruz, R.; Alvarez, A.; Gutierrez, D.; Skoreyko, F.; Card, S. Simulation Study for Designing an In-Situ Combustion Pilot in the Orinoco Belt of Venezuela: From Laboratory Studies to Field Scale. SPE—Canadian Unconventional Resources and International Petroleum Conference; CSUG/SPE-137491-MS, 2010.

(17) Mendoza, A.; Perozo, H.; Oliveros, D.; Reyes, N. Study for Improving the In-Situ Combustion of Venezuela Extra-Heavy Crude Oil Using Unconventional Additive. *SPE Latin American and Caribbean Petroleum Engineering Conference; SPE-138339-MS*, 2010.

(18) Arturo, J.; Mendoza, R.; Oliveros, D.; Arellano, D.; Perozo, H.; Reinoza, J.; Rivas, A. New Approach to Upgrade the Combustion In Situ Process by using an Emulsified Additive on Heavy Oil from Orinoco Belt. SPE Enhanced Oil Recovery Conference; SPE-145056-MS, 2011.

(19) Hincapie, R.; Tovar, F.; Alvarez, C. Feasibility for the Application of In Situ Combustion in Faja Petrolifera del Orinoco (FPO) Based in a Novel Screening Criteria for the Technology. *SPE Enhanced Oil Recovery; SPE-144027-MS*, 2011.

(20) Vargas, D.; Garcia, J.; Rodriguez, J.; Reverol, H. 2009. Drilling and Completion of Wells of the Pilot Test in the In Situ Combustion Project, Bare Field; World Heavy Oil Congr., 2009. WHOC-526.

(21) Perozo, H.; Mendoza, A.; Teixeira, J.; Alvarez, A.; Marquez, J.; Ortega, P.; Vasquez, P. The In Situ Combustion Pilot Project in Bare Field, Orinoco Oil Belt, Venezuela. *SPE Enhanced Oil Recovery Conference; SPE-144484-MS*, 2011.

(22) Amaro, J. Estudio del Efecto de Nanoparticulas Combinadas con el Proceso de Combustión In Situ, sobre un Crudo Extrapesado de La Faja Petrolifera Del Orinoco (FPO). Thesis Dissertation for the Degree in Petroleum Engineering, Univ. Cent. Venez. (UCV), 2013.

(23) Llamedo, M.; Zamora, O.; Mendoza, A. Comparative Study of the Temperature Profiles for Spontaneous and Induced Ignition on the Pilot Area of In Situ Combustion (ISC) on Bare Field of Venezuela. *Heavy Oil Latin America Conference & Exhibition, HOLA-153,* 2015.

(24) Yao, J.; Li, G.; Wu, J. Application of In-Situ Combustion for Heavy Oil Production in China: A Review. J. Oil Gas Petrochem. Sci. 2018, 1, 69–72.

(25) Chen, Y. f.; Pu, W. f.; Liu, X. l.; Li, Y. b.; Varfolomeev, M. A.; Hui, J. A Preliminary Feasibility Analysis of In Situ Combustion in a Deep Fractured-Cave Carbonate Heavy Oil Reservoir. *J. Pet. Sci. Eng.* **2019**, *174*, 446–455.

(26) Popov, E.; Askarova, A.; Mukhametdinova, A.; Maksakov, K.; Usachev, G.; Darishchev, V.; Mehta, S. A.; Cheremisin, A. Evaluation of the Applicability of In-Situ Combustion in a Heavy Oil Carbonate Field with High Initial Oil Saturation. *J. Pet. Sci. Eng.* **2021**, *207*, 109146.

(27) Cavanzo, E. A.; Muñoz, S. F.; Bottía R, H.; Niz V, E.; Ordoñez R, A. Combustión In Situ Húmeda: Alternativa para el Recobro Mejorado en Colombia. *Rev. Fuentes, Reventon Energ.* **2016**, *14*, 5–18.

(28) Alamatsaz, A.; Moore, G. R.; Mehta, S. A.; Ursenbach, M. G. Analysis of Dry, Wet and Superwet In Situ Combustion using a Novel Conical Cell Experiment. *Fuel* **2018**, *234*, 482–491.

(29) Ado, M. R.; Greaves, M.; Rigby, S. P. Simulation of catalytic upgrading in CAPRI, an add-on process to novel in-situ combustion, THAI. *Pet. Res.* **2022**, *7*, 297–307.

(30) Hart, A.; Wood, J.; Greaves, M. Laboratory Investigation of CAPRI Catalytic THAI-add-on Process for Heavy Oil Production and In Situ Upgrading. *J. Anal. Appl. Pyrolysis* **2017**, *128*, 18–26.

(31) Turta, A.; Kapadia, P.; Gadelle, C. THAI Process: Determination of the Quality of Burning from Gas Composition taking into account the Coke Gasification and Water-Gas Shift Reactions. *J. Pet. Sci. Eng.* **2020**, *187*, 106638.

(32) Quijada, J. Estudio Comparativo de Métodos de Ignición para el Proceso de Recuperación Mejorada Térmica de Combustión en Sitio. Thesis Dissertation for the Degree in Chemistry, Univ. Cent. Venez. (UCV), 2015.

(33) Mahinpey, N.; Ambalae, A.; Asghari, K. In Situ Combustion in Enhanced Oil Recovery (EOR): A Review. *Chem. Eng. Commun.* 2007, 194, 995–1021.

(34) Bottia-Ramirez, H.; Aguillon-Macea, M.; Lizcano-Rubio, H.; Delgadillo-Aya, C. L.; Gadelle, C. Numerical Modeling on In-Situ Combustion Process in the Chichimene Field: Ignition Stage. *J. Pet. Sci. Eng.* **2017**, *154*, 462–468.

