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CATALYSIS ON BULLETIN

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CONTENT

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CATALYSIS ON TERMAL OIL RECOVERY

César Patiño

The world's oil demand is forecasted to be at about 95 mn bbl/d for the Sustainable Development Scenario until 2025 and at 105 mn bbl/d for an extended period of time according to the Stated Policy Scenario of the IEA (IEA 2020 "The Oil and Gas Industry in Energy Transition"). The oil production decline from existing fields is about 8 %. Therefore, substantial effort needs to be made to ensure that the world's oil demand is met. Enhanced Oil Recovery (EOR) is contributing to the world's oil production, and significant progress has been made on these technologies. In addition, the commercial EOR technologies which have been implemented in different fields like steam and gas injection and chemical EOR have to be optimized to become economically feasible.

Accordingly, processes which work at microscale level to improve some properties like rock wettability and oil mobility are required to optimize EOR methods. Some nanomaterials can work at this scale, shown catalytic activity on some reaction to produce an upgrading in the oil, giving it better mobility. Thus, combining the catalytic nanoscience with EOR processes is possible to get a better forecast of these technologies. The nanoparticles have proven to be potential solutions or improvements to a number of challenges associated with the traditional EOR techniques. Generally, the nanoparticles are functionalized with metals, that consists of a nanoscale part with their active phase groups. The latter provides the capabilities to perform specific tasks such as adsorbing at the oil-water interface to modify properties like wettability and interfacial tension. Latin America projects with cases in Argentina, Brazil, and Colombia had been taken in lab-scale and some field applications.

Especially in Colombia, the recovery factor is around 17%, with 18 current field applications (1). These projects had been increasing our experiences with (16) water+improved injection projects, Steam injection (1), Gas injection (1); All of them had been developed into the country, giving the capabilities that companies like Ecopetrol, Parex, Gran Tierra, Frontera Energy required. These projects have been putting in place with the contribution of the academia, including different research groups from our universities like Universidad Nacional, Universidad SurColombiana, Universidad de Los Andes, Fundacion Universidad America y la Universidad Industrial de Santander. The latter is achieved with the support of the ANH within the strategy of PPI "PPI – Proyecto de Producción Incremental y Recobro Mejorado (EOR e IOR) and, ANH and Minciencia the inter-administrative agreements ANH No. 321 of 2016 and ANH No. 556/ 833 of 2018. The fundamental objectives of these government strategies are aimed at strengthening the research and experimental development work carried out systematically to increase scientific and technological knowledge in innovative techniques and various areas of the industry, specifically in EOR topic s.

Thanks to this Bulletin into the editorial part. The invitation today from our work at the Technology collaboration program IEA EOR TCP Colombia committee is to continue working on this perspective and developments of R&D with significant impact in reserves and production. Developments like the Catalysis group with the tasks are covering the important areas for EOR technology developments ranging from microscopic scale to research and field implementation of the key EOR methods, Chemical, Gas flooding, and Thermal recovery.

MAKING CATALYTIC NANOMATERIALS FOR RESERVOIR

Donaldo Fabio Mercado

Due to its relatively high surface/volume ratio, nanomaterials have gained attention above its analogs macroscopic solids. Interestingly, the reduction of the sizes to this scale may also result in the appearance of news or more intense chemical, mechanical, magnetic or catalytic properties (among others) but also by suitable controlling the chemical identity of the surface, it is possible to enhance, inhibit or evidence new properties, thus modifying the application field of the specific core nanomaterial.

One of these new fields of application which have huge expectations is the hibrid thermal - catalitic oil recovery processes. It is due to the need to transport the catalyst into the reservoir. Then, the nanocatalyst surface could be modified to get amphiphilic properties in order to prepare Oil/Water emulsions stabilized by the catalysts. This emuslions could be successfully inject into the reservoir.

In that regard, the Centro de Investigaciones en catalisis (CICAT) have successfully executed the research project: "*Preparación de nanomateriales basados en metales de transición para procesos ligados al recobro térmico de crudos colombianos y análisis de su comportamiento catalítico en procesos de combustión in-situ*" financed by MinCiencias and Asociación Nacional de Hidrocarburor - ANH (Colombia), in which the research team has developed skills in the synthesis, non-typical functionalization and characterization of metal oxide-based Janus nanomaterials able to stabilize oil-water emulsion without significantly losing catalytic activity. Depending on the metal oxide – core material, the effect of several parameters such as crystal phase, size, geometry, morphology, and synthesis route over the emulsion stability and catalytic performance have also been tested.

