

NANOTECHNOLOGY AND THE OIL INDUSTRY: POTENTIAL APPLICATIONS IN ECUADOR

NANOTECNOLOGÍA Y LA INDUSTRIA PETROLERA: APLICACIONES POTENCIALES EN EL ECUADOR

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Resumen

Consideramos algunas aplicaciones de la nanotecnología a la industria petrolera a nivel mundial y discutimos, en particular, algunas aplicaciones recientes en Colombia. Consideramos algunas aplicaciones potenciales de la nanotecnología en la industria petrolera del Ecuador y describimos en forma sucinta un proyecto para diseñar, sintetizar, caracterizar y probar catalizadores basados en nano estructuras para la industria petrolera ecuatoriana. Discutimos algunas perspectivas y dificultades relacionadas con estas aplicaciones.

Palabras Clave: Nanotecnología, industria petrolera, proyecto de catalizadores en Ecuador.

Abstract

We consider some applications of nanotechnology to the oil industry worldwide and in particular we discuss some recent applications in Colombia. We consider some potential applications of nanotechnology to the oil industry in Ecuador and succinctly describe a project to design, synthesize, characterize and test nanostructure-based catalysts for the Ecuadorian oil

industry. We discuss perspectives and difficulties related to these applications.

Keywords: Nanotechnology, oil industry, catalyst project in Ecuador.

Introduction

The impressive development of nano science and nanotechnology during the last three decades has had and will continue to have an important impact in many areas of industry and manufacturing. These areas may be roughly cataloged as: medical/pharmaceutical, chemical/advanced materials, information and communication technologies, energy, automotive, textiles and agriculture [1]. Of course, these areas involve many specialized subareas. For example, in agriculture we have agricultural production comprising: nutrient, plant hormones, agricultural waste treatment. In medicine: new nano ways of detecting and curing tumors, new drugs and nano drug delivery methods. A sub-branch of the energy area is oil drilling and refining, just to mention a few related activities [2]. Although it took some time for nanotechnology to reap benefits from market production its potential to change manufacturing was already appreciated quite early. As to its impact on oil industry already in 2006, Krishnamoorti predicted: "... nanotechnology is an enabler that has proved to be a game changer for exploiting fossil-based fuels and, over the next 30 years, will be a critical component in developing fossil-based energy technologies" [3].

Nanoscience emerges from the realization that as size diminishes to the order of nanometers, quantum effects become predominant. As a consequence, it is observed that the properties of bulk matter no longer characterize those of nanoparticles. Besides, as quite perspicuously noticed by Feynman [4], "There's plenty of room at the bottom", meaning that the size of nano-objects is such as to provide the means to construct devices and structures of uncanny complexity and minimal size. Of course, nature has already endowed us with the outcome of such complexity by creating living structures out of the nano-molecules of life.

Hand by hand, nano science and nanotechnology are changing the face of the world. Nano science by creating the theoretical tools and the crucial experiments to provide an understanding of the quantum phenomena taking place in nano systems, and nanotechnology by setting up the instruments for the synthesis, development and handling of nano structures. A short list of the latter embraces, for example: nanoparticles, nanotubes, nanoporous materials, fullerenes, graphenes, quantum dots, nanostructured materials, nanofibers, nanocapsules, nanofilms, nanofluids, etc.

In Section II, we concentrate on reviewing some of the current and prospective applications of nanotechnology to different processes taking place in the oil

industry. In Section III, we comment on recent regional applications such as those being implemented in Colombia. Finally, in Section IV, we discuss on prospective applications in Ecuador, describe the innovative catalyst project presented by ESPOL, and advance some conclusions.