(35) Alade, O. S.; Hamdy, M.; Mahmoud, M.; Al Shehri, D.; Mokheimer, E.; Al-Nakhli, A. Experimental and Numerical Analysis of using Thermochemical Injection for Preheating to Improve In-Situ Combustion of Bitumen. *Fuel* **2020**, *275*, 117894.

(36) Changbin, K.; Xiaocong, Y.; Wenlong, G.; Junshi, T.; Miao, W.; Yan, A.; Jian, S.; Xinjun, D.; Yu, H.; Shilin, T.; Qili, X.; Ding, M. Unveiling the Mechanisms of In-Situ Combustion of Post-Steam Driven Heavy Oil by Electric Heating Method Induced Auto-Ignition. *J. Pet. Sci. Eng.* **2022**, *212*, 110181.

(37) Zhu, Z.; Liu, Y.; Liu, C.; Kovscek, A. R. In-Situ Combustion Frontal Stability Analysis. SPE J. (Soc. Pet. Eng.) 2021, 26, 2271–2286.
(38) Anderson, T. I.; Kovscek, A. R. Analysis and Comparison of In-

Situ Combustion Chemical Reaction Models. *Fuel* **2022**, *311*, 122599. (39) Varfolomeev, M. A.; Yuan, C.; Bolotov, A. V.; Minkhanov, I. F.; Mehrabi-Kalajahi, S.; Saifullin, E. R.; Marvanov, M. M.; Baygildin, E. R.; Sabiryanov, R. M.; Rojas, A.; Emelianov, D. A.; Al-Muntaser, A. A.; Ganiev, B. G.; Zaripov, A. T.; Beregovoi, A. N.; Shaihutdinov, D. K.

Effect of Copper Stearate as Catalysts on the Performance of In-Situ Combustion Process for Heavy Oil Recovery and Upgrading. *J. Pet. Sci. Eng.* **2021**, *207*, 109125.

(40) Li, Y.; Liao, G.; Wang, Z.; Su, R.; Ma, S.; Zhang, H.; Wang, L.; Wang, X.; Pan, J.; Shi, Q. Molecular Composition of Low-Temperature Oxidation Products in a Simulated Crude Oil In-Situ Combustion. *Fuel* **2022**, *316*, 123297.

(41) Zhao, S.; Pu, W.; Varfolomeev, M. A.; Yuan, C.; Pan, J.; Wang, R.; Chen, L.; Kan, N. Low-Temperature Oxidation of Light and Heavy Oils via Thermal Analysis: Kinetic Analysis and Temperature Zone Division. *J. Pet. Sci. Eng.* **2018**, *168*, 246–255.

(42) Yuan, C.; Emelianov, D. A.; Varfolomeev, M. A.; Abaas, M. Combustion Behavior of Aromatics and their Interaction with n-Alkane in In-Situ Combustion Enhanced Oil Recovery Process: Thermochemistry. *J. Ind. Eng. Chem.* **2019**, *76*, 467–475.

(43) Wang, Y.; Zhou, Y.; Fan, S.; Lang, X.; Li, G. Influence of Low Temperature Oxidation on Heavy Oil Coking by Thermal Pyrolysis during In Situ Combustion Process. *Fuel* **2022**, *316*, 123314.

(44) Yuan, C.; Emelianov, D. A.; Varfolomeev, M. A. Oxidation Behavior and Kinetics of Light, Medium, and Heavy Crude Oils Characterized by Thermogravimetry Coupled with Fourier Transform Infrared Spectroscopy. *Energy Fuels* **2018**, *32*, 5571–5580.

(45) Yuan, C.; Sadikov, K.; Varfolomeev, M.; Khaliullin, R.; Pu, W.; Al-Muntaser, A.; Saeed Mehrabi-Kalajahi, S. Low-Temperature Combustion Behavior of Crude Oils in Porous Media under Air Flow Condition for In-Situ Combustion (ISC) Process. *Fuel* **2020**, *259*, 116293.

(46) Zhao, R.; Chen, Y.; Huan, R.; Castanier, L. M.; Kovscek, A. R. An Experimental Investigation of the In-Situ Combustion Behavior of Karamay Crude Oil. *J. Pet. Sci. Eng.* **2015**, *127*, 82–92.

(47) Pu, W.; Zhao, S.; Hu, L.; Varfolomeev, M. A.; Yuan, C.; Wang, L.; Rodionov, N. O. Thermal Effect Caused by Low Temperature Oxidation of Heavy Crude Oil and Its In-Situ Combustion Behavior. *J. Pet. Sci. Eng.* **2020**, *184*, 106521.

(48) Kittel, J.; Ropital, F.; Grosjean, F.; Joshi, G. Evaluation of the Interactions between Hydrogen and Steel in Geothermal Conditions with H_2S ; World Geothermal Congress 2020+1, 2021.

(49) Shargay, C.; Moore, K.; Colwell, R. Survey of Materials in Hydrotreater Units Processing High TAN Feed. NACE Int. Corros. Conf. Expo; NACE-07573, 2007.

(50) Liu, L.; Case, R. The Influence of H_2S on Hydrogen Absorption and Sulfide Stress Cracking Resistance of High Strength Low Alloy Carbon Steel C110. J. Nat. Gas Sci. Eng. **2022**, 99, 104418.

(51) Uzcategui, D.; Lamoureux-Var, V.; Berger, E. H2S and CO2 Generation Mechanisms on a Steam Injection Project on Petrocedeno Field, Orinoco Belt; World Heavy Oil Congr., 2011. WHOC11-112.

(52) Ayache, S.; Gasser-Dorado, J.; Michel, P.; Preux, C.; Lamoureux-Var, V. Tailor-Made Workflow to Understand and Forecast H₂S Production Risks in Thermal Projects. *SPE Western Regional Meeting; SPE-200776-MS*, 2021.

