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Cover photo: Phu My Fertilizer Plant. Photo: PVFCCo



FOCUS

OIL AND GAS CO-OPERATION with Kazakhstan and Algeria to be boosted

On the occasion of the signing ceremony of the Free Trade Agreement between Vietnam and the Eurasian Economic Union (EAEU) in Kazakhstan and his official visit to Algeria from 29 May to 2 June 2015, Prime Minister Nguyen Tan Dung held talks with senior leaders of Kazakhstan and Algeria on many important issues to promote co-operation in the mainstay fields of bilateral relations, including the field of oil and gas. The leaders of Kazakhstan and Algeria pledged to create favourable conditions for the Vietnam Oil and Gas Group (Petrovietnam) to boost investment in exploration and production of oil and gas, and increase their participation in the provision of petroleum services to the projects.



Leaders of Petrovietnam and KazAlas welcomed Prime Minister Nguyen Tan Dung. Photo: VNA

In the framework of the official signing ceremony of the Free Trade Agreement between Vietnam and the Eurasian Economic Union, Prime Minister Nguyen Tan Dung held talks with Kazakh President Nursultan Nazarbayev on 29 May 2015. The two leaders emphasised the signing of the Free Trade Agreement is a breakthrough in promoting economic co-operation and trade between Vietnam and the five member states of the Union in general, as well as with Kazakhstan in particular. Prime Minister Nguyen Tan Dung and President Nursultan Nazarbayev agreed that the two sides should continue to maintain and strengthen co-operation in key sectors, including oil and gas. Both sides expressed support for the Vietnam Oil and Gas Group (Petrovietnam) and the Kazakhstan National Oil and Gas Company (KazMunaiGas) to join the oil and gas exploration and production projects on each other's territory.

On 30 May 2015, Prime Minister Nguyen Tan Dung and the senior officials of the Government of Vietnam witnessed the signing of a co-operation agreement on oil and gas exploration, production and service provision between Petrovietnam and KazTransGas.

Accordingly, Kazakhstan will create favourable conditions for Petrovietnam to co-operate with KazTransGas in exploration and production at several blocks with oil and gas potential. At the same time, Petrovietnam may participate in the provision of drilling services, gas exploration and transportation for the projects.

In recent years, Vietnam - Kazakhstan oil and gas co-operation has developed positively. In April 2012, Petrovietnam and KazMunaiGas signed an additional agreement to extend the "strategic co-operation agreement between Petrovietnam and KazMunaiGas" and initially achieved a specific co-operation project via the Agreement on joint investigation at Usturt Block near the border with Uzbekistan where Petrovietnam has been implementing the Kosov Block contract. In September 2012, Petrovietnam and KazMunaiGas signed a Memorandum of Understanding on the negotiations for conclusion of an oil and gas contract for Usturt Block area. In addition to the projects in Vietnam and Kazakhstan, the two sides discussed the possibility to participate in some projects in third countries. Chairman of Petrovietnam Board of Directors Nguyen Xuan Son emphasised that

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FOCUS

CO-OPERATION IN THE FIELD OF OIL AND GAS with Russia to be strengthened

Petrovietnam President and CEO Nguyen Quoc Khanh attended the 19th Saint Petersburg International Economic Forum (SPIEF 2015) from 18 - 20 June 2015. In the framework of this important event, Petrovietnam and Gazprom signed an agreement on major terms and conditions for implementing the Nagaiorskoye and Severo-Purkovskoye fields development projects, and meetings and working sessions with major partners took place, contributing to strengthening and promoting co-operation between Petrovietnam and Russia's oil and gas companies.



Gazprom and Petrovietnam signed an agreement on major terms and conditions for implementing the Nagaiorskoye and Severo-Purkovskoye fields development projects. Photo: PVO

SPIEF is an annual economic forum which is considered Russia's Davos, which gathers many government leaders and executives of leading enterprises around the world. With over 6,000 delegates from more than 100 countries, the event is evaluated as positively contributing to the building of macro-economic development models and promoting comprehensive co-operation between Russian companies and foreign partners.

In the framework of this important event, Petrovietnam's delegation joined the discussions on oil and gas, energy and the special events of SPIEF 2015 such as the meeting of International Energy Companies' leaders and the meeting of Russian President Vladimir Putin with leaders of foreign companies.

In the framework of the Forum, Petrovietnam's President and CEO Nguyen Quoc Khanh and Gazprom's Chairman of the Management Committee Alexey Miller signed an agreement on major terms and conditions for implementing the projects to develop the Nagaiorskoye (Drenburg region) and Severo-Purkovskoye fields (Yamal-Nenets autonomous area). Mr Nguyen Quoc Khanh said "This agreement is a very important step to promote the implementation of the

Nagaiorskoye and Severo-Purkovskoye fields projects in Russia and a testament to the strategic partnership between Petrovietnam and Gazprom".

The two leaders also gave positive assessment of the implementation of the first-stage projects in the territory of Vietnam (Blocks 112, 129-132, 05-2, 05-3, etc) and of Russian Federation (Nagaiorskoye and Severo-Purkovskoye fields). In addition, the two sides committed to make efforts to promote co-operation in petrochemical and refining as well as producing gas for motor fuel, agreed to actively study and consider the possibility for co-operation in the field of importing LNG and the electricity market in Vietnam.

During the time participating in SPIEF 2015, the Petrovietnam leader also had meetings and bilateral working sessions with the senior leaders of Russia's major oil and gas corporations and international oil and gas companies.

At the meeting with Zarubezhneft, Petrovietnam's President & CEO Nguyen Quoc Khanh and Zarubezhneft's General Director Sergey Kudryashov, acknowledged the efforts of Vietsovpetro and Rusvietpetro in the production and business activities, which have been negatively affected by the decline of world oil prices and

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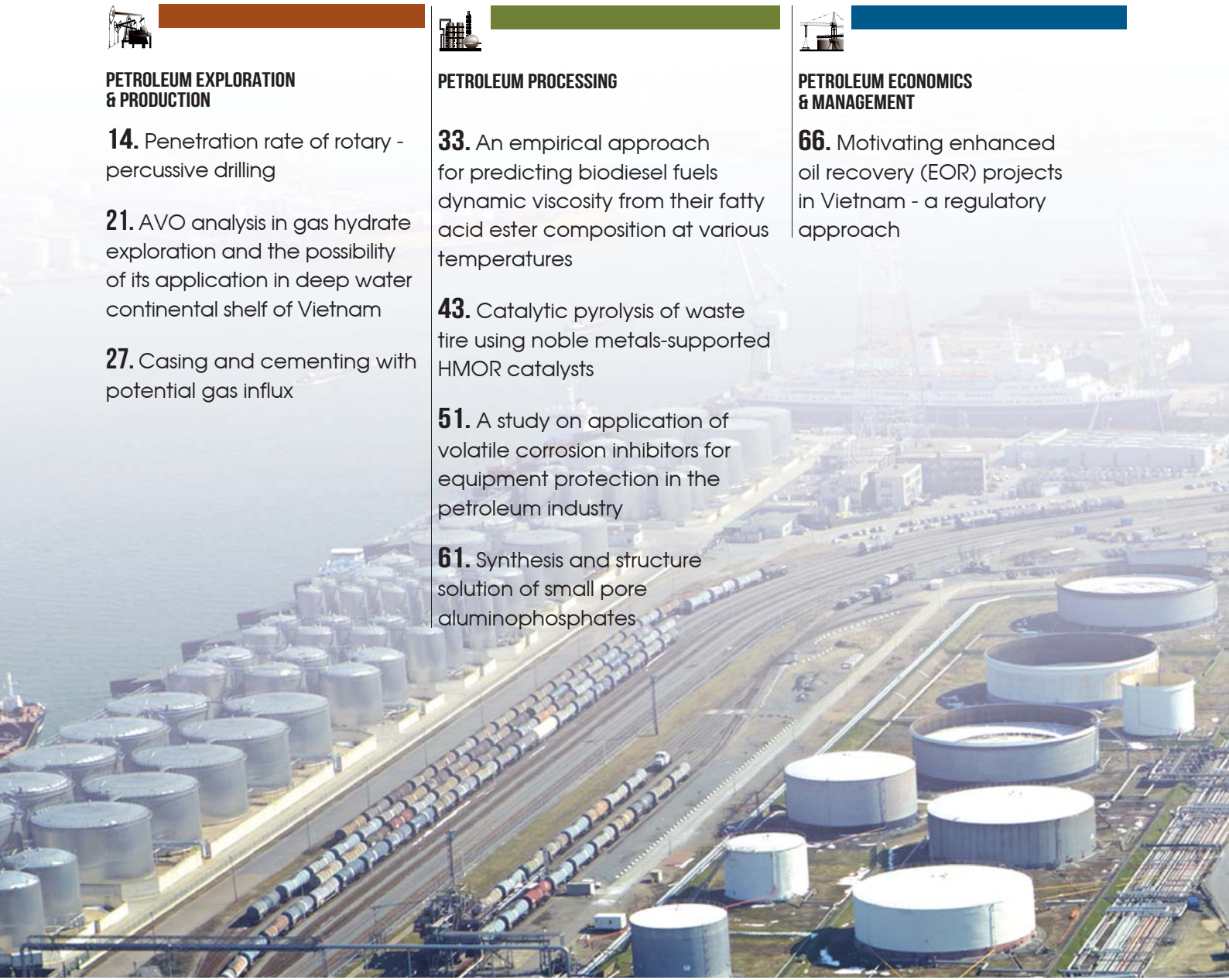
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PETROLEUM EXPLORATION & PRODUCTION

PENETRATION RATE OF ROTARY - PERCUSSIVE DRILLING

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Summary

This paper presents a study to improve hard rock drilling performance through emerging technologies. An effort to test called 'tricone roller cone drill bits' and drilling hammer or percussive drilling (with rotary) as one emerging technology that shows promising to increase penetration rates in hard rock formation. First, six hard rock types were collected and the mechanical properties of the rocks were determined in the laboratory. Then, a program of investigation of tricone and rotary percussive drilling has been conducted on the six hard rocks at simulated depths. The results show that the rate of penetration has been improved by a factor of two or three in certain hard rock formation with drilling hammer compared with tricone. The penetration rates were correlated with the rock properties. The reaction tensile strength shows a strong correlation with the penetration rate. The elastic modulus, the uniaxial compressive and triaxial compressive values exhibit a fairly good correlation with the penetration rate. Future work includes the single cutter impact tests to understand the rock knowledge process and cutting removal under high borehole pressure conditions in order to improve bit design and technology based on the knowledge gained from this test programme.

Key words: Penetration rate, ROP, rotary drilling, percussive drilling.

1. Introduction

It has been widely recognised that percussive drilling has a potential to provide faster penetration than conventional rotary drilling (7.5 times faster with the same rotation and WOB) or diamond drilling, especially in some hard rock formations such as granite, sandstone, limestone, and dolomite, etc. Besides a large increase in the rate of penetration (ROP), percussive drilling improves hole geometry, reduces drilling stress, generates better and larger cuttings, and lowers the cost per foot substantially [2]. At high borehole pressures, the pseudo-plastic behavior of cuttings can appear and that will limit the ROP [25]. An economical comparison between hammer drilling and other techniques in this case is necessary to decide the technique which will be used in the field.

In this study, the penetration rates of the rotary percussive drilling were measured under simulated borehole conditions. First, the paper presents the rock

mechanical properties and drilling tests setup. Then, the result of penetration rate in rotary percussive drilling will be presented and compared with the tricone's result. Finally, the penetration rates will correlate with the rock properties for the development of reliable equations in order to allow engineers to predict the penetration rate from rock characteristics.

2. Rock property determination

First, hard rock formations that are probably found at very deep reservoir were collected. Six rock types were chosen and tested: Calcaire150, Anhydrite220, Gypse70, Brèche280, Sandstone210, Gabbro280. Uniaxial compression tests, Brazilian tensile strength test, and triaxial compression tests were firstly selected as the basis for determining the rock mechanical properties. Their mechanical properties include Young's modulus (E), Poisson's ratio (ν), unconfined strength (UCS), and confining pressure strength (TCS).

Table 1. Rock properties

No	Rock	Pu (MPa)	UCS 1 (MPa)	Pu (MPa)	UCS 2 (MPa)	Pu (MPa)	TCS 1 (MPa)	Pu (MPa)	TCS 2 (MPa)
1	Calcaire150	0	150	0	145	5	153	10	166
2	Anhydrite220	0	164	0	278	5	326	10	364
3	Gypse70	0	74	0	69	5	130	10	167
4	Brèche280	0	284	0	275	5	402	10	422
5	Sandstone210	0	225	0	205	5	294	10	296
6	Gabbro280	0	280	0	285	5	350	10	471

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Leaders of Petrovietnam and KazTransGas received Prime Minister Nguyen Tan Dung. Photo: VNA

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Prime Minister Nguyen Tan Dung witnessed the signing of co-operation agreement between Petrovietnam and KazTransGas. Photo: VNA

some countries in Central Asia, especially Kazakhstan, are regarded as the key areas for Petrovietnam's overseas investment.

Prime Minister Nguyen Tan Dung said Vietnam and Kazakhstan are continuing to develop the strength and potential of the two countries to promote multifaceted co-operation in depth and efficiency. Highly appreciating the results of co-operation between Petrovietnam and KazMunaiGas, the Prime Minister hoped the two corporations will further co-operation in the exploration and production of oil and gas to match the potential of each corporation and the expectation of the two countries' senior leaders. Besides oil and gas exploration and production activities, he also urged KazMunaiGas and Petrovietnam to promote joint projects and programmes providing technical services for these activities. The two sides could also consider co-operation in projects in Kazakhstan, Vietnam or in third countries. The Government and the State of Vietnam will create the most favourable conditions for Kazakh businesses to invest in Vietnam, Prime Minister Dung pledged.

Commercial oil production to start in 3rd quarter of 2015

On 1 June 2015, Prime Minister Nguyen Tan Dung held talks with his Algerian counterpart Abdelmalek Sellal in which the two leaders discussed measures to develop

a more suitable and effective model for co-operation, striving to increase bilateral trade from USD 250 million to USD 1 billion in the near future.

In the oil and gas sector, Algerian Prime Minister Abdelmalek Sellal said Algeria welcomes Vietnamese businesses, both in the fields of exploration, production and provision of petroleum services. In addition to joint venture projects between Petrovietnam and Sonatrach, Algeria is ready to grant licences for Petrovietnam to expand existing projects as well as to invest in projects in new locations.

On 2 June 2015, Prime Minister Nguyen Tan Dung and Algerian Prime Minister Abdelmalek Sellal witnessed the signing ceremony of the agreement on co-operation between Petrovietnam and Sonatrach. Accordingly, Sonatrach would facilitate Petrovietnam's exploration and production in the area adjacent to Bir Seba field and provide oil and gas services to the Vietnamese partner. Concurrently, the two sides would strengthen training activities and exchange of officials and technical experts.

Leaders of Petrovietnam informed that Vietnam and Algeria signed the oil and gas exploration and production contract for Blocks 433a and 416b on 10 July 2002. Petrovietnam discovered commercial oil reserves on 28 April 2008, and then carried out the development project.



Prime Minister Nguyen Tan Dung and Algerian Prime Minister Abdelmalek Sellal witnessed the signing of co-operation agreement between Petrovietnam and Sonatrach. Photo: VNA

On 10 February 2009, an agreement on establishment of the Groupement Bir Seba joint venture company to develop Bir Seba field under the Block 433a and Block 416b contract in Touggourt, the Sahara, Algeria was signed by Petrovietnam Exploration and Production Corporation - PVEP (40%), PTTEP Algeria Ltd. (35%) and Sonatrach (25%).

The parties involved in the project set the target to produce commercial oil in the 3rd quarter of 2015, realising the commercial viability of the project after 12 years of implementation. After that, the project is expected to go into stable operation with 20,000 barrels/day and will reach peak production of 40,000 barrels/day in the 2018 - 2021 period. With the participation rate of 40% in the Joint Venture, Vietnam will collect about USD 100 - 150 million/year from oil sales and will recoup its investment in this project after 6 years. This project is not only of economic importance but also the first overseas project where Petrovietnam acts as operator, and uses the drilling services of Petrovietnam Drilling and Well Services Corporation (PV Drilling).

Prime Minister Nguyen Tan Dung noted that the project's success is the result of an effective long-term co-operation, which contributes to the promotion of the

traditional friendship and excellent co-operation between Vietnam and Algeria, and paves the way for both parties to expand co-operation in new fields. He hoped that the Algerian Government would create further conditions for Petrovietnam and Sonatrach to strengthen oil and gas co-operation

Earlier, Prime Minister Nguyen Tan Dung and the Vietnamese high-ranking delegates had paid a visit to Petrovietnam's and PVEP's officers and employees who are implementing the oil production project in the Sahara. The Prime Minister appreciated the great efforts and bravery of petroleum workers in coping with the difficulties and hardships in the harsh desert, showing their determination to find oil to enrich the country. He asked Petrovietnam and PVEP to draw lessons and experiences in order to better perform other overseas projects in the future and to ensure the safety and security for officers and engineers directly working at the oil field.