Figure 1 summarizes some relevant results in this area. Obtention of α-MnO_2 nanorods (DRX results not shown) is feasible. However, upon derivatizing its surface with conventional reagent (3-Aminopropyl) triethoxysilane – (APTES) modification in its surface properties is evidenced. The water-air-solid static contact angle is not only modified by the anisotropic presence of the organic coating in the solid, increasing the hydrophobic behavior of the powder but also it changes the interfacial properties in such a way that the core MnO_2 material is well-dispersed in hexane rather than water, but the Janus materials are located in the liquid-liquid interface. Interestingly, the derivatization not only provides the materials with amphiphilic properties but also seems to modify the heat flow profile of the catalytic oxidation of asphaltenes with higher heat flow.

Thus, these results not only evidence of some study fields of nanotechnology application in petroleum engineering but also the opportunity of knowledge creation in this area. Of course, the financing of new related research projects might be managed to focus the application of this emerging technology in real conditions for real applications.

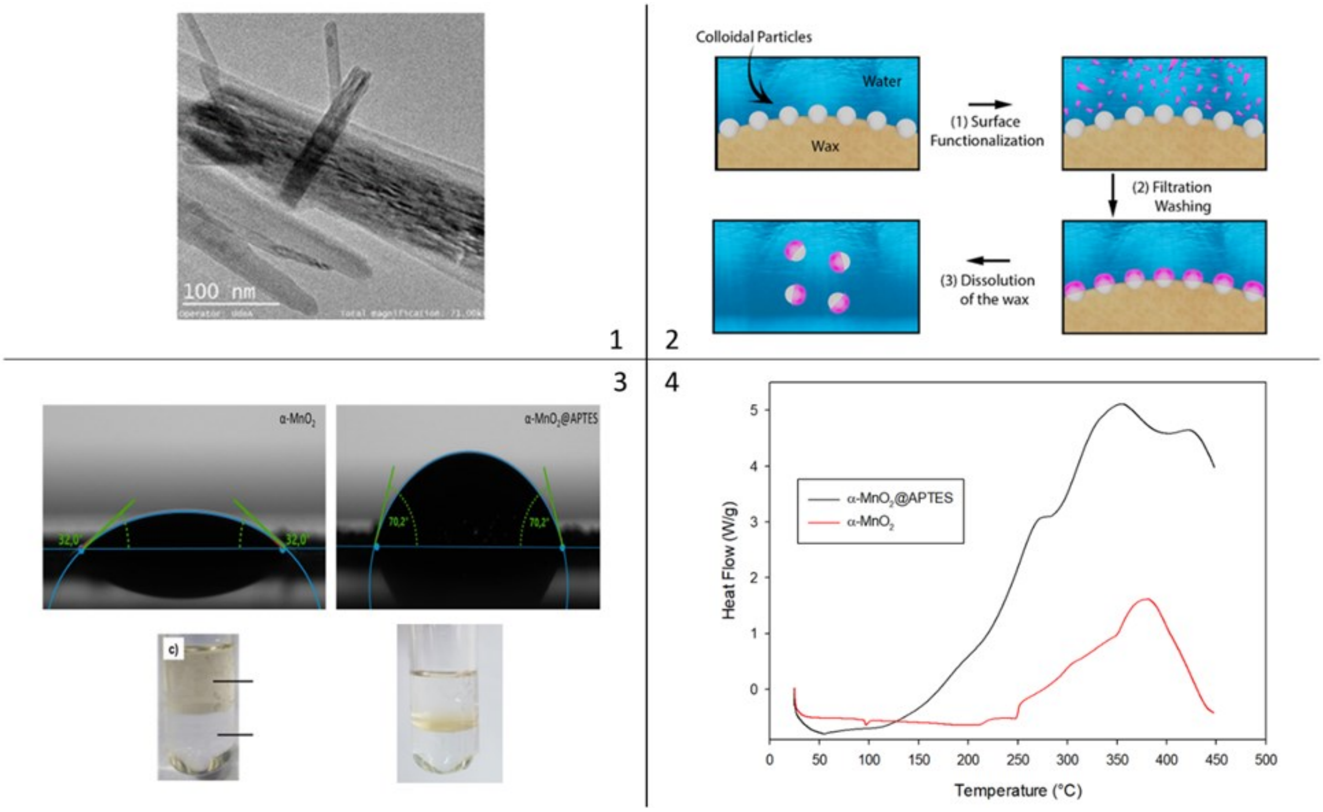

Figure 1. 1: *TEM micrograph of the core α-MnO_2 material.* ***2:*** *Schematic representation of the Pickering emulsion-based functionalization method.* ***3: Top:*** *Water-air-solid static contact angle of the α-MnO_2 core material and the Janus analog* ***bottom:*** *photographic evidence of the modifies interfacial properties in hexane/water interfaces of the solid upon the Janus derivatization and 4: Differential scanning calorimetry of asphaltenes oxidation catalyzed by the consider materials.*

COMMERCIAL APPLICATION OF CATALYTIC TECHNOLOGIES IN ENHANCED OIL RECOVERY: WHY ARE WE NOT THERE YET?

Edgar Mauricio Morales-Valencia

The financial support by government energy agencies and the petroleum industry for research and development projects focused on advanced technologies for enhanced oil recovery (EOR) has increased considerably [1]. This fact is directly related to the number of research groups that are working in this area and to the number of scientific papers published. According to a search done in Scopus using the keywords "enhanced oil recovery," we found 363 documents published in 2009, while ten years later, in 2019, 1450 were published. With the challenge of developing a technology for EOR in which a high recovery factor and a low amount of greenhouse gas emissions is achieved at a low cost, the