(53) Turta, A.; Coates, R.; Greaves, M. In-Situ Combustion in the Oil Reservoirs Underlain by Bottom Water. Review of the Field and Laboratory Tests. *Can. Int. Pet. Conf.; PETSOC-2009-150,* 2009.

(54) Kudryavtsev, P.; Hascakir, B. Towards Dynamic Control of Insitu Combustion: Effect of Initial Oil and Water Saturations. SPE Western North American and Rocky Mountain Joint Meeting; SPE-169542-MS, 2014.

(55) Zhao, R.; Sun, Z.; Sun, X.; Shi, X.; Chen, C.; Guo, W. Effect of Secondary Water Body on the In-Situ Combustion Behaviors. *Fuel* **2022**, *316*, 123303.

(56) Aleksandrov, D.; Kudryavtsev, P.; Hascakir, B. Variations in In-Situ Combustion Performance due to Fracture Orientation. *J. Pet. Sci. Eng.* **2017**, *154*, 488–494.

(57) Ovalles, C.; Vallejos, C.; Vásquez, T.; Martinis, J.; Perez-Perez, A.; Cotte, E.; Castellanos, L.; Rodriguez, H. Extra-Heavy Crude Oil Downhole Upgrading Process using Hydrogen Donors under Steam Injection Conditions. SPE Int. Therm. Oper. Heavy Oil Symp.; SPE-69692-MS, 2001.

(58) Ismail, N. B.; Hascakir, B. Impact of Asphaltenes and Clay Interaction on In-Situ Combustion Performance. *Fuel* **2020**, *268*, 117358.

(59) Garcia, H.; Velásquez, E. N.; Trujillo, M. Anticipating Operational Issues for the Field Pilot Test of Air Injection in Chichimene, Colombia. *Georesursy* **2016**, *18*, 289–298.

(60) Sharma, J.; Dean, J.; Aljaberi, F.; Altememee, N. In-Situ Combustion in Bellevue Field in Louisiana – History, Current State and Future Strategies. *Fuel* **2021**, *284*, 118992.

(61) Ovalles, C.; Rodriguez, H. Extra Heavy Crude Oil Downhole Upgrading Using Hydrogen Donors Under Cyclic Steam Injection Conditions: Physical and Numerical Simulation Studies. *J. Can. Pet. Technol.* **2008**, 47, 43–51.

(62) Goncalves, C. Evaluación Preliminar del Efecto de Nanoemulsiones y un Agente Hidrogenante, para Mejorar las Propiedades Fisicoquímicas del Crudo Producido, Mediante Recuperación Mejorada con Combustión en Sitio. Thesis Dissertation for the Degree in Chemistry, Univ. Cent. Venez. (UCV), 2015.

(63) Chen, Q.; Yin, M.; Zhang, L.; Liu, H.; Qin, Z.; Wang, Z. Hydrogen-Donated Thermal Upgrading of Venezuela Extra-Heavy Oil: Identifying the Role of Hydrogen Donor. *Pet. Sci. Technol.* **2020**, *38*, 550–555.

(64) Kok, M. V.; Bagci, S. Characterization and Kinetics of Light Crude Oil Combustion in the Presence of Metallic Salts. *Energy Fuels* **2004**, *18*, 858–865.

(65) Hosseinpour, N.; Mortazavi, Y.; Bahramian, A.; Khodatars, L.; Khodadadi, A. A. Enhanced Pyrolysis and Oxidation of Asphaltenes Adsorbed onto Transition Metal Oxides Nanoparticles towards Advanced In-Situ Combustion EOR Processes by Nanotechnology. *Appl. Catal., A* **2014**, *477*, 159–171.

(66) Simao, A.; Dominguez-Alvarez, E.; Yuan, C.; Suwaid, M. A.; Varfolomeev, M. A.; Ancheyta, J.; Al-mishaal, O. F.; Kudryashov, S. I.; Afanasiev, I. S.; Antonenko, D. A.; Petrashov, O. V.; Dubrovin, K. A. On the Use of Metallic Nanoparticulated Catalysts for In-Situ Oil Upgrading. *Fuel* **2022**, *313*, 122677.

(67) Hyndman, A.; Luhning, R. Recovery and Upgrading of Bitumen and Heavy Oil in Canada. *J. Can. Pet. Technol.* **1991**, *30*, DOI: 10.2118/91-02-03.

(68) Castanier, L.; Brigham, W. Upgrading of Crude Oil via In Situ Combustion. J. Pet. Sci. Eng. 2003, 39, 125–136.

(69) Kuhlman, M. The Benefits of In Situ Upgrading Reactions to the Integrated Operations of the Orinoco Heavy-Oil Fields and Downstream Facilities. *SPE/AAPG Western Regional Meeting; SPE-62560-MS*, 2000.

(70) Alvarez, C.; Marciano, C.; Pereira, C.; Larrauri, K.; Morros, F.; Bauduhin, P. The Orinoco Oil Belt Targets Light/Medium Crude Oil and Product Market Opportunities. *SPE Int. Therm. Oper. Heavy Oil Symp.; SPE-69734-MS*, 2001.

(71) Li, Y.; Wang, Z.; Hu, Z.; Xu, B.; Li, Y.; Pu, W.; Zhao, J. A Review of In Situ Upgrading Technology for Heavy Crude Oil. *Petroleum KeAi* **2021**, *7*, 117–122.

(72) Mateshov Experimental Study of In Situ Combustion with Decalin and Metallic Catalyst. Thesis Dissertation for the Master of Science Degree in Petroleum Engineering, Texas A & M University, 2010.