Petrovietnam Chairman Nguyen Xuan Son promised to strictly follow the Prime Minister's instruction and to make the best efforts for commercial oil to be produced in the 3rd quarter of 2015.

Nguyen Hoang

PETROVIETNAM COMPLETES acquisition of Chevron's assets in Vietnam

The Vietnam Oil and Gas Group (Petrovietnam) acquires two oil and gas exploration and production companies and a pipeline company owned by Chevron in Vietnam. Petrovietnam's completion of the acquisition of Chevron's assets in Vietnam will facilitate the acceleration of field development and the implementation of the component projects in order to make gas more quickly available to serve the development needs of the national economy.



Contract signing ceremony between Petrovietnam and Chevron. Photo: PVN

On 17 June 2015, Petrovietnam took over all the stakes of Chevron's companies with assets in Vietnam and operatorship at Block B, Block 48/95 and Block 52/97 of Vietnam's continental shelf. Chevron Vietnam (Block B) Ltd. has a 42.38% operating interest in a production-sharing contract (PSC) for Blocks B and 48/95, while Chevron Vietnam (Block 52) Ltd. holds a 43.40% operating interest in a PSC that covers Block 52/97 in Vietnam's continental shelf. Meanwhile, Chevron Southwest Vietnam Pipeline Co. Ltd. holds a 28.7% working interest in a pipeline project that would deliver natural gas to utility companies in the South of Vietnam.

Since 1996, intensive exploration in Blocks B, 48/95 and 52/97 offshore Vietnam has been conducted within the area covered by the PSCs. The contract area covers 3,200km² of the Malay - Tho Chu basin, southwest of Vietnam, with water depths ranging from 60m to 80m. As a result, important gas discoveries have been made that were declared commercial in 2002 and 2008 with a joint development agreement reached in 2007 to put the discoveries into development and production. Estimates reviewed and approved by the competent Vietnamese authorities include initially in-place gross gas at 170 billion m³ of gas, 4 million m³ of condensate (25.25 million barrels of condensate) and recoverable gas reserves (2P categories) at 107 billion m³ of gas, 2 million m³ of condensate (12.65 million barrels of condensate). These gas reserves will increase when additional exploration is conducted in the remaining area of the two PSCs.

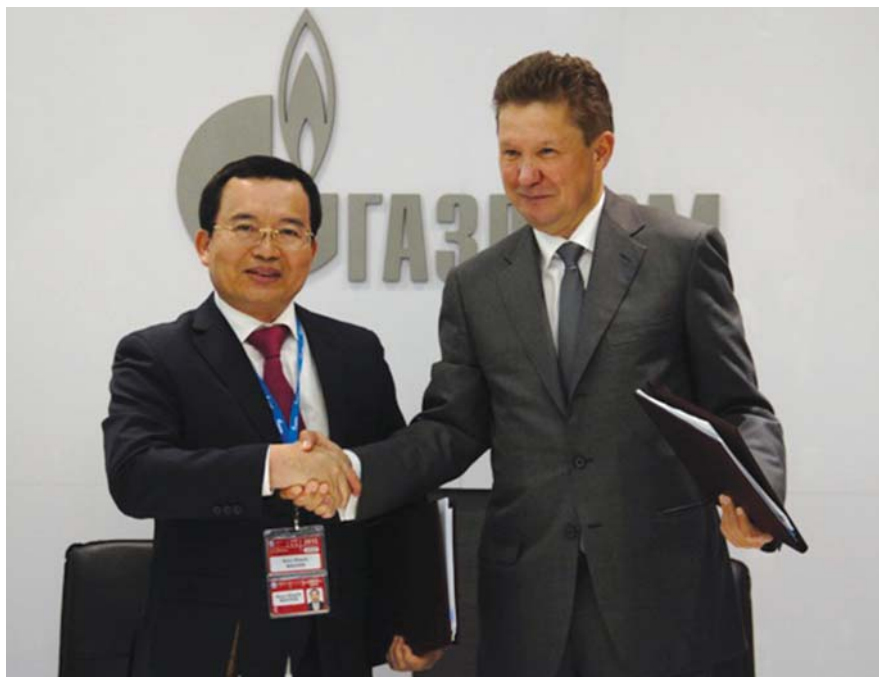
The Block B - O Mon project is designed to transport gas from Blocks B, 48/95 and 52/97 in the southwest waters of Vietnam to the O Mon power plant hub in Kien Giang province and to supplement gas supply to the Ca Mau Gas - Power - Fertilizer Complex. Total investment for field development and construction of the gas - power project utilising gas from Blocks B, 48/95 and 52/97 is estimated to exceed USD 10 billion and respond to the need to increase the generation capacity beyond 4,000MW. The series of projects will strongly contribute to the development of the Southwest region in Vietnam.

Mr. Nguyen Xuan Son, Chairman of the Board of Directors of Petrovietnam, stated: "The Block B gas project is Petrovietnam's main oil and gas project. The project is of major significance, contributing to ensuring the country's energy security and promoting the socio-economic development of the region. The construction and operation of the series of projects to produce, transport, and process gas and the construction and operation of power plants will stimulate the socio-economic development of the western provinces of the Southern region, contribute to the protection of the environment by using clean fuel, stabilise national power supply, and create an opportunity to link up with the gas transportation networks of countries in the region. Petrovietnam's completion of the acquisition of Chevron's assets in Vietnam will facilitate the acceleration of field development and the implementation of the component projects in order to make gas more quickly available to serve the development needs of the national economy."

Quang Hung

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At the meeting with Zarubezhneft, Petrovietnam's President & CEO Nguyen Quoc Khanh and Zarubezhneft's General Director Sergey Kudryashov acknowledged the efforts of Vietsovpetro and Rusvietpetro in the production and business activities, which have been negatively affected by the decline of world's oil prices and

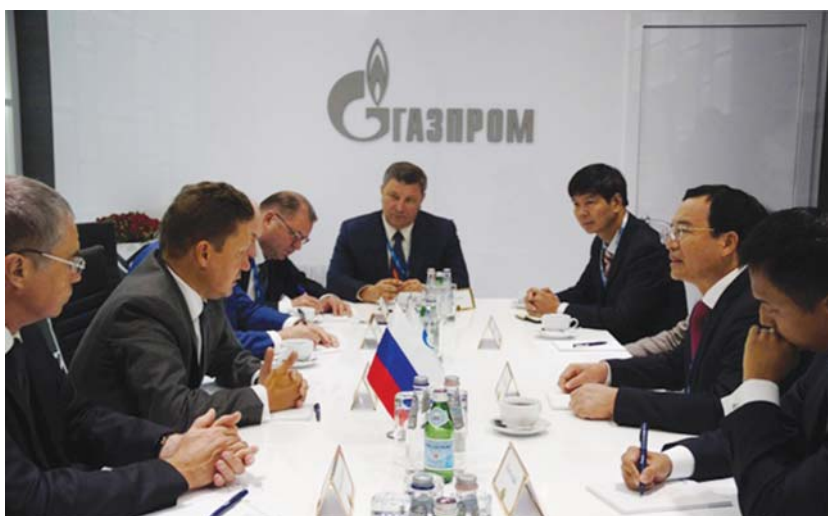
agreed to facilitate the further stable development of the joint ventures. In particular, the Petrovietnam's leader suggested that Zarubezhneft actively support and promote the extension of incentives for Rusvietpetro as soon as possible.

Petrovietnam's President & CEO Nguyen Quoc Khanh had a meeting with Rosneft leaders. He thanked Rosneft for introducing new investment opportunities in Russia and announced that Petrovietnam was conducting quick assessment of the above opportunities. Both sides discussed the prospects for expanding co-operation at Block 15-01/15 on the continental shelf of Vietnam and co-operation in the oil and gas services and trading (especially bunkering services).

At the Forum, Petrovietnam's President & CEO met with Socar's President Rovnag Ibrahim Abdullayev. The two sides agreed to further promote the implementation of the co-operation agreement in the Absheron field development project in the Caspian sea, and other co-operation projects of both sides' concern in Azerbaijan, Vietnam and third countries; actively prepare the contents of projects/opportunities for bilateral co-operation in the fields of oil and gas exploration and production, including provision of petroleum technical services, materials and manpower for the oil and gas industry.

At the same time, Petrovietnam's leaders also had meetings with PDVSA's President Eulogio del Pino to exchange views on the implementation of Junin 2 project as well as new investment opportunities in Venezuela; and with ONGC Videsh Ltd. (OVL)'s Managing Director Narendra Kumar Verma to discuss co-operation situation in Blocks 06-1 and 128 and continued deployment of new co-operation opportunities in Vietnam and India.

Ha Van



Mr. Nguyen Quoc Khanh, President & CEO of Petrovietnam, and Mr. Alexey Miller, Chairman of the Management Committee of Gazprom, committed to make efforts to promote co-operation. Photo: PVN



Petrovietnam's delegation at the meeting with Rosneft's leaders. Photo: PVN



Petrovietnam's leaders and PDVSA's President Eulogio del Pino. Photo: PVN



PETROVIETNAM TO DEVELOP SYNCHRONOUSLY AND SUSTAINABLY

After 40 years of establishment and development, the Vietnam National Oil and Gas Corporation has grown into a leading economic group in Vietnam, contributing to the assurance of national energy security and playing an important role in national industrialisation and modernisation. Petrovietnam has developed a complete oil and gas industry which covers exploration, production, transportation, processing, storage, distribution, import and export services. During the 2016 - 2020 period, Petrovietnam will focus on developing synchronously and sustainably into a corporation with sound financial, scientific and technological strength and high competitiveness.

With the mission "Energy for the country's development", Petrovietnam is focusing on improving its competitiveness, being pro-active in international integration, building itself into a corporation with sound financial, scientific and technological resources, and contributing to ensuring energy security for national development. In recent years, Petrovietnam is maintaining high rates of growth (average of 18 - 20%/year), contributing 25 - 30% of the State Budget revenues. In the 2010 - 2015 period, Petrovietnam earned an estimated total revenue of VND 3,675 trillion (USD 180 billion) and contributed to the State Budget VND 880.3 trillion (over USD 40 billion), made 19 new petroleum discoveries, put 29 new fields into operation and recorded a total oil and gas production of over 130 million tons of oil equivalent.

Petrovietnam is now focusing on five main areas: oil and gas exploration and production, gas industry, power generation,



In the first 5 months of 2015, Petrovietnam has kept up a good pace of development and over-fulfilled all its goals. Total oil and gas production reached 12.1 million tons of oil equivalent. Of this figure, crude oil accounted for 7.6 million tons, and gas 4.5 billion m³. Under the yearly plan set by the Government for 2015, Petrovietnam will produce 26.6 million tons of oil equivalent (16.8 million tons of crude oil and 9.8 billion m³ of gas); produce 18.5 billion kWh of electricity, 1.525 million tons of urea, and 5.55 million tons of petroleum products.

oil and gas processing, and high-quality petroleum services, of which exploration and production is the core area.

With a view to increasing oil and gas reserves and discovering new fields to meet the domestic demand and export, Petrovietnam has been effectively and deploying and implementing exploration and production activities both at home and abroad, making important petroleum discoveries, quickly bringing the discovered fields into production, and applying state-of-the-art technologies to increase production as well as oil and gas recovery rate, and protect the environment and natural resources.

Petrovietnam has been carrying out effective exploration and production of oil and gas with 65 petroleum contracts at home and 17 projects in 12 countries in the world. Petrovietnam aims to create the most favourable conditions for foreign contractors to carry out their petroleum activities in Vietnam, and pursues its strategy to expand overseas investment on the principle of ensuring cost effectiveness, concentrating on the key areas and high petroleum potential regions.

Besides, Petrovietnam is actively accelerating the progress of refinery, petrochemical and bio-fuel projects while at the same time studying the possibility of expanding and upgrading its existing plants to bring added value to petroleum resources in order to meet the domestic demand for fuel, petrochemicals and petrochemical materials. Petrovietnam has also implemented many mega-gas projects in order to supply gas for large consumers such as power plants and industrial plants using low-pressure gas and meet the gas demand of the chemical and fertiliser industries, transportation and household consumption...

The Group is investing strongly into power generation and has quickly become the second largest power producer in Vietnam, delivering more than 80 billion kWh accumulatively to the national power grid. Petroleum services have been greatly expanded, recording high growth rates (average 12.5%/year), representing a large proportion (over 30%) in the total revenues of Petrovietnam and step by step reaching out to foreign markets.

During the 2015 - 2020 period, Petrovietnam will focus on developing synchronously and sustainably into a corporation with sound financial, scientific and technological strength and high competitiveness. The Group has set the goal to increase reserves by 33 - 40 million tons of oil equivalent/year and produce 24 - 34 million tons of oil equivalent/year. Petrovietnam will continue to strictly control the progress of exploration, field development and production projects both at home and abroad, ensuring the fulfilment of plans to increase oil and gas reserves and production. At the same time, Petrovietnam will focus on enterprise restructuring, research and application of scientific and technological achievements, investment in new technologies to improve production and business efficiency, increase the added value of products in the value chain of petroleum products.

Ngoc Phuong

Construction starts for Phu Quoc petroleum service port and a bonded fuel warehouse

On 28 June 2015, Politburo member Le Hong Anh attended the launching ceremony of the construction of Phu Quoc petroleum service port and a bonded fuel warehouse in Kien Giang province. These are two important projects to be invested in and constructed by the Vietnam National Petroleum Group.



Mr. Nguyen Thanh Nghi, Deputy Secretary of the Party Committee and Vice Chairman of the People's Committee of Kien Giang province, highlighted the importance of two projects. Photo: PVN

The launch of the construction for the petroleum service port and the bonded fuel warehouse on Phu Quoc island is the first step in the development of gas fields in Blocks B, 48/95 and 52/97 (Southwest gas project), off the continental shelf southwest of Vietnam. This is a strong step of Petrovietnam after officially acquiring the equity participation of Chevron (USA) and becoming the operator of this petroleum contract, along with other partners: MOECO (Japan), Petrovietnam Exploration Production Corporation (PVEP) and PTTEP (Thailand).

Phu Quoc petroleum service port is built on 116.5ha of land and 60ha of sea, with investment from the Petrovietnam Technical Services Corporation (PTSC). Total investment of the project is about VND 4.2 trillion, divided into three stages, of which the first stage's investment is around VND 1 trillion. Once completed and put into operation, the project will facilitate the development of the gas fields in Blocks B, 48/95 and 52/97 as well as the oil and gas fields in the region, and provide cargo services for the construction and socio-economic development of Phu Quoc island district in particular and the region in general.

The bonded fuel warehouse project on Phu Quoc island to be invested by Petrovietnam Oil Corporation (PV

OIL) will be divided into two stages. In the first stage, PV OIL will invest VND 950 billion to build warehouses with total storage capacity of 70,000m³, the buoys for receiving vessels up to 80,000DWT and the port system which can receive ships of up to 10,000DWT. In the second stage, PV OIL will invest VND 450 billion to expand the storage capacity by 50,000m³.

The project would help PV OIL take advantage of the location to develop its bonded storage business. Domestic and foreign petroleum businesses could rent the warehouse to store products while waiting to transport them to third countries, including the ASEAN markets and other countries in the region. Also, the project will help to improve the capacity to store, transfer and distribute to dominate the domestic market and increase the market share of PV OIL in Phu Quoc island district, Kien Giang province and the neighbouring provinces of the southwest region.

Block B is Petrovietnam's main oil and gas project of important significance, which will contribute to ensuring the national energy security and promoting the socio-economic development of the southwest region. The process of construction and operation of the series of projects to produce, transport and process gas as well as construction and operation of power plants will strongly



Politburo member Le Hong Anh and delegates attended the launching ceremony of the construction of Phu Quoc petroleum service port and a bonded fuel warehouse. Photo: PVN

boost the socio-economic development of the southwest region, contribute to environmental protection by using clean fuels, stabilise the national power supply, and create the opportunity for linking up with the gas transportation network of countries in the region.

Mr. Nguyen Thanh Nghi, Deputy Secretary of the Party Committee and Vice Chairman of the People's Committee of Kien Giang province, said the two projects would not only improve the efficiency of the series of Block B gas projects, but also contribute to the socio-economic development of Phu Quoc island district, Kien Giang province in particular and the southwest region in general, thus contributing to ensuring the national energy security as well as promoting the socio-economic development of the country. He said the provincial authority would create favourable conditions for the projects to be safely and efficiently implemented.

Petrovietnam's Chairman Nguyen Xuan Son said the petroleum service port and the bonded fuel

warehouse on Phu Quoc island are two key pioneering projects which would assist in the development of southwest gas projects. To meet the drilling progress of the southwest gas projects, these projects must be completed and ready for operation in the second quarter of 2017.