Nanotechnology in the Oil and Gas Industry

Let us start by quoting Coccuza et al. [5], on some general reflections on this matter: “Nanotech applications in the oil industry are not completely new: nanoparticles have been successfully used in drilling muds for the past 50 years. Only recently all the other key areas of the oil industry, such as exploration, primary and assisted production, monitoring, refining and distribution, are approaching nanotechnologies as the potential Philosopher's stone for facing critical issues related to remote locations (such as ultra-deep water and arctic environments), harsh conditions (high-temperature and high-pressure formations), nonconventional reservoirs (heavy oils, tight gas, tar sands). “

The oil industry has undergone a quiet but substantial transformation due to some factors among which we may highlight the increase in oil consumption brought about by the rapid industrial development of countries such as China, India, Brazil, etc. Also, according to the US Department of Energy (DOE) about two-thirds of the oil remains un-extracted (cited by Coccuza et al. [5]). The increase in oil demand requires tapping this reserve. This is not an easy technical problem. Actually, its solution involves the development of enhanced oil recovery techniques which, in turn, rely on nanotechnology. Moreover, many reservoirs are located at considerable depths. Deep-drilling extraction techniques have been developed. But, for example, the usual sensing devices and images which work under milder conditions are not functional at high temperatures and pressures and so, new techniques, generally involving nanosensors, have to be resorted to. Hydraulic fracturing of shales, or fracking, has also opened previously untapped resources into production and has spurred the development of new techniques. Finally, environmental regulations have imposed much stricter standards on oil and gas derivatives and have promoted research on new catalysts also based on nano techniques for the removal of, for example, sulfur-containing compounds.

In general, strong and stable materials are needed in most processes employed in the oil and gas industry. There is, therefore, an important area of applications for nano materials designed and built to have these properties. For instance, nanoparticles of silicon carbide can be used to create exceptionally hard materials [6]. Similarly, there are many other examples of nanomaterials such as nanotubes, nanoporous materials, nanostructured materials, nanofibers, etc., which have been found useful in the oil and gas industry.

As reported by Kong and Ohadi [7], the need for the implementation of technological solutions to the problems facing the oil and gas industry prompted cooperation between academia and industry. To this purpose, the Advanced Energy Consortium (AEC) was set up in the US in 2008. The leading oil and service companies, such as BP, ConocoPhillips, Shell, Total and Schlumberger participated in this venture.

Some of the main areas of collaboration between the oil and gas industry and nanotechnology centers are listed below (for a more exhaustive and detailed description of these issues, see [6-14]):

1. Exploration
 - a. Improved techniques for remote sensing and improved resolution of subsurface imaging (nanosensors).
 - b. Controlled mobility of injectants and particle agglomeration (nano membranes).
2. Drilling
 - a. Increased strength, longevity and resistance to corrosion of drilling components (nanomaterials and coatings).
 - b. Light density and high strength cements, hermetic seals (nano materials and coatings).
 - c. Improved drilling fluids (nanofluids and nano membranes).
3. Production
 - a. In situ sensing (nanosensors)
 - b. Chemical detection (nanosensors)
 - c. Enhanced measurements in the borehole (nanosensors)
 - d. Leak detection and location in pipelines, downhole (nanosensors)
4. Enhanced oil recovery
 - a. Removal of oil droplets from pores in rocks (nanoparticles).
 - b. Removal of asphaltenes from pores in rocks (nanoparticles, nanodispersions)
 - c. In-situ heavy oil upgrading and recovery enhancement (nano catalysts).
5. Refining and processing
 - a. Oil refining (nano catalysts, mesoporous materials).
 - b. Removal of toxic or harmful substance from oil- derivatives (nano-catalysts, nano-filters).

Of course, not all applications of nanotechnology to processes occurring in the oil and gas industry are successful. The systems are so highly complex that harnessing the variables to optimize the nano application is, indeed, a great challenge. In this vein, let us quote Friedheim et al., [8]. "Initial studies have been producing interesting and exciting data, one example is the nanoparticle used to prevent water invasion into shales. More studies will be needed on

nanotechnology and applications the area of drilling fluids. Nanotechnology has potential uses due to the physical properties intrinsic to these materials. Additionally, the potential for modifications leading to new materials with unique properties is endless. Nevertheless, several considerations such as viscosity effect, flocculation tendencies and [Health, Safety and Environmental], HS&E, profiles must be addressed before any decision to use nanotechnology solution in a drilling fluid.”