(73) Mora, M. Evaluación Preliminar del Efecto de un Aditivo Sólido para la Mitigación de Gases Ácidos en Recuperación Mejorada mediante Combustión en Sitio. Thesis Dissertation for the Degree in Chemical Engineering, Univ. Cent. Venez. (UCV), 2015.

(74) Torres, M.; Flores, F. Evaluación Experimental del Efecto de la Mineralogía en el Mecanismo de Ignición con Vapor y Generación de Gases Ácidos para el Proceso de Combustión en Sitio (CES) de un Campo de la FPO. Thesis Dissertation for the Degree in Petroleum Engineering, Univ. Cent. Venez. (UCV), 2017.

(75) Hernández, N. Evaluación Experimental del Proceso de Combustión in Situ Empleando Crudo de la Faja Petrolifera del Orinoco. Thesis Dissertation for the Degree of Specialist on Integrated Management of Hydrocarbon Reservoirs, Univ. Cent. Venez. (UCV), 2003.

(76) Ron, A. Estimar la Reactividad Catalítica hacia Reacciones de Hidrotratamiento Empleando Catalizadores V-Ni-Mo/Alúmina. Thesis Dissertation for the Degree in Chemistry, Univ. Cent. Venez. (UCV), 2010.

(77) Retes, J. Tratamiento Aquatermolítico para el Mejoramiento de Crudos Pesados utilizando Aditivos Innovadores. Thesis Dissertation for the Degree in Chemical Engineering, Univ. Cent. Venez. (UCV), 2012.

(78) Alvarez, F. Desarrollo de Sistemas Catalíticos a Base de Óxidos Tipo Perovskitas e Hidrotalcitas para la Producción de Hidrógeno. Thesis Dissertation for the Degree of Doctor in Science, Univ. Cent. Venez. (UCV), 2016.

(79) Rodriguez, F.; Delamaide, E.; Rousseau, D.; Bekri, S. Which is the Most Attractive IOR Method to Produce the Venezuelan Highly Viscous Oil Resources in the Energy Transition Era? A Comprehensive Review of Research and Field Applications. *Abu Dhabi Int. Pet. Exhib. Conf.; SPE-211344-MS*, 2022.

(80) Rodriguez, F.; Belhaj, H.; AlDhuhoori, M. Opportunities for Producing Hydrogen and Low-carbon Fossil Fuels from Venezuelan Conventional and Unconventional Hydrocarbon Reservoirs: An Idea in Times of Energy Transition to Net Zero-Carbon. *Abu Dhabi Int. Pet. Exhib. Conf.; SPE-210998-MS,* 2022.

(81) Rodriguez, F. Surfactant Polymer Combinations for Chemical Enhanced Oil Recovery (EOR) Applied to Extra-Heavy Oil Reservoirs: Transport Properties in Porous Media and Recovery Mechanisms. Doctoral Dissertation, Sorbonne Paris Cité University, 2016.

(82) Brandl, A.; Bottiglieri; Han, J.; Garcia, J. Zonal Isolation in a High Stress Environment: A Case History in Venezuela's In-Situ Combustion Wells. *Int. Pet. Technol. Conf.; IPTC-18748-MS*, 2016.

(83) Huang, Y.; Luo, M.; Zhang, Z.; Li, W.; Zhang, Y. Research on Technology of Drilling in High Temperature and High Pressure Gas Field in South China Sea. *IOP Conf. Ser.: Earth Environ. Sci.* **2019**, *384*, 012024.

(84) Agha, K. R.; Belhaj, H. A.; Mustafiz, S.; Bjorndalen, N.; Islam, M. R. Numerical Investigation of the Prospects of High Energy Laser in Drilling Oil and Gas Wells. *Pet. Sci. Technol.* **2004**, *22*, 1173–1186.

(85) Odiete, W. E. New Wellbore Temperature Control Design for Preventing Failure and Poor Performance of Logging Tools in High Pressure-Temperature Wells. *Heliyon* **2022**, *8*, No. e09404. (86) Hand, E. Underground Oil Fires Liberate Carbon-Free Fuel. *Science* **2020**, 367, 617.

(87) Karlsdottir, S. N. Corrosion, Scaling and Material Selection in Geothermal Production. *Comprehensive Renewable Energy*, 2nd ed.; Elsevier, 2022; Vol. 7, pp 256–277.

(88) Arbad, N.; Emadī, H.; Watson, M. A Comprehensive Review of Geothermal Cementing from Well Integrity Perspective. *J. Pet. Sci. Eng.* **2022**, *217*, 110869.

(89) Kooper, R.; Kupecz, J.; Curtis, C.; Cole, T.; Dorn-Lopez, D.; Copley, J.; Munoz, A.; Caicedo, V. Reservoir Characterization of the Orinoco Oil Belt: Miocene Oficina Formation, Zuata Field, Eastern Venezuelan Basin. SPE Int. Therm. Oper. Heavy Oil Symp.; SPE-69697-MS, 2001.

(90) Bejarano, C.; Castillo, E.; Germain, P.; Mendoza, P.; Manrique, C.; Chacin, L.; Pineda, G.; Mendez, O. Challenging Complex Deltaic Reservoirs on the Orinoco Heavy-Oil Belt Aided by New-Generation Azimuthal Deep-Resistivity Tools and Advanced Real-Time Geosteering Techniques: Successful Case Study from the Eastern Venezuelan Basin. SPE Latin American & Caribbean Petroleum Engineering Conference; SPE-139134-MS, 2010.

(91) Farouq Ali, S. M. Non-Thermal Heavy Oil Recovery Methods. SPE Rocky Mountain Regional Meeting; SPE-5893-MS, 1976.