Therefore, Mr. Nguyen Xuan Son asked PTSC and PV OIL to monitor and follow the project progress as well as to remove all difficulties and obstacles to complete the projects according to the planned schedule. The leaders of Petrovietnam hoped to continue receiving support from the Government, the ministries, Kien Giang province and Phu Quoc island district to ensure that these works in particular and the southwest gas development projects in general would be successfully implemented and bring good impacts on the socio-economic development of the province of Kien Giang and the Southwest region.

Nguyen Ngoc

PENETRATION RATE OF ROTARY - PERCUSSIVE DRILLING

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Summary

This paper presents a study to improve hard rock drilling performance through emerging technologies. An effort to test called 'tricone roller cone drill bits' and drilling hammer or percussive drilling (with rotary) as one emerging technology that shows promising to increase penetration rates in hard rock formation. First, six hard rock types were collected and the mechanical properties of the rocks were determined in the laboratory. Then, a program of investigation of tricone and rotary-percussive drilling has been conducted on the six hard rocks at simulated depth. The results shown that the rate of penetration has been improved by a factor of two or three in certain hard rock formation with drilling hammer (compared with tricone). Yet, the penetration rates were correlated with the rock properties. The Brazilian tensile strength shows a strong correlation with the penetration rate. The elastic modulus, the uniaxial compressive and triaxial compressive values exhibit a fairly good correlation with the penetration rate. Future work includes the single cutter impact tests to understand the rock breakage process and cuttings removal under high borehole pressure conditions in order to improve bit design and technology based on the knowledge gained from this test programme.

Key words: Penetration rate, ROP, rotary drilling, percussive drilling.

1. Introduction

It has been widely recognised that percussion drilling has a potential to provide faster penetration than conventional rotary drilling (7.3 times faster with the same rotation and WOB) or diamond drilling, especially in some hard rock formations such as granite, sandstone, limestone, and dolomite, etc. Besides a large increase in the rate of penetration (ROP), percussion drilling improves hole geometry, reduces drillstring stress, generates better and larger cuttings, and lowers the cost per foot substantially [2]. At high borehole pressures, the pseudo-plastic behaviour of cuttings can appear and that will limit the ROP [25]. An economical comparison between hammer drilling and other techniques in this case is necessary to decide the technique which will be used in the field.

In this study, the penetration rates of the rotary-percussive drilling were measured under simulated borehole conditions. First, the paper presents the rock

mechanical properties and drilling tests setup. Then, the result of penetration rate in rotary-percussive drilling will be presented and compared with the tricone's result. Finally, the penetration rates will correlate with the rock properties for the development of reliable equations in order to allow engineers to predict the penetration rate from rock characteristics.

2. Rock property determination

First, hard rock formations that are probably found at very deep reservoir were collected. Six rock types were chosen and tested: *Calcaire150*, *Anhydrite220*, *Granite70*, *Basalt280*, *Sandstone210*, *Gabbro280*. Uniaxial compression tests, Brazilian tensile strength test, and triaxial compression tests were firstly selected as the basis for determining the rock mechanical properties. Their mechanical properties include Young's modulus (E), Poisson's ratio (ν), unconfined strength (UCS), and confining pressure strength (TCS).

Table 1. Rock properties

No	Rock	P _{c1} (MPa)	UCS 1 (MPa)	P _{c2} (MPa)	UCS 2 (MPa)	P _{c1} (MPa)	TCS 1 (MPa)	P _{c2} (MPa)	TCS 2 (MPa)
1	Calcaire150	0	150	0	145	5	153	10	166
2	Anhydrite220	0	164	0	278	5	326	10	304
3	Granite70	0	74	0	69	5	130	10	167
4	Basalt280	0	284	0	275	5	402	10	422
5	Sandstone210	0	225	0	205	5	294	10	296
6	Gabbro280	0	280	0	285	5	350	10	471

Table 2. Rock properties and ROP

No	Rocks	UCS (MPa)	TCS (MPa)	σ_T (MPa)	ROP (m/h)	Error bar ROP	Error bar σ_T
1	Calcaire150	147.5	166	9.10	12.5	0.4	0
2	Anhydrite220	221	304	9.03	11.9	0.4	0.24
3	Granite70	71.5	167	2.06	12.0	2.0	0.28
4	Basalt280	279.5	422	14.16	7.3	0.3	3.52
5	Sandstone210	215	296	17.80	6.5	0.5	1.26
6	Gabbro280	282.5	471	18.90	6.0	1.0	2.20

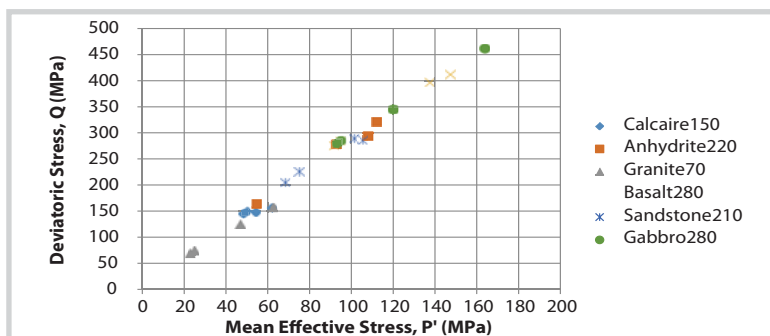


Figure 1. Effect of confining on rock strength

The deformation rate was controlled at 120mm/m. The cylindrical samples used in the uniaxial compression tests and triaxial compression tests have a diameter of 50mm and a length to diameter ratio of 2. The Brazilian tensile strength tests were conducted on core samples having a diameter of 25mm and a height to diameter ratio of 0.5. All tests were realised in dry condition; i.e. no pore pressure and at room temperature.

The rock properties were shown in Tables 1 and 2.

Figure 1 shows the failure envelope for six rocks; the Gabbro280 and Basalt280 are considerably stronger than other rocks. The Granite70 is the weakest. This figure and the fracture mode of samples show that six rocks have the brittle behaviour at confining pressures between 0MPa and 10MPa.

3. Drilling tests - Experimental setup

Drilling tests were performed on the ARMINES drilling bench in PAU, France as shown in (Figure 2). This allows full scale drill bit tests by simulating deep hole drilling conditions, up to 5km. The rock sample is loaded inside the pressure vessel, with constant overburden pressure up to 70MPa, confining pressure up to 50MPa, and pore pressure up to 50MPa. For the test here confining pressure was limited to 10MPa. Then the Weight on Bit (WOB) was varied from 0 to 18 tons, the rotary speed (RPM) from 42 to 87rev/min. The WOB, the RPM, injection pressure, pressure drop, penetration rate and the depth of tool were recorded. All data for each test were collected on a computer.

Drill bits were provided by Baker Hughes (STX50) and by Drillstar. The sample has the height of 350mm and the diameter of 240mm. A typical sample before and after test for six rocks tested are shown in



Figure 2. ARMINES drilling bench



Figure 3. Typical sample in hammer test (before test)



Figure 4. Typical sample in hammer test (after test)

Figure 3. These tests were run using water ($1,000\text{kg/m}^3$) as a drilling mud.

4. Drilling tests - Results

4.1. Well profile

Figures 5 and 6 show the hole in sample after drilling test, respectively for rotary drilling and rotary-percussive drilling. It can be seen that the profile obtained by the rotary-percussive drilling test is smoother than tricone test.

4.2. Performance

Figure 7 shows the comparison of performance between rotary-percussive drilling test and rotary drilling test of WOB 10T and 15T. The horizontal axe compounds the rock with the increase of their strength at 10MPa of confining.

In general, it is found that the performance does not follow the hardness of the rock. The detail of this result will be presented in the next part. It is also noted that the performances of rotary-percussive drilling test are always higher than those of tricone test of WOB 10T. Yet, with some of hard rocks (Basalt280, Gabbro280) significant difference of the performances in the tests is noted. In these cases, the performances of rotary-percussive drilling are even three times higher than those of the tricone 10T. Comparing the performance of rotary-percussive drilling test with tricone drilling test of WOB 15T, it is found that:

- Performance is almost two times higher for the hammer in the hardest rocks,
- Performances of rotary-percussive drilling test are substantially equal to those of tricone (except Anhydrite220 and Granite70).

The penetration rate (ROP) for all rocks is given in Table 3. The comparison of ROP to 'tricone roller cone drill bits' shows that percussion drilling results in faster penetration than tricone, especially in hard formations such as Basalt280 (ROP of 7.3m/h), Gabbro280 (ROP of 6m/h) compared to conventional drilling with Basalt280 (ROP of 2.1m/h) and Gabbro280 (ROP of 1.24m/h) at the condition of $\text{RPM} = 87$, borehole pressure of 10MPa, and WOB = 10T.

5. Rock properties affecting the penetration rate of rotary-percussive drilling

5.1. Background of study

The difference between brittle and ductile rock and the relationship of the failure mode to the crater

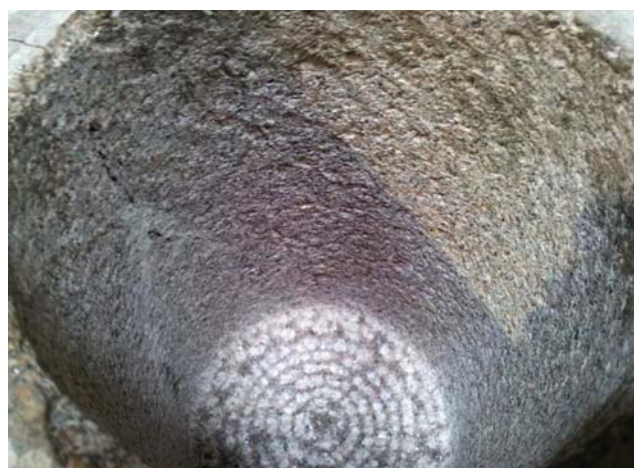


Figure 5. Typical well profile (tricone test)



Figure 6. Typical well profile (hammer test)

Table 3. Penetration rate of rotary-percussive drilling and tricone drilling

No	Rocks	Rotary-percussive	Tricone	
		ROP (m/h)	ROP (WOB10 T) (m/h)	ROP (WOB15 T) (m/h)
1	Calcaire150	12,5	7,74	11
2	Anhydrite220	11,9	6,14	16,84
3	Granite70	12	9,5	17,3
4	Basalt280	7,3	2,1	4,1
5	Sandstone210	6,5	2,82	4,9
6	Gabbro280	6	1,24	3,4

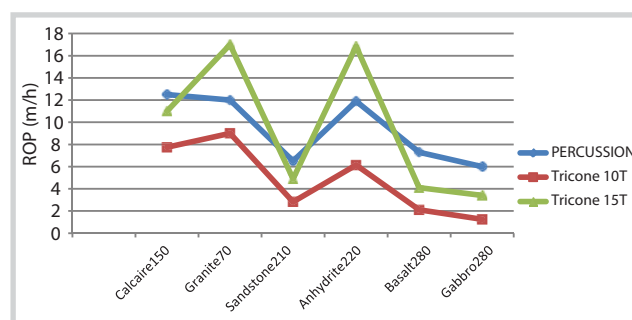


Figure 7. Penetration rate of rotary-percussive drilling and tricone drilling

volume produced by an impacting bit-tooth indentation has been studied by Maurer et al [25]. Often the rock fails in a brittle state but pseudo-plastic behaviour of cuttings on the bottomhole produces the equivalent of a ductile drilling effect. The result is that under comparable conditions, a ductile or pseudo-plastic bit tooth crater is smaller than a brittle crater which translates to a reduction in the drilling ROP [32].

Many researchers have investigated theoretically or experimentally the percussive drilling and correlated the penetration rate of percussive drills with various rock properties [7, 13, 15]. For percussion hammer in air drilling, they concluded that uniaxial compressive strength (UCS), tensile strength, and static Young's modulus correlated well with penetration rates in nine hard, abrasive rocks. However, recently oil wells have been drilled deeper and deeper, which creates a challenge to wellbore stability during drilling and cutting removal becomes more difficult. Yet, under high borehole pressures the rock strengthens and behaves in an apparent ductile manner [6]. So, it is important to know the rock strength and rock behaviour at each borehole pressure. After Winters [32], these strengths correlated closely to the triaxial compression of the rock at a confining pressure that is equal to the effective bottomhole differential pressure. These are accepted methods in the literature to calculate rock confined compressive strength based on rock unconfined compressive strength and pore pressure by: Mohr-Coulomb strength criterion (Liu [19]), Skempton [30] or Rampersad and Hareland [28].

The United States Government carried out two projects (DE-FC26-00NT40918 and DE-FC26-03NT41999) from 2000 to 2005. The objective is to optimise the hammer drilling performance and to advance the fundamental understanding of the physical mechanisms in percussion drilling. They showed that rotary-percussive drilling increases the rate of penetration (ROP) and decreases WOB and this is a cost-saving measure to replace more expensive rotary drilling applications. However at elevated wellbore pressures ($> 1,500$ psi), rate of penetration performance has not yet been optimised. Otherwise, by using numerical simulation they have shown that rock failure happens at three states: compression, tension, and shear loading. Yet, in the case tested ($K = 12,000$ MPa; $G = 7,200$ MPa; $\sigma_T = 1.2$ MPa), about 75% of elements have failed due to excessive tension stress and only 25% of rock elements have failed because of high compressive

loading. But they noted that these numbers depend also on stress state and rock properties (such as modulus, strengths, and friction angle, etc.).

We consider that ROP is a function of bit/cutter load, bit/rock interaction, borehole pressure, and cutter design and the rotary-percussive drilling mechanics is complex. But the understanding of rock fragmentation process by rotary-percussive drilling is really important in order to have the optimum line spacing of the neighbouring button-bits with a button-bit. This optimum line spacing has been proposed by Liu [19] as a function of the drilled rock properties, the diameter and shape of the button-bit, as well as the drilling conditions. This formula was established on the basis of quasi-static analyses.

5.2. Dominant rock properties affecting the penetration rate of rotary-percussive drilling

Literature shows that the drilling process involves a complex interaction of bit/rock, of which the rock mechanics and bit design are foremost. Many researchers try to study the impact energy transmitted into rock by using "Rigid impact" (Dongmin [5]) or stress wave theory (Hustrulid and Fairhurst [14]; Li et al. [17, 18]; Yinghui et al. [33, 34]; Lundberg [21 - 23]; Chiang and Elias [4]), but there are many questions which could not be answered; for example the mechanism of rotary-percussive rock drilling and how can we predict the ROP. Recently, some authors used numerical simulation to describe the rock fragmentation during percussive drilling [3, 8 - 12, 19, 20, 29, 31, 35]. One of their interesting results is to propose the optimum line spacing of button-bit in cutter design. Unfortunately, the dynamic interaction between the hammer and rock was not considered and not accounted into the borehole pressure. However, their results can help us answer the question: what happens in the rock during rotary-percussive drilling?

Although the drilling mechanics are complex, one should be able to consider which rock properties will govern failure, even in this complex dynamic case, and which properties will govern drilling. Thus, most published drilling models utilise grossly simplified assumptions about the bit along with empirical rock strength indicators such as drillability index, specific energy, modulus ratio, uniaxial compression strength, triaxial compression strength, and Brazilian tensile strength, etc. [1, 7, 15, 32].

In this paper, the relationship between penetration rates and the rock properties is presented. All results are shown in Figures 8, 9 and 10. The aim is to investigate and answer the

question: How and which rock properties dominantly affect the penetration of hammer. These tests were conducted at "Centre Géosciences des Mines, Pau, France".

Figure 8 shows the relation between penetrations rates of hammer studied and UCS, Eq. (1).

$$ROP = -0.0283UCS + 15.11 \quad (1)$$

where ROP is the penetration rate (m/h), and UCS is the uniaxial compressive strength.

The linear relationship gives a poor coefficient $R^2 = 0.5632$. However, some empirical models have shown that this linear relationship has a higher coefficient $R^2 = 0.94$ in the case of air drilling [7]. Thus, the uniaxial compressive strength is not performance for the prediction of ROP in petroleum drilling at condition of high borehole pressure. In this case, we can consider that the model utilising a triaxial compressive strength is more logical than the model utilising a uniaxial compressive strength. As presented previously, the triaxial compressive strength is equivalent to the drilling strength of a rock [32]. So the triaxial compressive strength at confining pressure of 10MPa has been determined at the laboratory of Ecole des Mines, Fontainebleau, France. These values used to similar the condition of drilling at 10MPa borehole pressure.

Figure 9 verifies the assumption about the relationship between the rates of penetration, ROP, and the triaxial compressive strength (TCS). It is found that this linear relationship is more improved than the investigation of UCS, by Eq. (2), but the relationship is still poor with a coefficient $R^2 = 0.6635$.

$$ROP = -0.0198TCS + 15.387 \quad (2)$$

where ROP is the penetration rate (m/h), and TCS is the triaxial compressive strength.