Nanotechnology Applications to Enhanced Oil Recovery in Colombia

Oil prices plummeted from 2014 on due to overproduction mainly caused by the incorporation of oil extracted by fracking from new shale reservoirs. This led to a worldwide reduction of production in oil fields which were no longer profitable due to the price collapse.

Of course, the profitability of any industry depends on the gap between production and market prices of the goods offered. However, when the market price cannot be changed, the smart answer is to reduce the production price. This is precisely the response given by Colombian oil and gas industry which reframed its goals by directing its investment toward strategies based on new technologies in order to improve the industry’s effectiveness. [15].

As we have mentioned in this short review, a significant portion of the new technologies having bearing on the oil and gas industry are founded on nanotechnology. The reason clearly emerges from the exceptional properties of nanoparticles. In addition, for processes involving the recovery of oil from micro pores in the rocks, namely, enhanced oil recovery, [16] the fact that nanoparticles are of the size from 1 to 100 nanometers allows them to freely flow through porous media without the danger of clogging the pores. Besides, nanoparticles show a highly increased ratio of surface area vs. volume, a property which renders them very active for catalytic purposes. For enhanced oil recovery, for example, nanoparticles have been used in order to change the wettability of the rock surfaces and to reduce the surface tension between water and oil interfaces. In addition, the use of surfactant and polymer mixtures can efficiently contribute to the removal of asphaltenes in heavy oil wells [9].

The use of nanotechnology and a concerted effort between academia and industry has been a successful story in the Colombian oil and gas industry. Let us quote to this purpose the conclusions set forward by Franco et al., [15] “Nanotechnology-based developments in Colombia have shown great potential for increasing the efficiency of different operations in the oil and

gas industry. Experimental efforts conducted by the academic sector have resulted in the realization of different nanoparticles and nanofluids specially designed according to the problem of interest. Thus, it can be said that the synthesis of smart fluids and particles is currently a reality. Approaches for formation damage inhibition have led to the expansion of these nano-based solutions in various wells and several fields in the country. NEOR [Nanoparticles/nanofluids for enhanced oil recovery] approximations are aligned with the current needs of the national oil and gas industry, and the academic sector is prepared for the challenges involved.”

In order to place the present discussion in a proper perspective, we present in Table 1, some comparative data concerning some oil-related facts plus the Gross Domestic Product, GDP, for Colombia and Ecuador. For comparison, Venezuela has also been included as a country in Latin America possessing very extensive oil resources.

Country	Proven Oil Reserves (million b)	Oil Production (1000 b/d)	Oil Demand (1000 b/d)	Oil Exports (1000 b/d)	Oil Exports (USD 10 ⁹ /y) *	GDP (USD 10 ⁶ /y) **
Colombia	2,002	883.3	324.4	613.5	8.0	282,357
Ecuador	8,273	549.0	247.0	414.7	5.1	98,0010
Venezuela	302,250	2,372.5	566.2	1,835.0	20.4	236,443

Source: OPEC Annual Statistical Bulletin 2017; * Source: World's Top Exports, <http://www.worldstopexports.com/worlds-top-oil-exports-country/>; ** Source: [https://en.wikipedia.org/wiki/List_of_countries_by_GDP_\(nominal\)](https://en.wikipedia.org/wiki/List_of_countries_by_GDP_(nominal))

TABLE 1. Comparative Chart of Oil-Related Data vs Gross Domestic Product, GDP 2016.