use of catalysts integrated with proven and emerging EOR methods such as thermal, chemical, and gas injection, has been a recurrent topic of study on the last years [2]. The experience of several research groups on the preparation and testing of catalytic materials has allowed a remarkable advance in the field, mainly in the synthesis of nanocatalysts for aquathermolysis [3]. However, beyond continuing to evaluate countless new materials, is imperatives to address the question: what does it take to achieve a commercial application of this kind of technology?

In this sense, the Centro de Investigaciones en Catálisis (CICAT), which has more than 30 years of experience in the preparation and evaluation of catalysts for oil refinery, especially for hydroprocessing of heavy oils, has the objective to analyze the challenges to the implementation of catalytic evaluation systems that simulate the real conditions of in-situ upgrading and recovery of heavy oil. In the framework of the project: "*Desarrollo de una estrategia catalítica para un proceso de in-situ upgrading acoplado con procesos de combustión in-situ para optimizar la producción y mejorar la calidad de crudos pesados y extrapesados colombianos por reacciones de transferencia de hidrógeno*" we will do a critical review of the experimental set-ups used to assess catalytic performances, considering variables such as type of reactor, temperature, pressure, residence times, catalysts loadings, hydrogen consumption, and hydrogen donors where applied.

Based on the experience and technical knowledge on the catalytic tests of synthetic and real crudes, and the facilities and equipment, i.e., two high-pressure batch reactor systems, four fixed bed reactors, two of them to operate at high pressure, and 3 GC equipped with TCD and FID detectors for quantification of reactor effluents. At the end of the project, we want to elucidate the answer for some questions that are currently being asked: i) are the laboratory scale reaction set-ups traditionally used for studying these processes adequate?; ii) how realistic are the reaction conditions used in the laboratory experiments as compared to those required in commercial applications?; iii) what are the possible sources for providing hydrogen for these processes?; and iv) is it possible to recycle the catalysts? For this reason, CICAT seeks to review the experimental conditions and configurations that are being used on a laboratory scale and thus identify and discuss the opportunities and challenges for evaluating catalysts under more realistic conditions.