(92) Kumar, R.; Socorro, D.; Pernalete, M. A.; Gonzalez, K.; Atalay, N.; Nava, R.; Lolley, C.; Kumar, M.; Arbelaez, A. Unique Infill Configuration to Unlock Additional Barrels in the Boscan Heavy-Oil Water-Injection Project. *SPE Reservoir Eval. Eng.* **2020**, *23*, 566–577.

(93) Dusseault, M. B. Comparing Venezuelan and Canadian Heavy Oil and Tar Sands. *Can. Int. Pet. Conf.*, 2001.paper 2001-061.

(94) Hajdo, L.; Hallam, R.; Vorndran, L. Hydrogen Generation During In-Situ Combustion. SPE California Regional Meeting; SPE-13661-MS, 1985.

(95) Kapadia, P. R.; Kallos, M. S.; Gates, I. D. Potential for Hydrogen Generation from In Situ Combustion of Athabasca Bitumen. *Fuel* **2011**, *90*, 2254–2265.

(96) Hart, A.; Wood, J. In situ Catalytic Upgrading of Heavy Crude with CAPRI: Influence of Hydrogen on Catalyst Pore Plugging and Deactivation due to Coke. *Energies* **2018**, *11*, 636.

(97) Anbari, H.; Robinson, J. P.; Greaves, M.; Rigby, S. P. Field Performance and Numerical Simulation Study on the Toe to Heel Air Injection (THAI) Process in a Heavy Oil Reservoir with Bottom Water. *J. Pet. Sci. Eng.* **2023**, *220*, 111202.

(98) Lopeman, T.; Anbari, H.; Leeke, G.; Wood, J. Numerical Modeling of Toe-to-Heel Air Injection and Its Catalytic Variant (CAPRI) under Varying Steam Conditions. *Energy Fuels* **2023**, *37*, 237–250.

(99) van der Vlis, A. On the Cause of Subsidence in Oil-Producing Areas; World Pet. Congr., 1967. WPC-12208.

(100) Adegbite, J. O.; Belhaj, H.; Bera, A. Investigations on the Relationship among the Porosity, Permeability and Pore Throat Size of Transition Zone Samples in Carbonate Reservoirs using Multiple Regression Analysis, Artificial Neural Network and Adaptive Neuro-fuzzy Interface System. *Pet. Res.* **2021**, *6*, 321–332.

(101) Finol, A. S.; Sancevic, Z. Chapter 7 Subsidence in Venezuela. *Dev. Pet. Sci.* **1995**, *41*, 337–372.

(102) Layrisse, I. Heavy Oil Production in Venezuela: Historical Recap and Scenarios for Next Century SPE Int. Symp. Oilfield Chem.; SPE-53464-MS, 1999.

(103) Belhaj, H.; Nouri, A. Reservoir Rock Behavior Pre and Post Pore Collapse during Production. *Int. Pet. Technol. Conf.; IPTC-11657-MS*, 2007.

(104) Fan, Z.; Yang, D.; Li, X. Quantification of Sand Production Using a Pressure-Gradient-Based Sand-Failure Criterion. SPE J. (Soc. Pet. Eng.) **2019**, *24*, 988–1001.

(105) Marquez, J.; Brito, A. How to Separate Sand in Heavy and Extra Heavy Oil Fields Surface Facilities; World Heavy Oil Congr, 2014. WHOC14-385.

(106) Ramirez, M.; Zubillaga, J. Applications of Well Logging for Compaction and Subsidence Studies in the Orinoco Oil Belt, Venezuela. SPE Annu. Tech. Conf. Exhib; SPE-16773-MS, 1987. (107) Perdona, P.; Rabe, C. Laboratory Test and Logging Campaign for Geomechanical Application in SAGD Process for Heavy Oil Reservoirs in Venezuela. *ISRM International Symposium-EUROCK* 2010; *ISRM-EUROCK-2010-171*, 2010.

(108) Li, Y.; Manrique, E. J.; Kovscek, A. R. Progress Toward Pilot-Scale Simulation of In-Situ Combustion Incorporating Geomechanics. *SPE Res Eval. Eng.* **2023**, *26*, 152–166.

(109) Marcos, J.; Pardo, E.; Casas, J.; Delgado, D.; Rondon, M.; Exposito, M.; Zerpa, L.; Ichbia, J.; Bellorini, J. Static and Dynamic Models of Formation Water in Sincor Area, Orinoco Belt, Venezuela. SPE Latin American and Caribbean Petroleum Engineering Conference; SPE-107378-MS, 2007.

(110) Martinius, A. W.; Hegner, J.; Kaas, I.; Mjøs, R.; Bejarano, C.; Mathieu, X. Geologic Reservoir Characterization and Evaluation of the Petrocedeño Field, Early Miocene Oficina Formation, Orinoco Heavy Oil Belt, Venezuela. *Am. Assoc. Pet. Geol.* **2013**, DOI: 10.1306/133715908t643559.

(111) Boschetti, T.; Angulo, B.; Quintero, F.; Volcán, J.; Casalins, A. Chemical and Stable Isotope Composition ($^{18}O/^{16}O, ^{2}H/^{1}H$) of Formation Waters from the Carabobo Oilfield. *Venezuela. Geol. Acta* **2018**, *16*, 257–264. I-III

(112) Chen, H.; Chen, H.; Li, C.; Wang, Y.; Li, J.; Huang, R.; Tian, C.; Hou, Q. Logging Response Characteristics and Formation Process of Flushed Zone in the Orinoco Heavy Oil Belt, Venezuela. *Pet. Explor. Dev.* **2020**, *47*, 585–593.

(113) Okocha, C.; Thornton, A.; Wylde, J. Novel Sulfide Scale Inhibitor Successfully Averts Challenging Sulfide Scale Deposition in Permian and Williston Unconventional Basins. *SPE/AAPG/SEG Unconventional Resources Technology Conference*, 2020.