Nanotechnology Projects for the Oil Industry in Ecuador

In Ecuador, the story is quite the opposite. In the first place there has been little interaction between academia and the oil sector, which is mostly controlled by the State-owned Petroecuador and PetroAmazonas. In addition, there are no research and development departments in these companies. There have been some isolated actions such as the installation by PetroEcuador of some equipment for catalyst characterization at the School of Chemical Engineering at the Central University of Ecuador and a training course in catalyst modeling given in Petroecuador by one of the authors of the present work (EV Ludeña). However, to our knowledge, there has been no sustained

and significant interaction with academia. There have been, nevertheless, outsourcing contracts for specific tasks related to oil production with service companies such as Schlumberger.

Aware of the importance both of applications of nano catalysts to the oil industry and the fact that Ecuador imports all of its catalysts, in 2016, the Center of Research and Development in Nanotechnology, CIDNA, of the Escuela Superior Politécnica del Litoral, ESPOL, presented a project to the Secretaría Nacional de Educación Superior, Ciencia y Tecnología, SENESCYT, the National Secretariat for Science, Technology and Higher Education, whose title was: “Design, modelling and synthesis of novel catalysts for the oil industry”. The purpose and scope of this project are given below, by quoting from the document submitted to SENESCYT:

“This Project focuses on the design, synthesis and testing of catalysts for hydrodesulfurization, HDS, processes [17] used in national refineries, promoting the change of the productive matrix and consolidating the technological sovereignty and efficiency of the strategic sectors. In this sense, it is aligned with Objectives 10 and 11 of the Plan Nacional del Buen Vivir, PNBV, (see below), and in particular policies 10.1, 10.2 and 11.1 and its policies 10.1f, 10.2a, 10.2 and 11.1f of the PNBV, as it will provide Ecuadorian society with novel catalysts made with our own technology and tailored to the country's refineries. In recent research [18] conducted by the proponent group it was found that structures isolated from sulfides containing Nb and V provide a viable alternative for the generation of HDS catalysts. The results of this research will be obtained through: 1. - Theoretical design of the structures of modified catalysts with niobium, Nb, and vanadium, V, through the combination of theoretical simulation techniques. 2. - Synthesis of the best prospects obtained in the theoretical design stage. 3. - Characterization and tests in micro reactors of the synthesized catalysts. As a result, at least one catalyst prototype based on Nb and V, suitable for the HDS process, will be obtained in the conversion of distillates, residuals, heavy crudes and fuels using domestic raw materials for both the catalyst and the support. The socio-economic impact would be the reduction of imports of catalysts, replacing them with a local alternative and the use of trained local personnel.” (PNBV is “El Plan Nacional del Buen Vivir”, or “National Plan for Good Living”, a document on policy priorities published by the government of Ecuador).

As an example of the kind of simulation of novel catalysts that is being performed in the context of this project, we present a graphical display of the type of nano structure of promoted niobium sulfide catalyst that has been used. In Fig. 1 we show a slab made up of 20 Nb atoms interconnected by a network of 40 sulfur atoms. In Fig 2 we show a graph of just the first two

upper rows of the slab, which in this case consists of 16 Nb atoms (in the four lower rows), of 4 V atoms (in the upper row) and 38 S atoms connecting the metal atoms. This slab has been used to determine the stability of the nanostructure subject to hydrogenation on the sulfur edge under working refinery conditions: 650K and a pressure ratio p_{H_2S}/p_{H_2} of 0.05. By an exhaustive modeling of a large number of structures, the relative stabilities brought about by the inclusion of promoting transition metal atoms is determined.