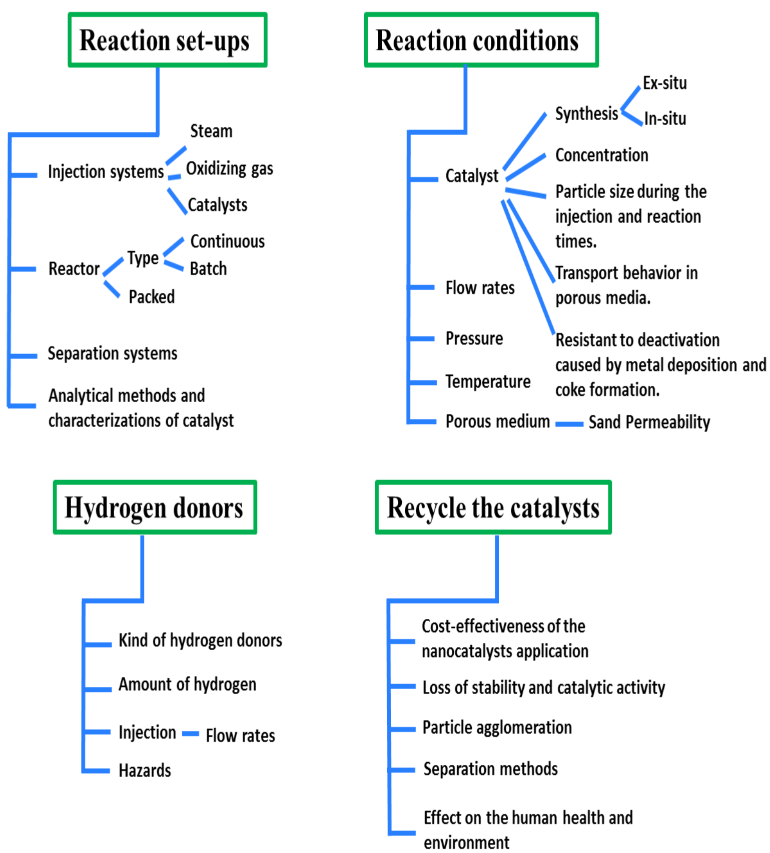

Figure 1. Mainly challenges for the implementation of nanotechnology on in-situ upgrading and recovery enhancement.

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UPGRADING HEAVY OILS AND VACUUM RESIDUES WITH NATIVE MINERALS AND SPENT CATALYSTS

Wilson Germán Oyola Naranjo

Oil production around the world has become a race to achieve technically and economically viable recovery processes . Projections in oil and natural gas production show a growing trend owing to improved recovery processes. However, with new oil production recovery techniques, the heavy fractions in oil have increased , affecting viscosity and the fluence of the oil for its transportation from the field , as well as in refinery processes, the increase of vacuum residues affects processes as thermal cracking and catalytic hydrocracking.

Through a technological and scientific cooperation agreement, the *Instituto Colombiano del Petróleo* of ECOPETROL S.A. (ICP-ECOPETROL) and the *Centro de Investigaciones en Catálisis* (CICAT-UIS) of the Universidad Industrial de Santander carried out a project to establish the bases for the development of the concept of a technology that allows upgrading Colombian heavy oils by hydrotreating reactions. The project studied the use of solid catalysts for upgrading heavy and extra-heavy oils and vacuum residue fractions. As a result, a homogeneous dispersion of catalysts was possible, that mainly impact polar structures of large molecular size, in this way, the viscosity of the heavy oil was reduced.

The catalysts were based on mineral sources and spent catalysts. They were conditioned as catalysts to obtain reaction products with suitable properties for different applications . The evaluation of metal catalysts in the upgrading of heavy oil was initially carried in batch reactors under conditions of high hydrogen pressure with a previous stage of activation by sulfidation with the sulfur compounds present in the fed in the presence of hy-