(114) Wang, X.; Deng, G.; Ko, S.; Lu, A.; Zhao, Y.; Dai, C.; Paudval, S.; Ouyang, B.; Mateen, S.; Kan, A.; Tomson, M. Improved Scale Prediction for High Calcium Containing Produced Brine and Sulfide Scales. SPE International Oilfield Scale Conference and Exhibition; SPE-200699-MS, 2020.

(115) Chen, T.; Wang, O.; Chang, F. New Insight into the Mechanism of Iron Sulfide Deposition in Carbonate Reservoir During Acid Stimulation. CORROSION 2018; NACE-2018-11141, 2018.

(116) Hamza, A.; Hussein, I. A.; Jalab, R.; Saad, M.; Mahmoud, M. Review of Iron Sulfide Scale Removal and Inhibition in Oil and Gas Wells: Current Status and Perspectives. *Energy Fuels* **2021**, *35*, 14401–14421.

(117) Manrique, E.; Trujillo, M.; Lizcano, J.; Cardenas, D.; Vanegas, J.; Portillo, F.; Salazar, H.; Caicedo, N. Comprehensive Fluid Compositional Analysis Program to Support the Interpretation of Chichimene Field In-Situ Combustion Pilot. SPE Improved Oil Conference; SPE-209390-MS, 2022.

(118) Rodriguez, F.; Rousseau, D.; Bekri, S.; Hocine, S.; Degre, G.; Djabourov, M.; Bejarano, C. Investigation and Interpretation of a Novel Surfactant-Polymer Approach to Increase Extra-Heavy Oil Recovery: Application to a Thin-Bedded Reservoir, Faja Petrolifera Del Orinoco, Venezuela. *SPE Improved Oil Recovery Conference; SPE-179624-MS*, 2016.

(119) Rodriguez, F.; Belhaj, H.; Rousseau, D.; AlDhuhoori, M. Generation of Complex Emulsions During the Application of Improved Recovery Methods in Venezuelan Heavy and Extra-Heavy Oil Reservoirs: A Critical Review. *Abu Dhabi Int. Pet. Exhib. Conf.; SPE-211106-MS*, 2022.

(120) Jurado, E.; Bravo, V.; Camacho, F.; Vicaria, J. M.; Fernandez-Arteaga, A. Estimation of the Distribution of Droplet Size, Interfacial Area and Volume in Emulsions. *Colloids Surf.*, A **200**7, 295, 91–98.

(121) Acevedo, S.; Escobar, G.; Ranaudo, M. A.; Khazen, J.; Borges, B.; Pereira, J. C.; Mendez, B. Isolation and Characterization of Low and High Molecular Weight Acidic Compounds from Cerro Negro Extra heavy Crude Oil. Role of These Acids in the Interfacial Properties of the Crude Oil Emulsions. *Energy Fuels* **1999**, *13*, 333–335.

(122) Lopez, L.; Lo Monaco, S. Geochemistry of Crude Oils from the Orinoco Oil Belt. *Rev. Fac. Ing. UCV* **2010**, *25*, 41–50. ISSN 0798-4065

(123) Meredith, W.; Kelland, S. J.; Jones, D. Influence of Biodegradation on Crude Oil Acidity and Carboxylic Acid Composition. *Org. Geochem.* **2000**, *31*, 1059–1073.

(124) Borges, B. Natural Surfactants from Venezuela Extra-Heavy Crude Oils – Study of Interfacial and Structural Properties. *Crude Oil Emulsions-Composition and Characterization*, 2012.

(125) Argillier, J.; Barré, L.; Brucy, F.; Dournaux, J.; Hénaut, I.; Bouchard, R. Influence of Asphaltenes Content and Dilution of Heavy Oil Rheology. SPE Int. Therm. Oper. Heavy Oil Symp.; SPE-69711-MS, 2001.

(126) Alvarez-Martínez, F. Emulsion Formation and Breaking during In Situ Combustion. Thesis Dissertation for the Master of Science Degree in Chemical Engineering, Univ. Nac. Colomb., Faculty of Mines, 2021.

(127) Morse, R. A. Upgrading Oil by In Situ Combustion. U.S. Patent 3,332,489 A, 1967.

(128) Shi, L.; Xi, C.; Liu, P.; Li, X.; Yuan, Z. Infill Wells Assisted In-situ Combustion following SAGD Process in Extra-heavy Oil Reservoirs. *J. Pet. Sci. Eng.* **2017**, *157*, 958–970.

(129) Zhao, R.; Yang, J.; Zhao, C.; Heng, M.; Wang, J. Investigation on coke zone evolution behavior during a THAI process. *J. Pet. Sci. Eng.* **2021**, *196*, 107667.

(130) Wylde, J. J.; Taylor, G. N.; Sorbie, K. S.; Samaniego, W. N.; Allan, B. N. Oxazolidine-Based H_2S and Mercaptan Scavengers: Uncovering the Myths. *Energy Fuels* **2021**, *35*, 12993–13010.

(131) Wylde, J. J.; Taylor, G. N.; Sorbie, K. S.; Samaniego, W. N. Scavenging Alkyl Mercaptans: Elucidation of Reaction Mechanisms and Byproduct Characterization. *Energy Fuels* **2020**, *34*, 13883–13892. (132) Wylde, J. J.; Taylor, G. N.; Sorbie, K. S.; Samaniego, W. N. Formation, Chemical Characterization, and Oxidative Dissolution of Amorphous Polymeric Dithiazine (apDTZ) during the Use of the H₂S Scavenger Monoethanolamine-Triazine. *Energy Fuels* **2020**, *34*, 9923–9931.