From Eq. (2) we can see that the higher TCS will result in the decrease of ROP. One interesting observation is that ROP is similar for the least hard rocks, Calcaire150 and Granite70, and these rocks also have the same TCS (~167MPa). But the result is opposite for harder rocks, like Anhydrite220 or Sandstone210. Their TCS is around of 300MPa, but ROP is very different, 6.5m/h for Sandstone210, and 11.9m/h for Anhydrite220. But we note that Sandstone210 is more ductile than Anhydrite220, as at the fracture, the vertical strain is 1.53% for Condroz, and 1.40% for Anhydrite220, and the radial strain is 0.34% for Sandstone210 and 0.25% for Anhydrite220. All these data were picked in the stress-strain curvature at a confining pressure of 10MPa. That means the brittle/ductile behaviour has an effect on ROP,

more brittle property of rocks will result in more value of ROP. Another result of ROP can be observed for Calcaire150 and Granite70. ROP is similar for these two kinds of rocks. It is noted that they have the same TCS (~166MPa to 167MPa), the strains at the rupture are axial strain of 1.23% and radial strain of 0.48% for Calcaire, and axial strain of 1.28% and radial strain of 0.51% for Granite70. Even a plastic deformation has been observed in Granite70 that can be caused by the deformation of 25% biotite in this rock. However, it should be noted that there was on stress drop on the stress-strain curvature for the triaxial test of 10MPa confining pressure, which was not observed in other test on this rock (uniaxial test with confining pressure of 5MPa). This can be caused by the pre-cracking on the sample during preparation of sample.

For many researchers, the compressive strength is not the only parameter which has the effect on the penetration rate and one of the other parameters is tensile strength ([7 - 9, 24, 27]. They confirmed that this parameter has strong effect on ROP. Yet, our measurement in the laboratory showed that the tensile strength is much lower than the compressive strength (on the order of seventeen for Condroz to one eighty for Amarello) (Table 3). So the rock failure is probably related to excessive tensile stress. By using the numerical modeling for percussion drilling, Han [8, 9] obtained that the bit impact caused 75% of elements failed due to excessive tension stress, and only 25% of the rock elements failed due to excessive critical compression. Our result in Figure 10 showed the significant correlation between the penetration rate and the Brazilian tensile strength value. This linear relationship is Eq. (3), with a high coefficient $R^2 = 0.8001$.

$$ROP = -0.4316\sigma_T + 14.478 \quad (3)$$

where ROP is the penetration rate (m/h), and σ_T is the Brazilian tensile strength (MPa).

We also found here the tendency of ROP evolution to decrease with the increase of σ_T . Other remark for Calcaire150 and Anhydrite220 is that the value of ROP is similar.

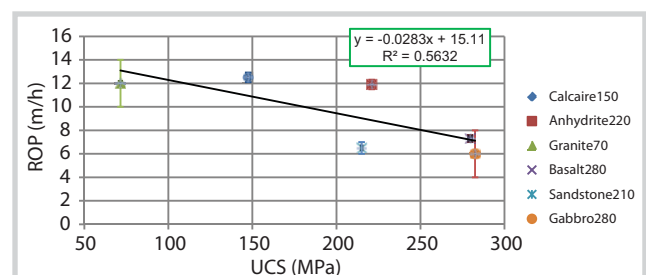


Figure 8. Penetration rate versus UCS

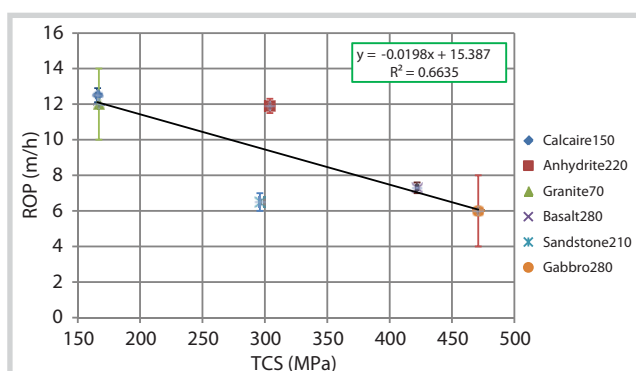


Figure 9. Penetration rate versus TCS

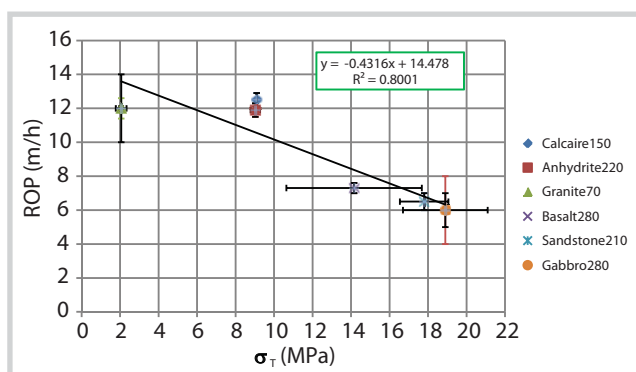


Figure 10. Penetration rate versus σ_T

6. Conclusions

It has been shown that the penetration of rotary-percussive drilling is faster than tricone, especially in hard formations.

Predicting the penetration rate is very important in percussion drilling. One of the important parameters affecting ROP is the rock properties. Among the rock properties adopted in this study, the uniaxial compressive strength, the triaxial compressive strength, and the Brazilian tensile strength are found as the rock properties affecting the penetration rate of rotary-percussive drilling. However, the most significant rock properties affecting the penetration rate is the Brazilian tensile strength. This can be explained that the tensile strength is much lower than the compressive strength so the criteria of tensile strength is likely occur under bit impact. The linear relationship can be described between ROP and the tensile strength. However, the compressive strength should be taken into account in the model in order to have the complete model of ROP prediction.

Further study is required to have more results of ROP for other rocks that have been tested for geomechanical parameters. The *in-situ* tested is recommended to verify our results of ROP with the borehole condition in the laboratory, also to validate the model of ROP prediction.

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AVO ANALYSIS IN GAS HYDRATE EXPLORATION AND THE POSSIBILITY OF ITS APPLICATION IN DEEP WATER CONTINENTAL SHELF OF VIETNAM

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Summary

AVO, which stands for Amplitude Variation with Offset - or more simply, Amplitude Versus Offset, is a seismic technique that looks for direct hydrocarbon indicators using amplitudes of prestack seismic data. The AVO technique became very popular in the petroleum industry, as one could physically explain the seismic amplitudes in terms of rock properties. For example, bright-spot anomalies (i.e. the high amplitude reflections seen on the P-wave stacked section) could be investigated before stack to see if they also had AVO anomalies. It can help us distinguish the geological objects that created bright-spot anomalies, such as gas-bearing sandstones, coal seams or volcanoes.

AVO analysis proved successful in certain areas of the world for gas hydrate exploration. In this paper we describe AVO analysis methods and some examples of using AVO in gas hydrate exploration in the world as well as the possibility to apply it in deep water areas on the continental shelf of Vietnam.

Key words: Gas hydrate, AVO, BSR, anomaly amplitude, deep water area

1. Introduction

Gas hydrate was considered by scientists as a curiosity and by the petroleum industry as a nuisance until its very recent recognition in the natural environment. Within more than thirty years of its first discovery, however, both industry and governments had begun to explore the potential of hydrate as an energy [10, 11]. Recent interest in gas hydrate has grown not only in the U.S but also in some European Union countries, Japan, South Korea, China and Taiwan. The primary interest is the potential of gas hydrate to supply large quantities of methane to commercial energy markets in this century and beyond.

Gas hydrate is found in the ocean because of a coincidence of rising pressure and diminishing temperature with increasing water depth (Figure 2), where there are huge quantities seismic data but very sparse well data. One of the primary issues for gas hydrate research is the interpretation of seismic data to determine the possible existence of gas hydrate.

Gas hydrate can be detected from seismic data by observations of Bottom-Simulating Reflectors (BSR). A BSR is parallel to the seafloor reflector with opposite polarity (Figure 3 and 4). A bottom-simulating reflector (BSR) is

clearly observed on the seismic section with a reversed polarity compared to that of the seabed reflection. Instantaneous amplitude section clearly shows lateral variations of the BSR. The zero-phase waveform of the BSR is distinct and weak reflectors above the BSR can be observed on the instantaneous phase section. AVO analysis shows the absolute values of the negative BSR amplitude increasing with offset. AVO analysis could also be useful in differentiating amplitude anomalies related to gas hydrate and those resulted from anomalous lithologies, because the amplitude anomalies induced by anomalous lithologies can be typically observed on both P- and S-wave sections. Unfortunately, S-wave is commonly not recorded. One solution to this problem is to use AVO method on conventional P-wave data, which allows us to derive S-wave data without actual recording (Figure 1).

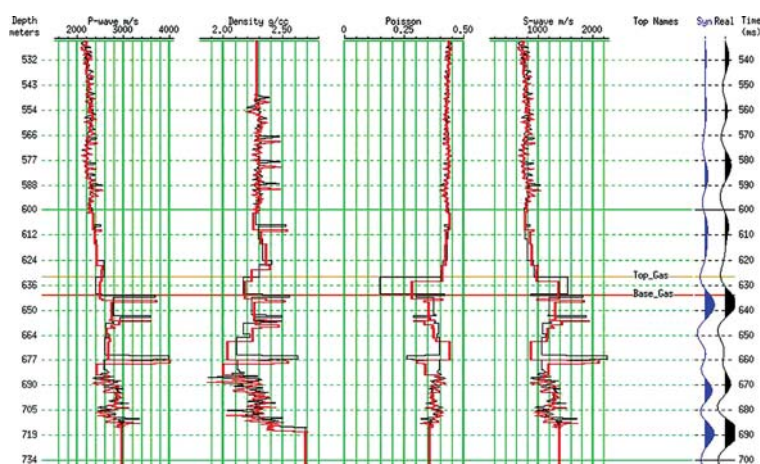


Figure 1. Quantitative AVO analysis to estimate P- and S-wave velocities and density. The black curves are before inversion while the red curves show the same logs after inversion. Synthetic seismic trace (blue) shows very good fit with real seismic data

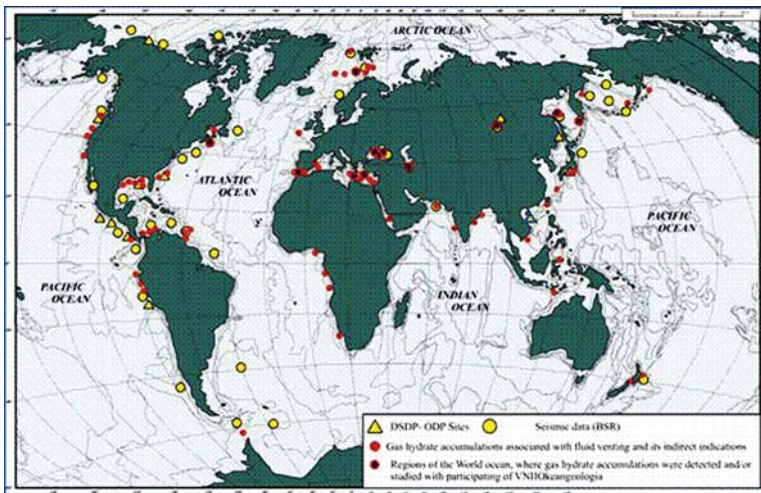


Figure 2. Map showing regions where gas hydrate accumulations were detected and studied [9]

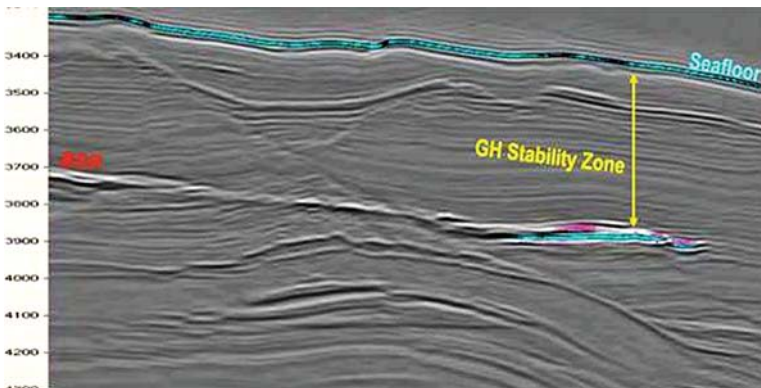


Figure 3. Seismic section in the deep water area of the Gulf of Mexico: BSR is a strong reflector and parallel to the seafloor [13]

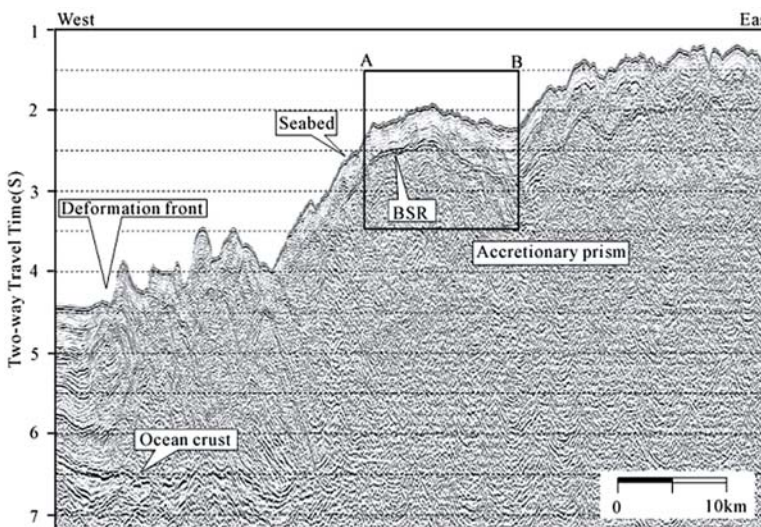


Figure 4. Seismic section in the deep water area of Taiwan BSR - is a strong reflector and parallel to the seafloor [14]

AVO analysis was first mentioned in 1984 when Ostrander published a break-through paper in "Geophysics" [1]. He showed that the presence of gas in a sandstone layer capped by a shale layer would cause an amplitude variation with offset in prestack seismic data. He also found that this change was related to the reduced Poisson's

ratio caused by the presence of gas. One year later, Shuey [2] confirmed mathematically via approximations of the Zoeppritz equations that Poisson's ratio was the elastic constant most directly related to the offset-dependent reflectivity for incident angles up to 30°.

AVO analysis is carried out after the raw seismic data have been processed using an amplitude-preserved processing sequence. In this paper we describe the AVO technique and some examples of using AVO in gas hydrate exploration in the deep water in the Gulf of Mexico and in Taiwan [13, 14] as well as the possibility to apply it in deep water areas on the continental shelf of Vietnam.

2. AVO intercept and gradient analysis

Analysis of AVO or amplitude variation with offset seeks to extract rock parameters by analysing seismic amplitude as a function of offset. The reflection coefficient for plane elastic waves as a function of reflection angle at a single interface is described by the complicated Zoeppritz equations [3]. For analysis of P-wave reflections, a well-known approximation is given by Shuey [2]. He linearly approximated the Aki-Richards equation and kept only the second-order term:

$$R(\theta) = R_p + G \sin^2 \theta \quad (1)$$

where: $R(\theta)$ is the reflection coefficient with incident angle θ

$R_p = \frac{1}{2} \left[\frac{\Delta V_p}{V_p} + \frac{\Delta \rho}{\rho} \right]$ is the P-wave reflection coefficient of normal incidence ($\theta = 90^\circ$)

$G = \frac{1}{2} \frac{\Delta V_p}{V_p} - 2 \frac{V_s^2}{V_p^2} \left[\frac{\Delta \rho}{\rho} + 2 \frac{\Delta V_s}{V_s} \right]$ describes the variation at intermediate offsets

Equation (1) is linear if we could plot $R(\theta)$ as a function of $\sin^2 \theta$. We could then perform a linear regression analysis on the seismic amplitude to come up with estimates of both intercept R_p and gradient G . When we perform this analysis at every sample on every gather, we create two sections, or volumes. The intercept section is similar to the conventional stack - except that it represents a better estimate of the vertical P-wave reflections (normal incident

P-wave reflections). The gradient contains information about both the P and S-wave reflections.

Assume that $V_p/V_s = 2$ then the formula for gradient G becomes:

$$G = R_p - 2R_s \quad (2)$$

where: $R_s = \frac{1}{2} \left[\frac{\Delta V_s}{V_s} + \frac{\Delta \rho}{\rho} \right]$ is the S-wave reflection coefficient of normal incident ($\theta = 90^\circ$).

Equation (2) can be rewritten as: $R_s = (R_p - G)/2$. From this formula, it is obvious that the difference between intercept and gradient, after scaling, is the approximate S-wave reflectivity. If the intercept (P-wave) section shows a strong "bright spot", whereas the pseudo-S-wave (intercept minus gradient) section does not show a "bright spot," it might indicate the presence of BSR.