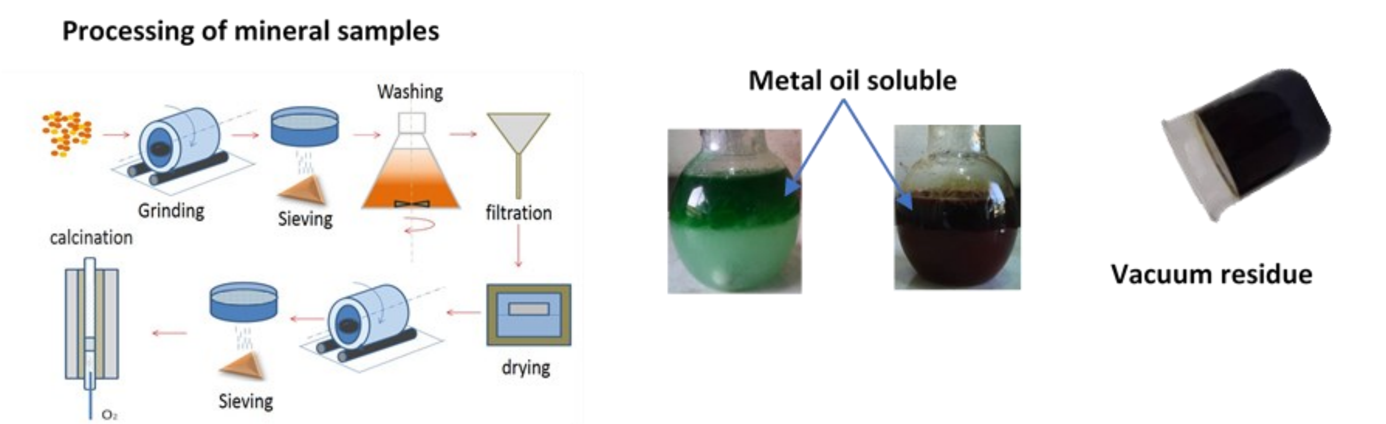

Figure 1. *Vacuum residue fraction and soluble oil Ni and Fe catalysts.*

drogen. Later, the process was carried on a pilot plant in a continuously dispersed bed for hydrocracking.

Mineral samples were converted into catalysts, both in liquid and solid phase, figure 1, and transformation methodologies were developed for the catalytic conversion of vacuum residues in fluidized bed . The evaluation was carried out based on the monitoring of hydrogen consumption both in the sulfidation stage and in the high-pressure hydrogenation of the vacuum residues, and the evaluation of the products following petroleum characterization techniques and instrumental analysis such as SimDis, density, viscosity, ICP - MS, sulfur content, PIONA, rheological behavior, among others.

The results of the evaluation of the catalysts for the upgrading of heavy oils include adequate operating conditions to reduce the content of insoluble materials in heptane and toluene, product stability, and the reaction products yield showed in figure 2.

This study allowed to obtain treatment methodologies for hydrocracking, that opening doors to new strategies to give value to heavy fractions obtained from new technologies applied to oil production processes.

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HOW TO EVALUATE HYBRID STEAM INJECTION – CATALYSTS PROCESSES BEFORE THEIR APPLICATION IN OIL FIELDS

Dr. Claude Gadelle

The recovery factor for heavy or extra-heavy oil reservoirs is low, even very low. This is due to the very high viscosity of these oils, meaning very low mobility in the reservoirs. Enhanced oil recovery methods have been developed for increasing production. The aim of thermal methods is to decrease the viscosity of the oil in place in order to increase its mobility. The thermal recovery methods are mainly steam injection and in-situ combustion. Their mechanisms are well known and their domain of application too. Recovery in these cases can reach 60 % but generally is of the order of 30 %.

On-going researches on thermal methods aim at increasing the sweep efficiency (injection of polymers or/and surfactants, foaming agent before or during the implementation of the thermal method), or at modifying the implicated chemical reactions by the use of catalysts. In this last case, the goal is to directly produce an upgraded oil that allows transportation by pipelines; whereas, normally, heavy and extra heavy oils have to be pretreated on the field or nearby before sending them to the pipe-lines grid.

Researches are carried out to develop catalysts for the reactions of this kind of applications; namely, oxidation, combustion, pyrolysis, hydrocracking, and aqua thermolysis of hydrocarbons. All these reactions are well-known in the refining area, but they must be studied under the conditions of the reservoir since the latter are very different from those prevailing in refinery reactors. Along with the difficulties of studying catalytic effects, there are other difficulties linked to the porous medium and its characteristics, meaning that experiments in physical models long enough to simulate a portion of the reservoir are needed.