(133) Taylor, G.; Wylde, J.; Samaniego, W.; Sorbie, K. Amorphous Polymeric Dithiazine apDTZ Solid Fouling: Critical Review, Analysis and Solutions of an Ongoing Challenge in Triazine-Based Hydrogen Sulphide Mitigation. SPE International Conference on Oilfield Chemistry; SPE-204397-MS, 2021.

(134) Wylde, J. J.; Taylor, G. N.; Sorbie, K. S.; Samaniego, W. N. Synthesis and Reaction Byproduct Characterization and Mechanistic Understanding of Hemiformal Based Hydrogen Sulfide Scavengers. *Energy Fuels* **2020**, *34*, 4808–4821.

(135) González, A. Efecto del Uso de Secuestrantes Líquidos para la Remoción de H2S en Sistemas de Producción de Crudo y Gas Natural. Thesis Dissertation for the Degree in Chemical Engineering, Univ. Cent. Venez. (UCV), 2004.

(136) Rodriguez, F.; Llamedo, M.; Belhaj, H.; Belhaj, A. Challenges Associated with the Acid Gases Production and Capture in Hydrocarbon Reservoirs: A Critical Review of the Venezuelan Cases. *SPE Thermal Well Integrity and Production Symposium*; Paper SPE-212146-MS, 2022.

(137) Rafferty, A.; Steward-Liddon, C.; Graham, G.; Baraka-Lokmane, S.; Nwankwo, C.; Hitta, J. Alternative Scavenger Chemistries: Impact of Scavengers on Carbonate Scaling. SPE International Oilfield Scale Conference and Exhibition; SPE-209513-MS, 2022.

(138) Perez, M.; Barrios, M.; Vasquez, P.; Losada, R.; Salcedo, M.; Perozo, H.; Ortega, P.; Diaz, M. Capture and Sequestration of CO_2 Produced by In-Situ Combustion Pilot Project, Orinoco Oil Belt, Venezuela: A Mineral Carbonation Assessment. SPE International Conference on CO_2 Capture, Storage, and Utilization; SPE-139661-MS, 2010.

(139) Yáñez Angarita, E. E.; Núñez-López, V., Ramirez Ramirez, A., Castillo Monroy, E., Faaij, A. Rapid Screening and Probabilistic Estimation of the Potential for CO_2 -EOR and Associated Geological CO_2 Storage in Colombian Petroleum Basins. *Pet. Geosci.* **2022**, *28*, DOI: 10.1144/petgeo2020-110.

(140) Tsopela, A., Bere, A., Dutko, M., Kato, J., Niranjan, S. C., Jennette, B. G., Hsu, S. Y., Dasari, G. R. CO₂ Injection and Storage in

Article

Porous Rocks: Coupled Geomechanical Yielding Below Failure Threshold and Permeability Evolution. *Pet. Geosci.* 2022, 28 DOI: 10.1144/petgeo2020-124.

(141) Ringrose, P. How to Store CO_2 Underground: Insights from Early-mover CCS Projects. *SpringerBriefs in Earth Sciences*; Springer, 2020.

(142) Langhi, L., Strand, J., Ricard, L. Flow Modelling to Quantify Structural Control on CO_2 Migration and Containment, CCS Southwest Hub, Australia. *Pet. Geosci.* 2021, 27, DOI: 10.1144/petgeo2020-094.

(143) Leslie, R.; Cavanagh, A. J.; Haszeldine, R. S.; Johnson, G.; Gilfillan, S. M. V. Quantification of Solubility Trapping in Natural and Engineered CO_2 Reservoirs. *Pet. Geosci.* **2021**, 27, DOI: 10.1144/petgeo2020-120.

(144) MacDowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C. S.; Williams, C. K.; Shah, N.; Fennell, P. An Overview of CO_2 Capture Technologies. *Energy Environ. Sci.* **2010**, *3*, 1645–1669.

(145) Belhaj, H.; Agha, K.; Butt, S.; Islam, M. Simulation of Non-Darcy Flow in Porous Media Including Viscous, Inertial and Frictional Effects. SPE International Improved Oil Recovery Conference in Asia Pacific; SPE-84879-MS, 2003.

(146) Tarkowski, R.; Uliasz-Misiak, B.; Tarkowski, P. Storage of Hydrogen, Natural Gas, and Carbon Dioxide – Geological and Legal Conditions. *Int. J. Hydrogen Energy* **2021**, *46*, 20010–20022.

(147) Dvoynikov, M.; Buslaev, G.; Kunshin, A.; Sidorov, D.; Kraslawski, A.; Budovskaya, M. New Concepts of Hydrogen Production and Storage in Arctic Region. *Resources* **2021**, *10*, 3.

(148) Heinemann, N.; Scafidi, J.; Pickup, G.; Thaysen, E.; Hassanpouryouzband, A.; Wilkinson, M.; Satterley, A.; Booth, M.; Edlmann, K.; Haszeldine, R. Hydrogen Storage in Saline Aquifers: The Role of Cushion Gas for Injection and Production. *Int. J. Hydrogen Energy* **2021**, *46*, 39284–39296.

(149) Almeida, J.; Espinoza, C.; Mosquera, J.; Todd, M. R. Reservoir Engineering Study of CO_2 Enhanced Oil Recovery for the Nipa 100 Field, Venezuela. *SPE Advanced Technology Series* **1994**, *2*, 86–94.

(150) Rivas, O.; Embid, S.; Bolivar, F. Ranking Reservoirs for Carbon Dioxide Flooding Processes. *SPE Advanced Technology Series* **1994**, *2*, 95–103.

(151) Manrique, E.; Ranson, A.; Alvarado, V. Perspectives of CO_2 Injection in Venezuela. 24th Annual Workshop & Symposium; IEA Collaborative Project on EOR, 2003.