Equation (1) was further approximated by Verm and Hiltermann [4] to:

$$R(\theta) = R_p \cos^2 \theta + R_s \sin^2 \theta \quad (3)$$

where: $PR = \left[\frac{\Delta \sigma}{(1 - \sigma_{avg})^2} \right]$ is the Poisson's reflectivity;

$\Delta \sigma$ is the change in Poisson's ratio;

σ_{avg} is the average Poisson's ratio.

Assuming that $\sigma_{avg} = 1/3$ we have $PR = \frac{9}{4} \Delta \sigma$ and equation (3) becomes:

$$R(\theta) = R_p + \left(\frac{9}{4} \Delta \sigma - R_p \right) \sin^2 \theta \quad (4)$$

Comparing equations (1) and (4) we have: $G = \frac{9}{4} \Delta \sigma - R_p$ or:

$$\Delta \sigma = (R_p + G) \times \frac{4}{9} \quad (5)$$

Equation (5) shows that the sum of the intercept and the gradient can be shown to represent the approximate Poisson's ratio change, where the Poisson's ratio is related to the square of the P-wave to S-wave velocity ratio $\left(\frac{V_p}{V_s} \right)^2$. Thus, a negative Poisson's ratio change is associated with the top of a gas zone, whereas a positive change is associated with the base.

Furthermore, the product of AVO intercept and gradient ($R_p \times G$) is a very helpful parameter in areas where we expect soft sands with hydrocarbons, which is AVO class III. Soft sand with hydrocarbons will have strong negative intercept and a strong negative gradient. The product will be a strong positive. Non-hydrocarbon reflectors will be weak or have negative products. Thus,

the product parameter is a nice attribute to distinguish BSR-related bright spots from "false" bright spots.

With the AVO analysis results from line AB in Figure 4 (deep water of Taiwan) [14], the BSR is negative in the R profile (Figure 5a), indicating that the impedance below the BSR is smaller than that above the BSR. The G -attribute values along BSR in section AB are also negative (Figure 5a), implying that the absolute value of the BSRs amplitude increases with incident angles. The AVO anomaly (Figures

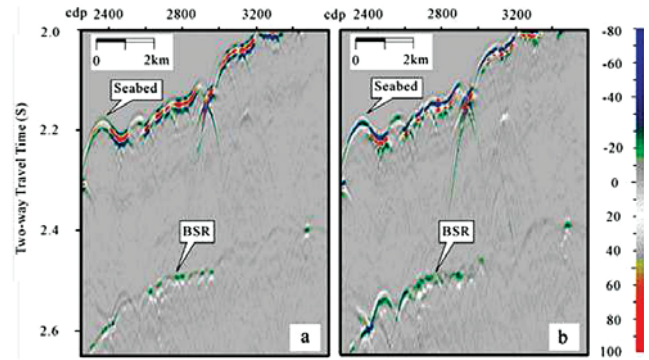


Figure 5. R (a) và G (b) section [14]

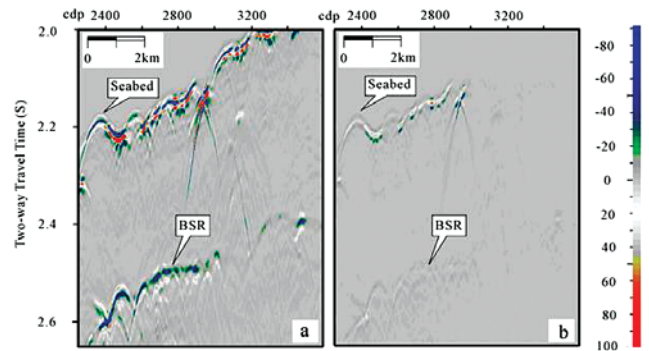


Figure 6. $R + G$ (a) và $R - G$ (b) section [14]

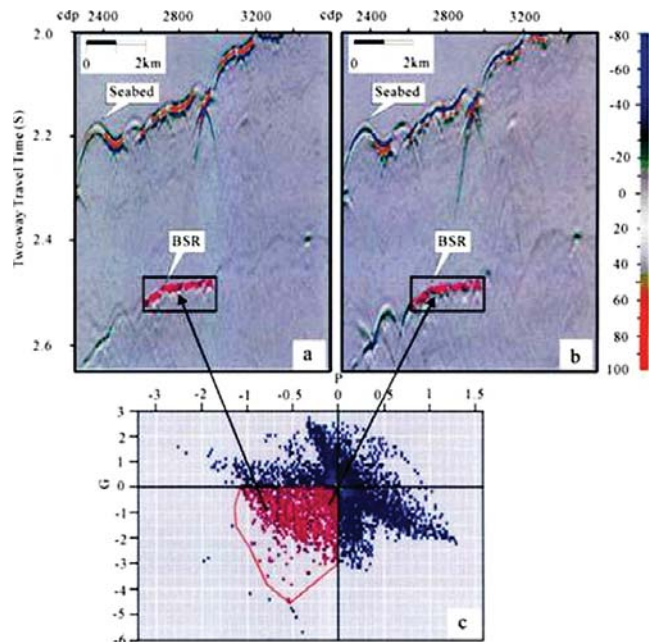


Figure 7. R section (a); G (b); R vs G crossplot (c) [14]

7a, b) of the BSR belongs to type III [5] and the BSR's value lies in the third quadrant of the crossplot of the R and the G sections [6] (Figure 7c), thus the sediments should contain a hydrate layer above the BSR and free gas below the BSR.

3. AVO analysis using seismic amplitude

Mathematical expressions of AVO are, in fact, usually presented in terms of *relative* amplitude, i.e., reflection coefficient, or reflection amplitude normalised with respect to incident-wave amplitude. In practice, however, AVO analysis is carried out using seismic amplitudes (*absolute* amplitude). This leads us to a very important question: how can we obtain such relative amplitudes if we only observe seismic-trace amplitudes?

For example, Smith & Gidlow [8] write:

$$R_{pp}(\theta_i) = A_i \frac{\Delta\alpha}{\alpha} + B_i \frac{\Delta\beta}{\beta} \quad (6)$$

where: $\alpha = V_p$ and $\beta = V_s$

$$A_i = \frac{5}{8} - \frac{1}{2} \frac{\beta^2}{\alpha^2} \sin^2 \theta_i + \frac{1}{2} \tan^2 \theta_i \text{ and } B_i = -4 \frac{\beta^2}{\alpha^2} \sin^2 \theta_i \quad (7)$$

Both of these expressions, (8) and (9), are clearly dimensionless; they involve relative amplitudes. However, Smith & Gidlow go on to say "if the actual amplitude of each offset sample is a_i , then the mean square error... is given by":

$$\varepsilon = \sum_{i=1}^n \left(A_i \frac{\Delta\alpha}{\alpha} + B_i \frac{\Delta\beta}{\beta} - a_i \right)^2 \quad (8)$$

Further, they give results of their least-squares regression analysis for α and β reflectivities in the form:

$$\frac{\Delta V}{V} = \sum_{i=1}^n a_i C_i \quad (9)$$

where V stands for α or β . C_i are weights that are clearly dimensionless, as they involve only sums and products of dimensionless A_i 's and B_i 's. Thus the a_i values must clearly also be dimensionless, or normalised with respect to incident-wave amplitude.

The actual trace-sample values could be written as Ka_i , where K is a scaling constant that we assume initially to be unknown. Then (11) becomes:

$$K \frac{\Delta V}{V} = \sum_{i=1}^n (Ka_i) C_i \quad (10)$$

in which Ka_i are trace-sample values. And (8) becomes:

$$KR_{pp}(\theta_i) = A_i \left[K \frac{\Delta\alpha}{\alpha} \right] + B_i \left[K \frac{\Delta\beta}{\beta} \right] \quad (11)$$

in which the bracketed quantities are known from the regression analysis.

Equation (13) shows that, in order to obtain relative amplitudes from seismic amplitudes we need to estimate the value of K . If we do not estimate this value and calibrate the seismic data prior to AVO analysis then we can only perform the qualitative AVO analysis but not quantitative analysis. AVO inversion of the seismic data without scaling them to the level of reflection coefficients will give incorrect elastic parameters such as P-wave and S-wave velocities and density.

Estimation of the value of K requires forward modeling to create multi-offset synthetic seismogram from dipole sonic information. For each offset trace the root-mean-square (RMS) amplitude is calculated and then matched to the corresponding seismic data.

In order to study the characters of gas hydrate in the deep area of the Gulf of Mexico [13] (Figure 3), qualitative AVO analysis can be performed directly using seismic amplitudes. To obtain relative amplitudes from seismic amplitudes, seismic data (Figure 9) is scaled, prior to AVO, from seismic velocity and density (Figure 8), then the AVO

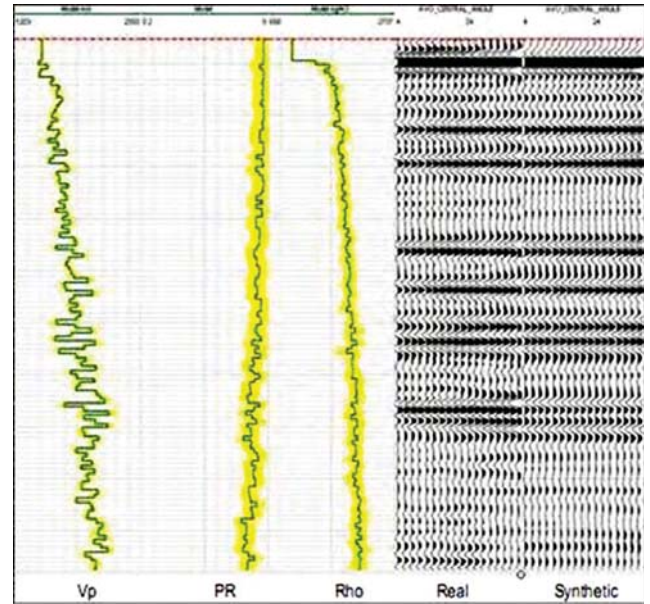


Figure 8. Synthetic seismogram established from data in the deep water of Gulf of Mexico [13]

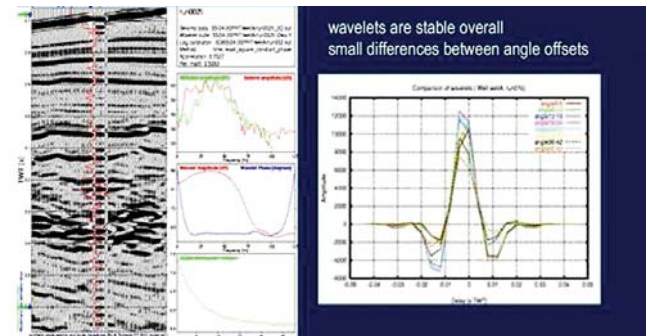


Figure 9. Amplitude correction with reflection coefficients [13]

is performed. As per integrated analyses above, the gas hydrate layer above the BSR and the free gas layer below the BSR may most probably occur in the place where strong BSRs are observed as a base of gas hydrate stability (Figure 10).

4. The possibility to apply AVO in deep water areas on the continental shelf of Vietnam

Beside the traditional petroleum resources that have an important role in the industrialisation and modernisation of the country, gas hydrate that may exist in deep water areas on the continental shelf of Vietnam can be another source of fossil fuels in the future.

Oil and gas exploration in Vietnam began in the 60s of the last century, but the research and investigation of gas hydrate potential has been a "Topical Question". Since 2006, Petrovietnam and the Ministry of Natural Resources and Environment have organised several conferences and seminars on the issue of gas hydrates, and proposed to the Government "an integrated research programme on gas hydrate potential in the continental shelf of Vietnam". On 24 September 2007, the Prime Minister issued Decision No. 1270/QĐ-TTg to add "The basic research and investigation programme of gas hydrate potential in Vietnam's territorial waters and continental shelf" programme to the tasks of the Master Plan for "Basic survey and integrated management of marine resources until 2010 and vision to 2020".

Several companies in Vietnam have conducted research, investigation and evaluation of gas hydrate potential in Vietnam and initially made statements about the presence of gas hydrate in the deep water areas on the continental shelf of Vietnam (from 500m of water) [15, 16].

On the basis of seismic data covering the Vietnam continental shelf and neighbouring areas (Figure 11) and under the direction of Petrovietnam, the Vietnam Petroleum Institute is currently carrying out a State Project to collect, analyse and integrate data to identify the indicators of gas hydrate in Vietnam's continental shelf".

Based on the seismic data analysis as well as integrated analysis, the results of the research conducted by the Vietnam Petroleum Institute allow the prediction of gas hydrate presence in the deep-water areas on the continental shelf of Vietnam. On some seismic sections in the study area (Figure 12), the presence of strong reflective surfaces that lie continuously parallel to the

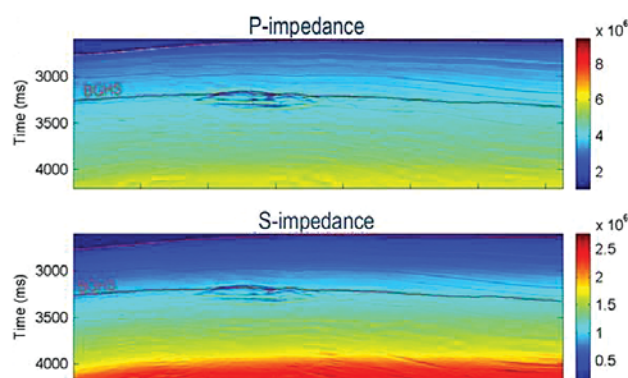


Figure 10. AVO result for studying the gas hydrate in the deep area of the Gulf of Mexico [13]

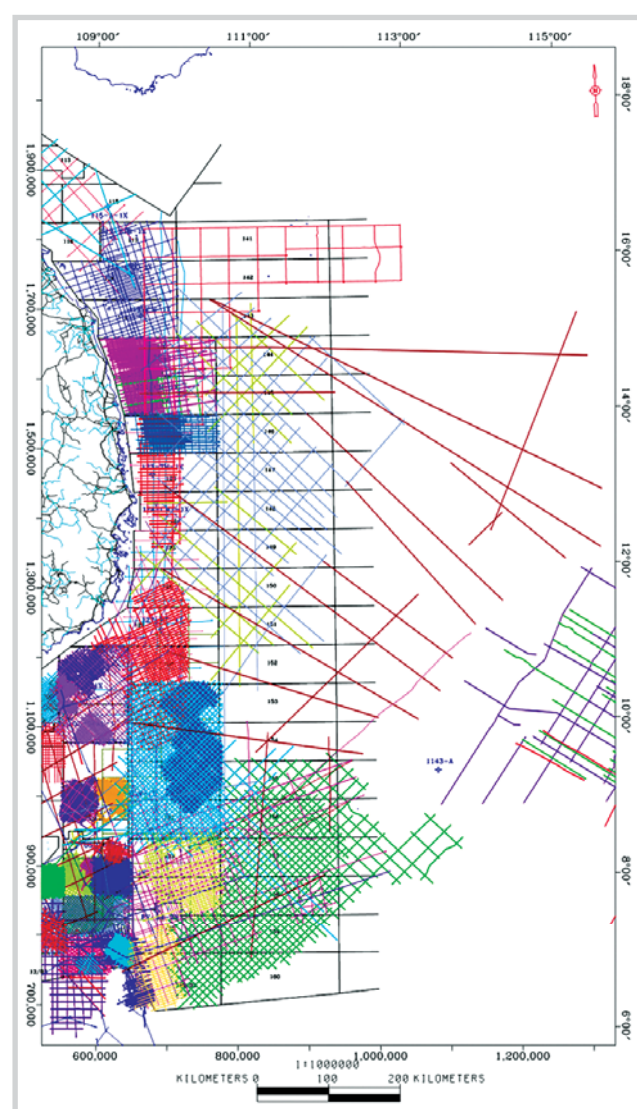


Figure 11. Location map showing seismic lines used in the gas hydrate project

sea floor (BSR) within the blank zones, gas chimneys, and amplitude anomalies can be related to gas hydrate.

From the seismic data with the gas hydrate indication as presented and in combination with related geological data, special analysis of seismic attributes, especially

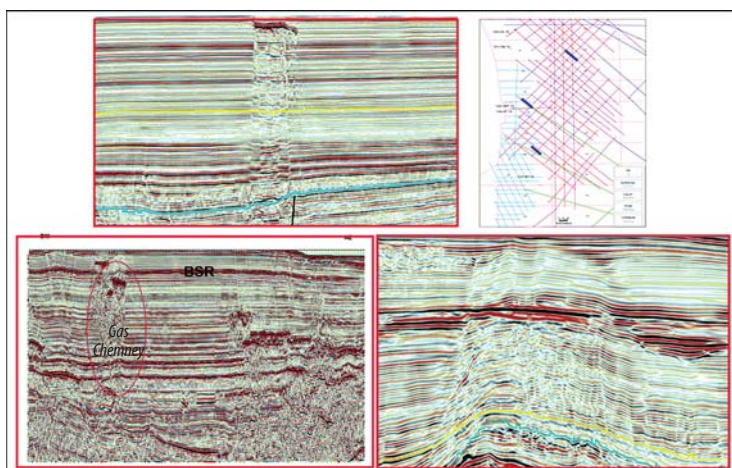


Figure 12. The BSR, gas chimney, and amplitude anomalies can be related to gas hydrate in deep water areas on the continental shelf of Vietnam

AVO analysis, can be conducted to predict the existence of BSR to explore gas hydrate in the deep water areas on the continental shelf of Vietnam.