This physical model must allow studying a fluid-rock system at the conditions of fluid saturations, pressure and temperature prevailing in the study reservoir. The model must also allow enough original oil to be contained in order to carry out the displacement while samples of produced liquids are taken in order to look for a possible upgrade as well as of produced gases to quantify important gases such as H_2 and H_2S. On the other hand, it is mandatory that the system works in adiabatic conditions to be sure that the energy is transfer to the rock-fluid system. This physical model must measure the temperature along the system to determine the velocity rate of the steam front. This would allow us to make energy balances to determine the amount of steam necessary to heat and displace a certain volume of fluids in the reservoir. This will allow evaluating if the addition of catalysts to the system reduces the steam requirements and / or the residual saturation of fluids, as well as determining the degree of upgrading and the amount of H2 or H2S produced .

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Donaldo Fabio Mercado Castro, Ph.D.

Chemical engineer graduated from Universidad Nacional de Colombia with a Ph.D. in Chemistry in Universidad Nacional de La Plata, Argentina. During his doctoral studies he worked at Università degli Studi di Torino, Italy and Universidad Politecnica de Valencia, Spain. His doctoral research was focused on the obtention of several nanocomposites using organic residues as raw-materials or additive in bottom-up synthesis processes. Later, he was vinculated to Georgetown University, USA, where he developed a magnetic polymer nanocomposite active to the dehalogenation of aromatic halogenated compounds in groundwater.

Actually he is associated to the Centro de Investigaciones en Catalisis (CICAT) and to the Grupo de investigación en Aplicaciones Fotoquímicas (GIAFOT), both in Colombia.

His experience is in the desing, synthesis, characterization and application of nanotechonology. Actually, he is the postdoctoral researcher of a project related to the obtention of metal oxide-based Janus nanomaterials to its application as catalyst in thermic oil recovery proceesses associated to the CICAT – UIS.

Edgar Mauricio Morales-Valencia

Edgar Mauricio holds a chemical engineering degree from Universidad Industrial de Santander and a Ph.D. from the same university. The research activities focused on evaluating experimentally and theoretically the influence of different inhibiting species such as H_2S, N-containing compounds and aromatic molecules on ultra-deep hydrodesulfurization (HDS) reactions for the production of ultra-low sulfur fuels. This research aimed at obtaining quantitative rather than qualitative results applying mathematical basis related to the development of kinetic models.

He is currently a postdoctoral researcher at the Centro de Investigaciones en Catálisis (CICAT). He is working in a project of Enhanced Oil Recovery related to the development of a catalytic strategy for an in-situ upgrading process coupled with in-situ combustion processes to optimize production and improve the quality of Colombian heavy and extra-heavy crudes by hydrogen transfer reactions

Wilson Germán Oyola Naranjo

Graduated in Chemistry from the *Universidad Industrial de Santander* (UIS), working in recovery and purification of gold and silver metals. He obtained a master's degree in Chemistry at the same institution, focusing his study on the development of models for predicting the properties of gasoils and its hydrocracking products from infrared absorption spectra using chemometry. Continued to investigate on processes for removing naphthenic acids from acidic crude oils, synthesis of oil-soluble catalysts, treatment of hydrocracking products, monitoring, and control of hydrocracking processes in discontinuous and continuous reactors, deactivation of catalysts for the petroleum industry, analysis and characterization of catalysts and products, among others. Currently, he is a student of the doctoral program of the UIS at the *Centro de Investigaciones en Catálisis* (CICAT) where he develops catalysts for the oxidation of sulfur compounds in the emulsion phase.

Dr Claude Gadelle

Dr Claude Gadelle has been involved in the design and manufacturing of the in-situ combustion laboratory for the Instituto Colombiano del Petroleo. He has been involved in the design of the in-situ combustion pilot test on the Chichimene field. During his career at IFP, he was involved in many aspects related to thermal recovery of heavy oils. He worked in Romania on fields exploited by in-situ combustion. He was involved in the preparation of injection and production wells prior to starting combustion. As a Project Leader in Underground Coal Gasification in France, he studied the ignition of a coal seam with gas burner or electrical ignitor. For deep coal seams, he selected an electrical ignitor, the design of which was patented. This ignitor was manufactured in France and successfully used.