(152) Belhaj, H.; Agha, K.; Butt, S.; Islam, M. A Comprehensive Numerical Simulation Model for Non-Darcy Flow Including Viscous, Inertial and Convective Contributions. *Nigeria Annual International Conference and Exhibition*; SPE-85678-MS, 2003.

(153) Wang, C.; Li, T.; Gao, H.; Zhao, J.; Li, H. A. Effect of Asphaltene Precipitation on CO_2 -Flooding Performance in Low-Permeability Sandstones: A Nuclear Magnetic Resonance Study. *RSC Adv.* **2017**, 7, 38367–38376.

(154) Shi, Y.; Zhao, W.; Li, S.; Yang, D. Quantification of Gas Exsolution and Preferential Diffusion for Alkane Solvent(s)-CO₂-Heavy Oil Systems Under Nonequilibrium Conditions. *J. Pet. Sci. Eng.* **2022**, *208*, 109283.

(155) Huang, L.; Wang, Y.; Zhang, L.; Pei, S.; Zhang, Z.; Su, Y.; Ren, S. Risk Assessment and Field Case Study on Oil/Natural Gas Explosion during High-Pressure air Injection Process. SPE J. **2022**, *27*, 806–819.

(156) Zheng, S.; Li, H.; Yang, D. Pressure Maintenance and Improving Oil Recovery with Immiscible CO₂ Injection in Thin Heavy Oil Reservoirs. J. Pet. Sci. Eng. **2013**, 112, 139–152.

(157) Lake, L.; Lotfollahi, M.; Bryant, S. Fifty Years of Field Observations: Lessons for CO_2 Storage from CO_2 Enhanced Oil Recovery. International Conference on Greenhouse Gas Control Technologies; GHGT-14, 2018.

(158) Belhaj, H.; Abu Khalifeh, H.; Javid, K. Potential of Nitrogen Gas Miscible Injection in South East Assets, Abu Dhabi. *North Africa Technical Conference and Exhibition; SPE-164774-MS*, 2013. (159) Shi, S.; Belhaj, H.; Bera, A. Capillary Pressure and Relative Permeability Correlations for Transition Zones of Carbonate Reservoirs. J. Pet. Explor. Prod. Technol. **2018**, *8*, 767–784.

(160) Caballero, M. Estudio Geológico para el Almacenamiento de CO_2 en Yacimientos de Petróleo y Gas, Ubicados en el Área Mayor de Anaco y Oficina Estado Anzoátegui. Thesis Dissertation for the Degree in Geologist Engineer, Univ. Cent. Venez. (UCV), 2010.

(161) Pens, M. Estudio de Factibilidad para Almacenamiento Geológico de CO_2 en Yacimientos Agotados Ubicados en el Campo Santa Rosa Municipio Anaco, Estado Anzoátegui. Thesis Dissertation the Degree in Master Geosciences, Univ. Cent. Venez. (UCV), 2009.

(162) Rodriguez, I.; Hernandez, E.; Velasquez, R.; Fernandez, J.; Yegres, F.; Martinez, R.; Contreras, R.; Korabelnikov, A. Characterization of the Stratigraphic Column in an Extra Heavy Oil Field to Optimize Production Costs, From the Disposal of Wastewater Effluents to the Evaluation of Shallow Aquifer for Water Production. Cerro Negro Area, Venezuela. SPE Int. Heavy Oil Conf. Exhib.; SPE-193732-MS, 2018.

(163) Erickson, D.; Haghighi, H.; Phillips, C. The Importance of CO_2 Composition Specification in the CCUS Chain. *Offshore Technology Conference; OTC-31844-MS*, 2022.

(164) Dong, B.; Liu, W.; Zhang, Y.; Banthukul, W.; Zhao, Y.; Zhang, T.; Fan, Y.; Li, X. Comparison of the Characteristics of Corrosion Scales Covering 3Cr Steel and X60 Steel in CO_2 -H₂S Coexistence Environment. *J. Nat. Gas Sci. Eng.* **2020**, *80*, 103371.

(165) Zafra, A.; Harris, Z.; Sun, C.; Martínez-Pañeda, E. Comparison of Hydrogen Diffusivities Measured by Electrochemical Permeation and Temperature-Programmed Desorption in Cold-rolled Pure Iron. *J. Nat. Gas Sci. Eng.* **2022**, *98*, 104365.

(166) Zelmati, D.; Bouledroua, O.; Ghelloudj, O.; Amirat, A.; Djukic, M. B. A Probabilistic Approach to Estimate the Remaining Life and Reliability of Corroded Pipelines. *J. Nat. Gas Sci. Eng.* **2022**, *99*, 104387.

(167) Yu, H.; Peng, X.; Lian, Z.; Zhang, Q.; Shi, T.; Wang, J.; Zhao, Z. Experimental and Numerical Simulation of Fatigue Corrosion Behavior of V150 High-Strength Drill Pipe in Air and H₂S-Dilling Mud Environment. *J. Nat. Gas Sci. Eng.* **2022**, *98*, 104392.

(168) Gonser, M.; Allan, B.; Wylde, J. Simultaneous Control of Surface Scale, Corrosion, and H_2S Using a Single Capillary String: A Real-World Chemical Application in the Permian Basin. SPE Annu. Tech. Conf. Exhib.; SPE-210140-MS, 2022.

(169) Ben Seghier, M. E. A.; Höche, D.; Zheludkevich, M. Prediction of the internal corrosion rate for oil and gas pipeline: Implementation of ensemble learning techniques. *J. Nat. Gas Sci. Eng.* **2022**, *99*, 104425.

(170) Wasim, M.; Djukic, M. B. External corrosion of oil and gas pipelines: A review of failure mechanisms and predictive preventions. *J. Nat. Gas Sci. Eng.* **2022**, *100*, 104467.