5. Conclusion

In this paper we presented an overview of AVO analysis method and the results of applying AVO analysis in gas hydrate research. AVO analysis results indicate that the absolute value of the BSR amplitude increases with offset. The gas hydrate layer above the BSR and the free gas layer below the BSR may probably occur in the place where strong BSRs are observed as a base of gas hydrate stability (BGHS).

Based on the results of the State Project carried out by the Vietnam Petroleum Institute to collect, analyse and integrate data to identify the indicators of gas hydrate in the Vietnam continental shelf, it can be concluded that the AVO analysis can be conducted to predict the distribution of BSRs to explore gas hydrate in deep waters of the continental shelf of Vietnam.

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CASING AND CEMENTING WITH POTENTIAL GAS INFLUX

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Summary

It is well known that wells should be reinforced by running the casing and cementing the annulus to create a competent cement sheath that helps to prevent the caving of the bore-hole. Other than supporting the casing, cementing the annulus also provides zonal isolation. The presence and migration of gas into the well annulus have been known as a problem in hydrocarbon exploration when complete isolation has not been achieved.

This report presents the general concept of gas migration in the well annulus and introduces some practical examples from experience of running casing and cementing in production and exploration wells in abnormally high pressure formations with substantial risks of gas migration in Vietsovpetro's fields.

Key words: Well cementing, annular gas migration, phase transition period, hydrostatic pressure reduction of cement slurry column, preventive methods of gas influx.

1. Introduction

Drilling wells create channels from a reservoir up to the surface. To produce oil and gas from the reservoir, one has to build sustainable channels that connect the reservoir to the surface and the storage tanks. For effectiveness and safety in the lift of oil and gas in the well from the reservoir to the surface, the wells have to be reinforced and all formations in the ground isolated. Only then, the wells can be competent for long-term production.

In casing and cementing jobs, steel pipes are thread-joined to form a casing string which is then lowered to the designed depth of the bore-hole. The process of dropping the casing string into the bore-hole is called running the casing. A cased well will be able to maintain the circular shape during drilling and production of oil and gas in the future. To anchor the casing string and isolate the reservoir, cement slurry is injected into the annulus. It displaces the drilling fluid, rises to the designed depth and sets to form a solid cement sheath. That process is called well cementing.

In fact, most of oil and gas production fields around the world have found traces of gas flow in the annulus after cementing and during production. Over a long time, this gas may migrate into another reservoir or up to the surface (Figure 1). In some cases, high pressure inside the cement sheath is created and becomes impossible to control, causing a blowout from the wellhead, which leads to tremendous damage both economically and environmentally [5, 7].

There are possibilities to greatly reduce the material costs and the time to overcome the problems above

(the most serious is oil and gas blowout), if the source, causes and nature of the phenomenon of gas migration in channels through the cement sheath are clarified, and then there is timely application of the technical measures to prevent them.

This report discusses casing and cementing in an abnormally high pressure reservoir with a high risk of gas migration.

2. Fundamentals of gas influx and migration into the annulus

2.1. Practical consequences of gas influx and migration into the annulus

The annulus of a oil and gas well is defined (constructed and limited) by nested casing strings, borehole wall, casing head on the wellhead, cement sheath, and liquid column consisting of drilling mud, buffer fluid wash (in cases that cement slurry does not rise onto the surface) [3]. A cement sheath is formed only after the casing and cementing process is completed.

Gas intrusion and migration into the cement sheath in the annulus is a potential cause of several dangerous complications and occurrences. However, these are not always immediately detectable. The first indication of this phenomenon on the surface is the appearance and increase in pressure between casing strings or gas flow at the wellhead. Usually, remedial cementing is performed to force the cement into gas channels until the gas flow is stopped and casing pressure is reduced to a level compatible with the operator's safety policy and local regulations. However, the efficiency of squeeze cementing in such circumstances is very low for three essential reasons:

- Gas channels are difficult to locate, especially if they are less than 1mm in size;
- Gas channels may be too small to be effectively filled by cement;
- The pressure exerted during the squeeze job is sometimes sufficient to break the cement bond or even to initiate formation fracturing, creating problems in down-hole communication.

Gas migration between two or more subsurface zones, with no surface manifestations, is very difficult to detect (Figure 1). In such cases, gas production may be impaired; gas may migrate to an upper depleted zone (possibly followed by gas migration to the surface through another well), or the efficiency of stimulation treatments may be reduced.

Usually, cement repairing operations to fix the above problems are expensive, especially offshore or in remote locations. Therefore, preventing gas migration is definitely preferable to attempting to repair it [5].

There have been many subjective and objective causes in the oil spill disaster of Deepwater Horizon platform, offshore the Gulf of Mexico in April 2010. However, the investigation report indicated the main cause appears to be that the cement sheath did not maintain the isolation of oil and gas in the high-pressure reservoir, causing the gas to enter the annulus between casing strings and wellbore wall and then up to the wellhead [7].

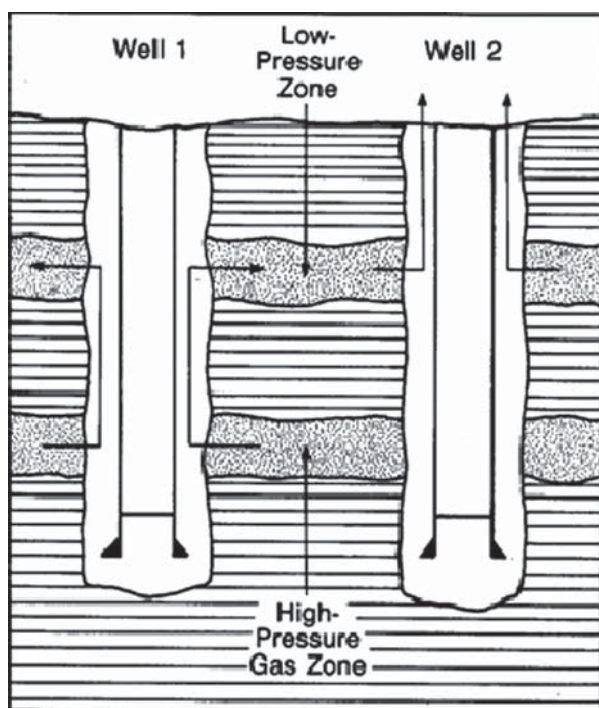


Figure 1. Two scenarios for gas migration in the annulus

2.2. Root causes for gas migration in the annulus

In principle, where there is a source (reservoir) of gas, annular gas migration has three distinct root causes:

- The hydrostatic pressure in the annulus falls to a level that is less than or equal to the pore pressure of a gas-bearing zone.
- Space in the annulus allows gas entry.
- A path is present in the annulus through which the gas can migrate.

2.3. Paths for gas migration in the annulus

Gas migration in a cement sheath requires paths. Gas migrates in the annulus between a cement sheath and casing strings, the cement sheath and wellbore wall, or directly through the cement. Some investigations state these three gas migration mechanisms, but also claim that it is impossible to use this concept to classify or indicate the gas intrusion phenomenon in any particular circumstance. There is almost no circumstance whereby only one mechanism took place.

2.4. Gas migration categories

Understanding and modeling the gas migration phenomenon is difficult because the conduit through which the gas can channel (i.e., an annular column full of cement, with possibly some spaces and drilling fluid left in the hole) evolves with times. The physical state of the cement progresses from a liquid slurry during placement to a permeable gel during a limited static period, then to a permeable-weak solid when setting, and finally to an impermeable solid after hardening. Therefore, the physical process of gas migration is conveniently categorised according to the timing of its occurrence during the cementing operation (Figure 2) [5].

2.4.1. Immediate gas migration (during the cementing process)

Gas intrusion during the cementing process occurs in the period from when cement pumping starts until the top plug is set on the bottom plug in the float collar. In this stage, gas migration into the cement slurry column is caused by the imbalance between hydrostatic pressure in the column and reservoir pressure. Preventing gas intrusion during this stage is similar to well control. The first method is to increase the drilling fluid density in the annulus. However, this method increases the risk of lost circulation or broken formation. The most reasonable method is annulus cleanout treatment before pumping cement.

Controlling gas migration while cementing is differentiated from well control in the drilling process via the phenomenon of gravity due to the “U-tube” effect. Due to the density difference between drilling fluid, buffer fluid and cement slurry, hydrostatic and hydrodynamic pressure of column fluid in the well always changes during pumping cement.

Sliding up and down casing strings will reduce hydrostatic pressure in the annulus when cementing due to the piston effect.

The fluctuation of cement density also causes gas intrusion during the cementing process. Inhomogeneous cement slurry develops the solid setting of cement slurry, free water...

2.4.2. Short-term gas migration (post placement gas migration)

This form of gas migration occurs between the end of the primary cementing operation (normally marked by the landing of the top wiper plug) and the setting of the cement (this time also is called as period of phase transition). Most of research suggests that the phase transition period of the cement slurry (waiting on cement) after cement placement is a dangerous time for gas intrusion. Thus the theory of gas migration and prevention methods often focus on this form [6]. The main reason for this is hydrostatic pressure reduction of the cement slurry column in the annulus after cement placement while cement is creating the structure and converting the phase from liquid to solid [2, 3, 4]. The reduction of pressure here is the combination of a variety of factors including free water, gel strength development and chemical shrinkage of cement hydration. It can also result from the formation of annular bridges or the setting of mechanical devices such as packers that isolate hydrostatic pressure transmission. Spaces for gas intrusion are generated by free water, chemical shrinkage and porosity of cement. At first, gas migrates through cement filter cake then through cement pores..

For the cement slurry as liquid and the cement rock as solid, there are many comprehensive methods



Figure 2. Categories of gas migration

for experimentation and study to determine their characteristics. However, the phase transition period between liquid and solid has not yet been fully investigated. Therefore, the gas intrusion phenomenon during this period is seen as the most complex form and is difficult to realise and forecast.

The following formula is used to describe and estimate the value of pressure reduction:

$$\Delta P = \frac{4 \times L \times SGS}{D_h - D_p} \quad (1)$$

L: Length of the cement slurry column;

SGS: Static gel strength;

D_h (D_p): Hole diameter (casing diameter).

In fact, it is often assumed that cement begins to develop static gel strength at the time of cement slurry so as to allow itself to support its own weight. Meanwhile, the pressure between cement particles reduces to the equivalent of static hydraulic pressure. After this time, the cement slurry becomes solid and able to prevent normal gas intrusion. Therefore, for calculation simplicity, we can consider pressure at this moment as the lowest pressure values of cement column that can be achieved (i.e. ΔP achieves maximum). Then the following formula is used:

$$\Delta P_{max} = (\rho_{cem} - \rho_w) \times g \times L \quad (2)$$

ρ_{cem} : Cement slurry density;

ρ_w : Water density;

g: Gravitational coefficient.

2.4.3. Long-term gas migration

In recent years, a growing technical interest has been shown in the long-term form of gas migration due to the increased awareness of environmental protection. The reason for this is gas leakage into the environment from gas wells after their abandonment. The main cause of intrusion is the formation of gas channels after cement setting. After solidification, normal cement will become a low permeability solid (microdarcy). Gas cannot migrate through these pores, especially when it is saturated with water in the cement structure. A lightweight cement system (low density) containing a lot of water often has high permeability (0.5 - 5.0mD). Therefore, gas can migrate through the cement structure, although in small flows. However, over a long time, it can move onto the wellhead. This phenomenon can take a few weeks or months to reach the wellhead when sustained casing pressure in

the annulus appears and increases. Paths for gas influx after cement solidification are cracks, mud channels, channels caused by poor displacement of mud by cement slurry, channels due to cement dehydration, mud filter cake dehydration, or due to mechanical stress or temperature changes on the cement sheath in the annulus. The space that contains the gas is the chemical shrinkage, shrinkage of bulk cement, shrinkage due to channel liquid, and clay or mud filter cake dehydration. Due to cement solidification, at this stage the cement column does not transmit hydrostatic pressure to the gas reservoir.

3. Well casing and cementing with potential gas influx of Vietsovpetro's fields

3.1. Engineering geological conditions

Currently Vietsovpetro is producing oil mainly from three fields in the Cuu Long basin. They are Bach Ho, Rong and Gau Trang. Although there are various geological factors, they also have common characteristics, i.e.:

Source of gas with high reservoir energy in Vietsovpetro fields from Oligocene formations can influx or migrate into wells during drilling, casing, cementing and production.

The bore-holes in Oligocene formations are cased (reinforced) by running the liner or production casing strings in two types of well schemes (Figure 3).

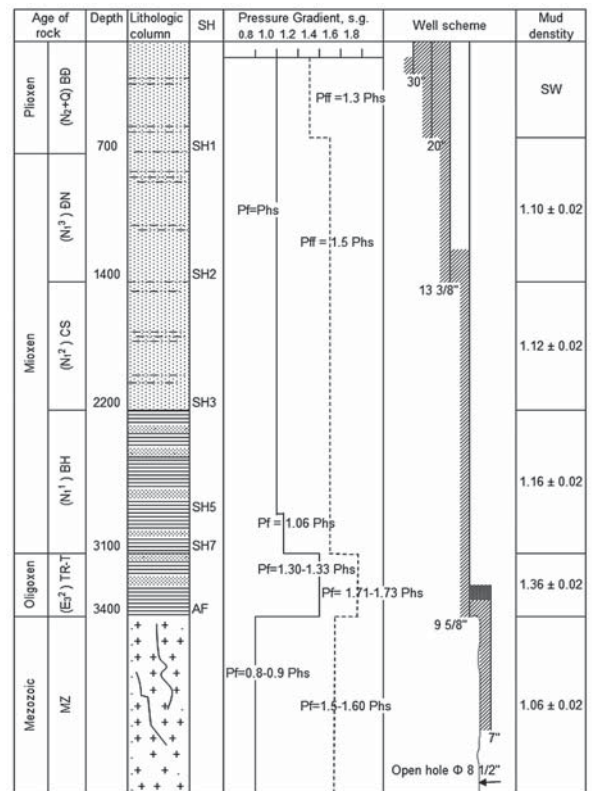
3.2. Reinforcement of wellbore through formations with gas migration risk by running the production (intermediate) casing onto the surface

For the location of the geological cross-section with not-too-high abnormal reservoir pressure in the Oligocene formation (up to 1.40), we could use the production casing string Ø 245mm to support the wellbore to the top of the basement. The wellbore in the Oligocene formation is drilled and cased (reinforced) with the wellbore in the Miocene formation by running one casing string and cementing (Figure 3a).

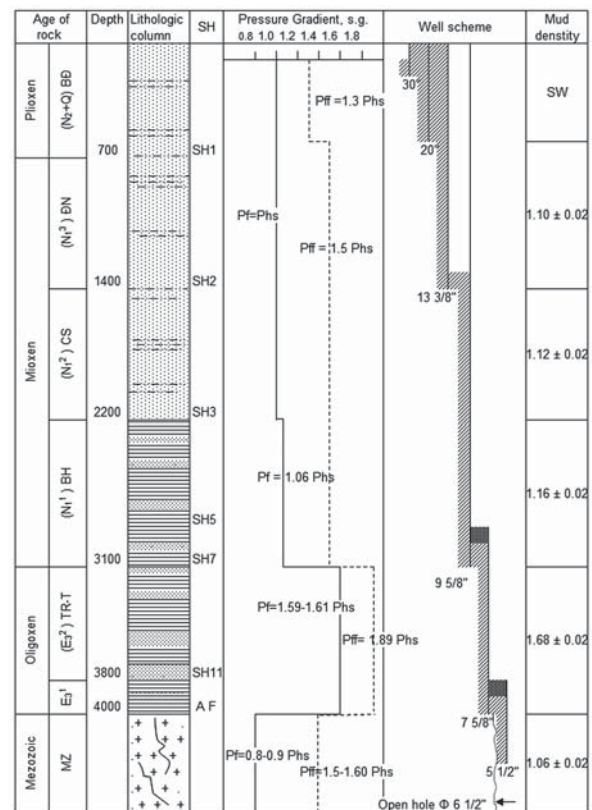
Gas migration risk factors include: (i) high pressure gas source from the Oligocene formation; (ii) cement slurry column length of approximately 2,000m being affected by the phenomenon of hydrostatic pressure reduction during the phase transition period. If using cement density of 1.53g/cm³ for the 2,000m length, according to the formula number (2), the hydrostatic pressure may be decreased by:

$$\Delta P_{max} = 0.1 \times (1.53 - 1.0) \times 2,000 = 106 \text{ kg/cm}^2$$

Measures to prevent gas migration can include the design of two types (lead and tail) of cement slurry that have different properties to minimise gas intrusion due to the hydraulic pressure reduction of the slurry column.