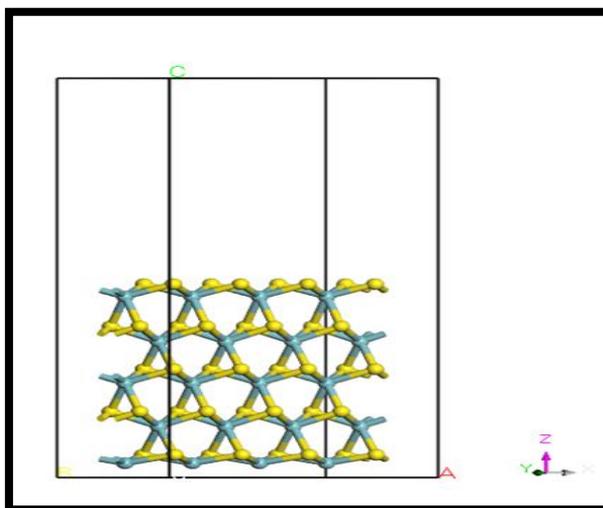


FIGURE 1. Schematic view of the slab of NbS_2

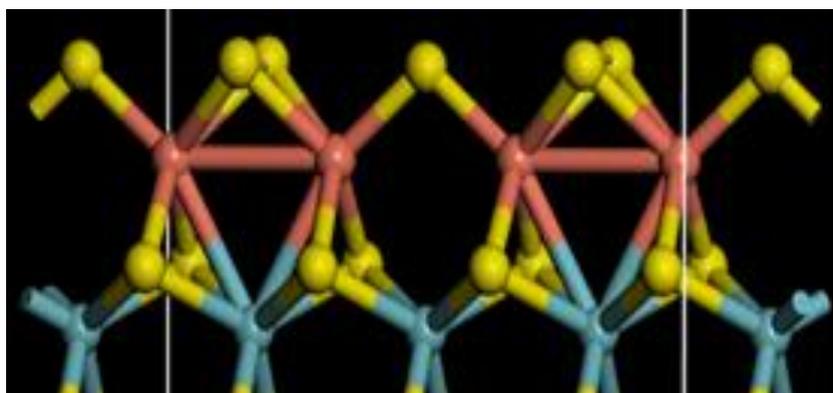


FIGURE 2. Schematic view of the 100V 75S corresponding to a 100 % replacement of the first row with V and a sulfur coverage of 75% on the sulfur edge of the slab.

The above project, having passed the technical and economic evaluation by SENESCYT was finally not funded as a result of a negative review on its relevance by reviewers from one of the state-owned oil companies. Clearly, a more proactive collaboration between academia and the state-owned companies in Ecuador, would be desirable to set up common goals. This might also help to avoid practices such as those recently revealed by the press [19]. In the absence of open calls for projects during the present year, the project has been reintroduced to the consideration of the Secretary- General of SENESCYT.

Summing up: Ecuador is in the same condition as Colombia concerning the many problems related to lower oil prices. For this reason, it should follow Colombia's example and promote a strong connection between industry and academia (which not necessarily has to be local) for applying nanotechnology to the problems inherent to the local oil industry. Ecuador should create a Petroleum and Energy Institute to foster and canalize research and to update scientific applications of nanotechnology and other fields to the oil industry. Engagement with the private sector in these endeavors might help to enhance transparency in management and reduce improper use of resources.

Conclusions

Nanotechnology offers many actual and possible solutions to problems that emerge when the oil and gas industries have to depart from the traditional methods of drilling, refining and recovering. In fact, as a result of a combined effort involving academic research centers, industrial labs and field applications, some novel processes, materials and instruments which heavily rely on nanotechnology, have been developed.

Nanotechnology has the power to contribute to optimization and cost lowering in many of the areas making up the oil and gas industries. Hence, it can be used to mitigate some of the effects of price collapse and ensure adequate revenues for countries whose economy depends substantially on oil production. This has been the case of Colombia, where a wise use of nanotechnology has been crucial to maintaining a profitable production.

In Ecuador very little effort has been invested in the inclusion of nanotechnology in the oil industry. There is a dire need to incorporate nanotechnological solutions in the industry as well as to tighten relations between the industry and existing research groups. The creation of a petroleum and energy institute to monitor these efforts would be highly desirable.

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