(a)



(b)

Figure 3. Casing programs to reinforce the wellbore through formations with the risk of gas migration (a: by running the production (intermediate) casing to surface; b: by running the liner)

As shown above, the cementing process in Vietsovpetro's fields almost never has any problem of gas migration. Gas can influx when cementing by using buffer fluid (cushion water) at the time when cement starts to flow out of the casing shoe, and then the pressure will be balanced when cement reaches the bottom hole and out of the casing shoe and goes up in the annulus. Gas influx into slurry can occur while pumping cement. However, before the end of the cementing process, gas does not reach the wellhead and hence it may not be seen at the surface.

Short-term gas migration after the cementing process of production (intermediate) casing strings in Vietsovpetro's fields has generally been controlled by two types of different cement properties (thickening and setting time) (Table 1). Essentially, when the above cement slurry column (first type-lead cement) is still liquid and transmits hydrostatic pressure to the gas reservoir, the type below (second-tail cement) covering the gas-source formation must set before that. In addition, the second type should have extra isolation properties compared to normal. This technique is simple and seems to work effectively for Vietsovpetro.

However, application of this technique failed in two cases, i.e. Well 440-BK-4 when cementing the casing Ø 245mm on Xakhalin rig and 20-DR RC-4 when cementing casing Ø 194mm on rig West Larissa. In these cases, casing design and cementing were the responsibility of other contractors.

3.3. Reinforcement of wellbore in high pressure formation by liner

When drilling through Oligocene formations with high abnormal formation pressure, heterogeneous conditions occur on drilling between Miocene and Oligocene formations. In this case wellbore through the Oligocene formation is reinforced by liner (Figure 3b).

In principle, the well is reinforced in abnormal high pressure conditions by running and cementing the liner, so the risk of gas migration due to hydrostatic pressure reduction of the cement slurry column in the phase transition period is very little. Because the cement slurry column length is short, there is always the drilling fluid

column (its length is long when comparing with cement) that impacts on the top of cement. If the overlap distance between the liner top and the previous casing shoe is 200m and the cement density 1.73, the largest reduction value of the hydrostatic pressure exerting on the top of the Oligocene formation is calculated as:

$$\Delta P_{max} = 0.1 \times (1.73 - 1.0) \times 200 = 14 \text{ kg/cm}^2$$

Thus value ΔP is very much smaller than the hydrostatic pressure of the drilling fluid column (length 3,000m) above the cement slurry column. If the drilling fluid density is 1.65, the column hydrostatic pressure is approximately:

$$P = 0.1 \times 1.65 \times 3,000 = 495 \text{ kg/cm}^2$$

Measures to prevent gas intrusion when casing and cementing through high pressure formations by liner in Vietsovpetro are using packer on the top of the liner and keeping wellhead pressure after cement placement on WOC period. However, these measures appear to be ineffective.

According to the 2010-2011 Annual Report, there were many problems in the process of casing and cementing liner. Table 2 presents the level of success when casing and cementing liners [1] of Vietsovpetro's fields.

There are many possible reasons, but most failures are related to abnormal conditions of casing and cementing liner (before cementing and while cementing there was occurrence of both gas intrusion and loss circulation, cementing without return). The liner is sliding to the hole bottom after its hanging. The liner top packer is not sealed after primary cementing and so compels secondary cementing (squeeze job) to fill and seal completely or running an additional casing-liner linkup (tieback) above. The cost is therefore increased.

Thus, the principle of well reinforcement in formations with risk of gas intrusion by casing and cementing liner in Vietsovpetro (save the casing) can prevent the dangerous phase transition period if compared to running casing up to the surface. However, there are still many complicated problems. It is shown that existing techniques and technology of casing and cementing liner are incomplete, and not in accordance with the engineering geological conditions of the field.

Table 1. Properties of cement slurry for production (intermediate) casing

Interval (m)	Slurry density (g/cm ³)	Spread of slurry (cm)	Thickening time (hours-mins)	Setting time (hours-mins)		Free water (%)	Bending strength (kg/cm ²)
				start	finish		
3,457-1,106	1.53	25	7 - 10	10 - 35	11 - 10	1.5	24.6
3,957-3,457	1.57	21.5	5 - 05	8 - 50	9 - 35	0	26.5

Table 2. Percentage of success (no complexity) when running and cementing liner (12/2010-12/2011) in Vietsovpetro's fields

Diameter of liner (mm)	Number of times casing & cementing liner	Number of operation with complexity	Success rate (%)
194	14	8	43
178	6	3	50
140	9	3	70

4. Problems in prevention of long-term gas migration after cement setting

There are two types of gas migration, that during immediate and that after (short-term) the cementing process of casing strings, in which preventive measures (though simpler) were noted and applied. This is understandable because at this time the wells are still not complete and are in the process of drilling - building wells (wells have not been accepted, not yet put into production). If gas flow or fluid is detected in the annulus, it will have to be fixed/repared immediately. This is the job of drilling team (contractors).

The phenomenon of gas migration after cement solidification (long-term) is often discovered long after the cementing, sometimes even months or years after the well has been put online. Then management responsibilities are no longer placed upon the drilling contractor. This is why works to prevent gas migration of the third type is unnoticed and seldom done in the well-construction process (in the cementing process).

Thus, from the process of running casing and cementing in formations with a high risk of gas migration in Vietsovpetro's fields, we also realise that during the drilling process, we do not have any measures to prevent long-term gas migration after cement solidification.

5. Conclusion

- Practice and theory have confirmed that the presence, intrusion and migration of gas in the annulus are a particularly complex problem which is difficult to fix and repair and may lead to serious consequences when it happens. Therefore prevention before this occurs is the most practical and economic measure.

- In Vietsovpetro's fields, reinforcement of wells in high risk of gas migration is carried out by two methods: running production casing up to the surface or a liner to isolate the high pressure zone.

+ The reinforcement of wells by production casing (technical) up to the surface with high cement slurry

column will be affected by the rule of pressure reduction in the dangerous phase transition phase period. However, this rule has been effectively controlled by cementing application with a different setting time of cement slurry, and a combination to improve isolation properties of the cement stone in Vietsovpetro.

+ In principle, reinforcement of a well by a liner prevents a dangerous period of phase transition. However, running casing and cementing liner in Vietsovpetro are still complicated and further research is needed to find the root cause and to improve the efficiency.

- Measures to prevent long-term gas migration after cement solidification have not been applied during the drilling period.

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AN EMPIRICAL APPROACH FOR PREDICTING BIODIESEL FUELS DYNAMIC VISCOSITY FROM THEIR FATTY ACID ESTER COMPOSITION AT VARIOUS TEMPERATURES

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Summary

The purpose of this work was to develop an empirical model for predicting temperature dependent dynamic viscosities of biodiesel, based on their fatty acid ester composition. The Vogel equation [1] was used to describe the viscosity-temperature relationship of pure fatty acid esters (FAME-Fatty acid methyl ester/FAEE-Fatty acid ethyl ester) commonly present in biodiesel fuels, and a modified mass fraction based mixing equation was used to predict viscosity of 47 biodiesel mixtures based on their FAME/FAEE composition. The accuracy of this simple method was better than the other mass-based semilog blending equation reported in the literature.

Key words: Biodiesel, viscosity, prediction, empirical approach, dynamic viscosity.

1. Introduction

The stringent emissions law, the depletion of fossil fuels and the interrelation of fossil fuels with politics have forced the world to find alternatives to fossil fuels [2]. Biodiesel is a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel is one of the renewable and environmentally friendly alternative biofuels that can be used in a diesel engine with little or no modification in the engine. It is an oxygenated fuel that is essentially sulfur-free and biodegradable, significantly reducing particulate matter, hydrocarbon, carbon monoxide and life-cycle net carbon dioxide emissions from combustion sources. Because of these advantages, biodiesel has gained considerable attention in recent years. However, engine manufacturers are concerned about biodiesel's higher viscosity compared with diesel fuel because a high viscosity could cause excessive fuel injection pressures during engine warm-up [2].

Viscosity is one of the most important fuel properties as it impacts the performance of fuel injection system. The effect of viscosity can also be seen in the quality of atomisation and combustion as well as engine wear. Different publications showed that the higher viscosity of biodiesel could increase fuel penetration in the chamber, consequently affecting combustion and emissions from the engine; fuels with high viscosity tend to form larger droplets upon injection, which may result in poor fuel atomisation during spray, increases in engine deposits, greater energy demands for the fuel pump and wear in fuel pump elements and injectors [2 - 4]. On the other hand, fuels with

low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear [5, 6]. In the synthesis process, the knowledge of physical properties including viscosity is of great importance. Design of pipes, reactors, pumps, mixers, settlers and other equipment involved in unity operations related to alkyl esters and/or biodiesel production is highly dependent on this property. Biodiesel's characteristics strongly depend on various plant feedstock. Among the biodiesel's properties, viscosity, density and heating value are the most important parameters that affect the engine performance and the emission characteristics [7].

Reliable biodiesel viscosity data as well as accurate viscosity models that incorporate the dependence on temperature are very important in the development of combustion models [8, 9]. Apart from that, viscosity models are also very useful for design purposes, as well as for simulation and optimisation of process equipment such as heat exchangers, reactors, mixing vessels and process piping [10]. Some researchers have experimentally measured viscosity for some biodiesel fuels and their diesel blends [11 - 18]. These measurements, however, are for specific biodiesel fuels. Because there are numerous biodiesel source materials and the composition of each type of material may vary substantially, it is impractical to determine experimentally the viscosity of fuels produced from each material source. The aim of the present work is to improve the accuracy in the prediction of biodiesel dynamic viscosity for wide ranges of temperature and composition, by using a simple equation and a limited

number of adjustable parameters. In this way, it will be possible to predict with acceptable accuracy the viscosity of biodiesels blends.

According to Krisnangkura et al. [28] viscosity may be considered the integral of the interaction forces of molecules. Viscosity increases with carbon chain length and decreases with the number of double bonds of fatty compounds [19]. The Andrade equation [20] can be considered as the most well-known empirical correlation for the viscosity of the liquids and is given by:

$$\ln(\mu) = A + \frac{B}{T} \quad (\text{Eq. 1})$$

Although the correlation was proposed empirically based on observation, the form of the correlation and the description of the parameters were later suggested by the less rigorous semi-theoretical reaction rate theory by Eyring [21]. Nonetheless, the Andrade correlation is most commonly used by regression of the constants to experimental liquid viscosity data. Several modifications of Andrade equation were made to extend the temperature range. For example, the three-parameter Vogel equation, by adding a third variable parameter as shown:

$$\ln(\mu) = A + \frac{B}{T+C} \quad (\text{Eq. 2})$$

Many authors tried to generalise the parameters of the Andrade and Vogel equations to make the equations predictive rather than completely correlative. The developments were mostly correlations of the parameters to the structure of the molecules based on group contributions. Van Velzen et al. [22] method requires complicated calculations of the group contributions and commonly predicts the viscosity of the lighter compounds of the homologous series with an average deviation of 15%. Orrick and Erbar [23] developed another group contribution method to estimate the parameters of the Andrade equation using the molecular weight and density at 20°C, with overall average deviation of 15% compared to experimental data.

Yaws [24] used the following extension of the Andrade equation to represent the liquid viscosity of hundreds of hydrocarbons and non-hydrocarbons with tabulated regressed parameters:

$$\ln(\mu) = A + \frac{B}{T} + C \ln T + DT^E \quad (\text{Eq. 3})$$

In 1992, Liew et al. [25] proposed a function of temperature on kinematic viscosity as:

$$\log(\mu) = A + (B \times T) \quad (\text{Eq. 4})$$

In 1999, Tat and Van Gerpen [4] modified Andrade equation to determine the viscosity of the biodiesel at different temperatures. They concluded that the kinematic viscosities of biodiesel blends were well fit by equation as shown below:

$$\ln(\mu) = A + \frac{B}{T} + \frac{C}{T^2} \quad (\text{Eq. 5})$$

In 1999, by considering the carbon number, Krisnangkura et al. [18] proposed different equations to determine viscosity of biodiesels with long and short carbon structure at different temperatures. In 2006, Krisnangkura et al. [9] presented two different equations based on thermodynamic parameters, which use two and four adjusted parameters in the determination of unsaturated and saturated kinematic viscosity of pure methyl esters, respectively. The large relative deviations in relation to experimental data were 9.2%.

In 2007, Ceriani et al. [26] developed a group contribution model to predict viscosity as a function of temperature and chemical compound formula. In 2011, these authors [8] applied this group contribution method to predict the viscosity of fatty compounds, the relative deviations in relation to experimental data ranging up to 16.43 % were obtained on pure fatty alkyl esters.

More recently, in 2013, Ramirez-Verduzco [27] proposed an empirical model with four adjustable parameters (A, B, C, D) to predict the dynamic viscosity of FAMES.

$$\ln(\mu) = A + B \ln(M) + C.N + \frac{D}{T} \quad (\text{Eq. 6})$$

His model had the advantage of being a single equation for saturated and unsaturated species. However, this model exhibited some significant deviations between experimental and calculated viscosities. The author reported minimum, maximum and average absolute deviations of 0.09%, 29.63% and 6.04%, for 259 data points corresponding to samples of fifteen methyl ester at different temperatures.

Most of the empirical correlations described above are dependent on some constants and vary with type of biodiesel and percentage of blends. It is very important to have a simple, stable and reliable estimation method of viscosity as a function of weight/molar fraction and temperature of biodiesel. In all of the above equations, μ is the kinematic viscosity expressed in and T is the temperature; A, B, C, D, E, N are regression coefficients specific for each compounds.

2. Mixing rule for predicting the viscosity of biodiesel

Empirical viscosity methods for liquid mixtures are either interpolative mixing rules or pure component viscos-

ity models where the parameters of the model are calculated using mixing rules applied to the parameters of the mixture constituents. Although, viscosity is an important factor for biodiesel, methods for estimation of biodiesel viscosities are few [28] compared to those for petroleum. In addition, biodiesels are marketed mostly as the blends for uses in diesel engines and the methods for estimation of the viscosity of biodiesel blends are even fewer [29].

The first proposed mixing rules were mole, mass, or volume averages of a function of the viscosity of the pure components [30] which is widely used [4, 31] to calculate the viscosity of a mixture. It is formulated as:

$$\ln(\mu_{mix}) = \sum_i z_i \ln(\mu_i) \quad (\text{Eq. 7})$$

Molar fractions instead of mass fractions can also be used in this equation and this does not have a significant effect on the prediction of biodiesel viscosity, according to Ramirez-Verduzco [27]. Irving [32] reviewed more than 75 liquid viscosity equations including the above and other developed methods and evaluated them against experimental data for binary mixtures. He found that the simple predictive interpolative methods in the form of equation eq. 7 are only effective for the mixtures of the similar components with the viscosities of the same magnitude. Among the other mixing rules with adjustable constants, Irving [32] concluded that the most effectual yet simple methods are the additive parabolic equations with one adjustable constant. This is why the Grunberg - Nissan [33] equation, which considers the interactions among components, is usually recommended to calculate the viscosity of a mixture.

$$\ln(\mu_{mix}) = \sum_i z_i \ln(\mu_i) + \frac{1}{2} \sum_i \sum_j z_i z_j G_{ij} \quad (\text{Eq. 8})$$

The values of the adjustable parameters, G_{ij} depend on the binary compounds and are generally considered to be pressure or components and/or temperature dependent and this is very difficult to specify. Isdale et al. [34] proposed a complex group contribution method to estimate the G_{ij} values at 298 K. They found that the binary interaction parameter is slightly temperature dependent.

Another method of predicting viscosity of biodiesel based on its fatty acid ester composition was first studied by Allen et al. [17], who measured viscosities of some pure fatty acid esters and applied a mixing rule to predict viscosities of biodiesel fuels based on their component composition. This method was reasonably accurate but only applicable to the viscosity at 40°C. Similar alternatives to the Grunberg and Nissan method are the predic-

tive UNIFAC-VISCO method (Chevalier et al. [35]; Gaston-Bonhomme et al. [36]), the multi-parameter McAllister [37] mixing rule, and the mixing rule of Teja and Rice [38]).

In 1998, Graboski and McCormick [39] pointed out that kinematic viscosity of the blend was lower than would be predicted from a linear combination model (eq. 7), because dissolution of biodiesel minimised intramolecular interactions. The underpredictions led us to hypothesise that components with higher viscosities contributed more than predicted in a mixture using their pure value, thus leading to underpredicted viscosities, this hypothesis was inspired by Allen et al. [17]. The exact mechanism of the more significant effect of the higher-viscosity components on mixture viscosity is unknown, however, it is generally accepted that the interactions between non-associated components always exist. Therefore, when non-associated components are mixed, in this case biodiesel, their interaction makes the internal friction larger than accounted for by equation (eq. 7). On the contrary, in 2005, Yuan et al. [40] reported that the kinematic viscosities of biodiesel blends estimated by equation (eq. 7) were generally lower than the measured values. Hence, a correction parameter should be used for prediction of the kinematic viscosity of biodiesel blend.

Although biodiesel fuels are non-associated liquids that are composed of mixtures of fatty acid esters with similar structures, interactions among the esters do exist, since we expect that the polar interactions are strong enough. Our observations showed that, if the correction factor was neglected, mixture viscosity was always underestimated. Inspired by the conclusion of Allen et al. [17], in this work, a correction factor (or *binary interaction parameter*) was introduced to correct the difference between experimental and predicted values and the equation took the form:

$$\ln(\mu_{mix}) = \sum_i (1 - w_i) z_i \ln(\mu_i) \quad (\text{Eq. 9})$$

w_i is the correction factor. To account for the effect of the higher viscosity component, biodiesel, in this study, the correction factor was determined empirically by minimising the difference of measured and predicted data, the value for different type of fatty acid compounds were reported in Table 1.

3. Results and discussion

Many of the scientific publications relating to biodiesel have reported the FAME/FAEE profile on a mass base [13, 14, 41 - 45]. In this work, we have chosen the

mass fraction as it is the most common way to report the concentration of biodiesel in the literature, the prediction of the biodiesel viscosity is indistinguishable to the use of the mol fraction or mass fraction, as it has been previously observed by Ramirez-Verduzco et al. [41]. The newest experimental data of dynamic viscosity of the ethyl and methyl esters here studied are reported in Table 1.

As expected, the viscosity of all esters increases with the ester chain length and decreases with its level of unsaturation. The ethyl esters also present a higher viscosity than the corresponding methyl ester of the equivalent fatty acid.

The development of the proposed model was performed as follows.

- The Vogel equation was chosen to describe the experimental viscosities as a function of temperature;

the equation's constants were estimated using an optimisation algorithm based on the least squares method. The values of the parameters and the average absolute deviations (AAD) of the regression are reported in Table 1, Figures 1, 2 and 3. The results show that the Vogel equation provides an excellent description of the experimental data of viscosity with a maximum value of AAD of 0.77% and an average deviation of 0.22%, this is comparable to the uncertainty of experimental data.

- The modified mass fraction mixing equation (eq. 9) is used to determine the correction factor. This unique value is used to predict viscosity of all biodiesel mixtures considered in this work.

To assess the predictive ability of the model, the average absolute deviations (AAD) between the predicted and the experimental data of the dynamic viscosity were calculated at different temperatures according to:

Table 1. Parameter values to calculate the dynamic viscosity of pure FAMES/FAEs that are commonly present in biodiesel fuels using Vogel equation and correction factor, w in equation (eq. 9) to predict mixture's dynamic viscosity

	Compound	A	B	C	AAD (%)	Npt	T _{min} (K)	T _{max} (K)	Correction factor, w	Ref. data
Fatty acids methyl esters (FAME)										
C8:0	methyl-caprylate (C ₉ H ₁₈ O ₂)	-3.47	856.42	69.39	0.05	15	283	353	-0.04	[46]
C10:0	methyl-caprate (C ₁₁ H ₂₂ O ₂)	-3.32	814.90	93.34	0.19	19	278	372	-0.04	[29, 46]
C12:0	methyl-laurate (C ₁₃ H ₂₆ O ₂)	-3.30	857.10	100.84	0.17	16	283	372	-0.04	[29, 46]
C14:0	methyl-myristate (C ₁₅ H ₃₀ O ₂)	-3.09	823.48	114.17	0.08	13	298	372	-0.04	[46]
C16:0	methyl-palmitate (C ₁₇ H ₃₄ O ₂)	-3.09	880.48	113.61	0.05	12	308	363	-0.04	[46]
C16:1	methyl-palmitoleate (C ₁₇ H ₃₂ O ₂)	-3.04	818.87	109.26	0.51	18	278	363	-0.04	[44]
C18:0	methyl-stearate (C ₁₉ H ₃₈ O ₂)	-3.61	1173.32	87.97	0.37	14	313	513	-0.04	[29, 46]
C18:1	methyl-oleate (C ₁₉ H ₃₆ O ₂)	-2.78	778.85	125.41	0.09	16	283	363	-0.04	[29, 46]
C18:2	methyl-linoleate (C ₁₉ H ₃₄ O ₂)	-3.03	904.55	97.92	0.38	16	278	353	-0.04	[29, 46]
C18:3	methyl-linolenate (C ₁₉ H ₃₂ O ₂)	-3.12	962.63	84.70	0.73	20	278	373	-0.04	[44]
C20:0	methyl-arachidate (C ₂₁ H ₄₂ O ₂)	-2.76	824.91	132.98	0.02	11	323	373	-0.04	[44]
C20:1	methyl-gadoleate (C ₂₁ H ₄₀ O ₂)	-2.55	737.30	136.72	0.07	20	278	373	-0.04	[44]
C22:0	methyl-behenate (C ₂₃ H ₄₆ O ₂)	-2.56	781.24	143.37	0.03	9	333	373	-0.04	[44]
C22:1	methyl-erucate (C ₂₃ H ₄₄ O ₂)	-2.51	753.18	138.80	0.30	18	278	363	-0.04	[44]
C24:0	methyl-lignocerate (C ₂₅ H ₅₀ O ₂)	-2.54	809.36	144.42	0.07	8	338	373	-0.04	[44]
Fatty acids ethyl esters (FAEE)										
C10:0	ethyl-caprate (C ₁₂ H ₂₄ O ₂)	-3.57	954.79	76.71	0.11	16	278	353	+0.05	[46]
C12:0	ethyl-laurate (C ₁₄ H ₂₈ O ₂)	-3.24	859.64	100.52	0.10	15	283	353	+0.05	[46]
C14:0	ethyl-myristate (C ₁₆ H ₃₂ O ₂)	-3.14	866.33	108.57	0.14	15	283	353	+0.05	[46]
C16:0	ethyl-palmitate (C ₁₈ H ₃₆ O ₂)	-3.42	1045.30	95.11	0.57	18	298	513	+0.05	[46]
C18:0	ethyl-stearate (C ₂₀ H ₄₀ O ₂)	-3.04	920.00	115.98	0.01	11	313	363	+0.05	[46]
C18:1	ethyl-oleate (C ₂₀ H ₃₈ O ₂)	-2.65	761.20	126.97	0.10	18	278	363	-0.09	[46]
C18:2	ethyl-linoleate (C ₂₀ H ₃₆ O ₂)	-2.64	754.47	119.01	0.44	18	278	363	-0.09	[44]
C18:3	ethyl-linolenate (C ₂₀ H ₃₄ O ₂)	-2.68	800.68	100.87	0.05	20	278	373	-0.09	[44]
C20:0	ethyl-arachidate (C ₂₂ H ₄₄ O ₂)	-2.96	933.05	119.32	0.17	12	318	373	+0.05	[44]

$$AAD = \frac{\eta_{cal} - \eta_{exp}}{\eta_{exp}} \times 100 \quad (\text{Eq. 10})$$

The overall average absolute deviation (OAAD) was calculated as a summation of the modulus of AAD over N_p experimental data points. The OAAD was calculated by:

$$OAAD = \frac{\sum AAD}{n_{exp}} \quad (\text{Eq. 11})$$

3.1. Viscosity of individual FAMES

Viscosities of FAME commonly present in biodiesel fuels were correlated to temperatures by the Vogel equation. The Vogel equation constants in Eq.2 for dynamic viscosity are given in Table 1.

The experimental data published in the literatures was compared for the same systems. The relative deviations for the FAMES and FAEEs are within 3%, at high temperatures that show large deviations when compared from different authors.

3.2. Viscosity of biodiesel fuels

The proposed mass fraction mixing rule in this work was applied to predict the viscosity of 47 biodiesel mixtures whose FAME/FAEE compositions at different temperatures were taken from the literature. The FAME/FAEE compositions of these fuels are listed in Tables 2 and 3.

Using Vogel equation constants and correction factor (listed in Table 1), viscosities of biodiesel fuels at a given temperature can be easily calculated. Prediction of dynamic viscosity at different temperatures for 47 biodiesel mixtures is given in Tables 4 and 5 and Figure 4 for some samples. For these 47 biodiesels, minimum and maximum absolute deviations between experimental and predicted values of 0.58 - 9.48% were obtained respectively (except for 3 mixtures).

In most of the cases, predicted values for biodiesel mixtures are in close agreement with the measured data, with prediction errors of less than 4% in the temperature range of 293 - 373K. However, at high temperature (higher than 373K, up to 393K) for the three biodiesel fuels (BioD 32, 33, 34), maximum errors were underestimations of around 12 - 18% compared to experimental data. Figure 4 shows the dynamic viscosity of some sample biodiesels as obtained in the present study.

These results indicate that viscosity prediction of FAMES/FAEEs biodiesel can be performed with good accuracy from the empirical approach proposed in this

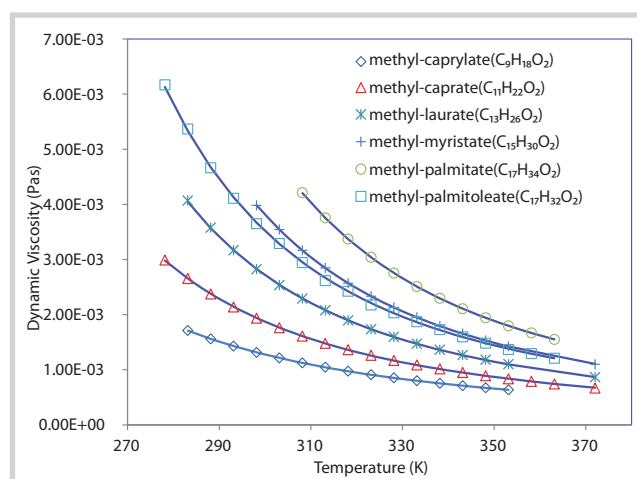


Figure 1. Dynamic viscosity of FAMES as a function of temperature. Experimental data (symbols) gathered from the literature (Table 1) and calculated values (lines) obtained in this work

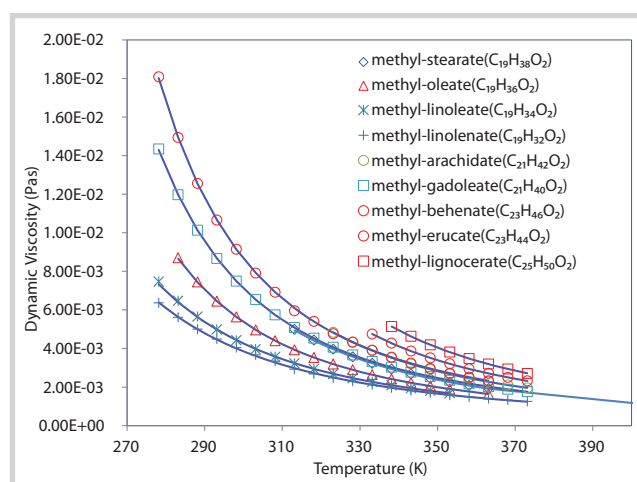


Figure 2. Dynamic viscosity of FAMES as a function of temperature. Experimental data (symbols) gathered from the literature (Table 1) and calculated values (lines) obtained in this work

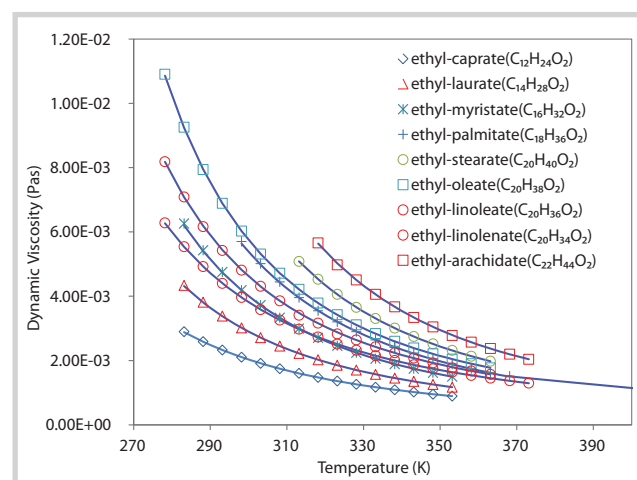


Figure 3. Dynamic viscosity of FAEEs as a function of temperature. Experimental data (symbols) gathered from the literature (Table 1) and calculated values (lines) obtained in this work

work. The results obtained for the complete data sets of biodiesels are summarised in Tables 4 and 5, in which AADs are compared with the corresponding values obtained for previously reported models.

Various studies were conducted to estimate viscosity of different biodiesel mixtures at various temperatures. The effect of the biodiesel blends' fraction and temperature on the dynamic viscosity of

Table 2. Composition of the biodiesel studied, FAME in mass fraction

Mixture	C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1	C24:0	Ref data
BioD-1	-	-	-	-	0.1129	-	0.0396	0.1998	0.5839	0.0586	-	-	0.0052	-	-	[12]
BioD-2	-	-	-	-	0.4150	-	0.0490	0.4010	0.1350	-	-	-	-	-	-	[13]
BioD-3	-	0.0010	-	0.0010	0.1510	0.0090	0.0710	0.4470	0.3140	0.0020	0.0020	-	0.0020	-	-	[13]
BioD-4	-	0.0460	0.2533	0.2303	0.1500	-	0.0493	0.2071	0.0578	0.0058	-	-	0.0005	-	-	[12]
BioD-5	-	0.0359	0.1976	0.1797	0.1419	-	0.0472	0.2055	0.1734	0.0174	-	-	0.0015	-	-	[12]
BioD-6	-	0.0304	0.1675	0.1523	0.1375	-	0.0460	0.2046	0.2359	0.0237	-	-	0.0021	-	-	[12]
BioD-7	-	0.0254	0.1403	0.1275	0.1335	-	0.0450	0.2038	0.2925	0.0294	-	-	0.0026	-	-	[12]
BioD-8	-	0.0201	0.1110	0.1010	0.1292	-	0.0439	0.2030	0.3533	0.0355	-	-	0.0031	-	-	[12]
BioD-9	-	0.0100	0.0551	0.0501	0.1210	-	0.0417	0.2014	0.4695	0.0471	-	-	0.0042	-	-	[12]
BioD-10	-	0.0050	0.0278	0.0253	0.1170	-	0.0407	0.2006	0.5261	0.0528	-	-	0.0047	-	-	[12]
BioD-11	-	0.0425	0.2344	0.2142	0.1685	-	0.0463	0.1995	0.0946	-	-	-	-	-	-	[12]
BioD-12	-	0.0410	0.2260	0.2067	0.1711	-	0.0455	0.1980	0.1117	-	-	-	-	-	-	[12]
BioD-13	-	0.0358	0.1971	0.1810	0.1801	-	0.0430	0.1928	0.1704	-	-	-	-	-	-	[12]
BioD-14	-	0.0358	0.1971	0.1810	0.1801	-	0.0430	0.1928	0.1704	-	-	-	-	-	-	[12]
BioD-15	-	0.0161	0.0888	0.0850	0.2135	-	0.0334	0.1734	0.3898	-	-	-	-	-	-	[12]
BioD-16	-	0.0099	0.0548	0.0548	0.2240	-	0.0304	0.1672	0.4588	-	-	-	-	-	-	[12]
BioD-17	-	0.0051	0.0281	0.0311	0.2322	-	0.0281	0.1625	0.5129	-	-	-	-	-	-	[12]
BioD-18	-	0.0510	0.2811	0.2556	0.1541	-	0.0504	0.2079	0.0000	-	-	-	-	-	-	[12]
BioD-19	0.0002	-	-	0.0008	0.1049	0.0012	0.0427	0.2420	0.5136	0.0748	0.0036	0.0028	0.0040	0.0007	0.0014	[14]
BioD-20	-	-	-	0.0170	0.1947	-	0.1438	0.5467	0.0796	0.0069	0.0025	0.0052	0.0021	-	-	[14]
BioD-21	0.0920	0.0640	0.4870	0.1700	0.0770	-	0.0220	0.0540	0.0220	-	-	-	-	-	-	[14]
BioD-22	-	-	-	-	0.4060	-	0.0510	0.4280	0.1100	0.0050	-	-	-	-	-	[14]
BioD-23	-	-	-	-	0.0420	-	0.0170	0.5680	0.2170	0.1570	-	-	-	-	-	[14]
BioD-24	-	-	-	0.0062	0.2409	-	0.0256	0.1574	0.5699	-	-	-	-	-	-	[12]
BioD-25	-	-	-	-	0.1618	-	0.0382	0.2880	0.5046	-	-	-	-	-	-	[15]
BioD-26	-	-	-	0.0007	0.1078	0.0007	0.0395	0.2302	0.5366	0.0703	0.0038	0.0023	0.0080	-	-	[15]
BioD-27	-	-	-	0.0180	0.0470	0.0470	0.0190	0.7113	0.0989	-	0.0589	-	-	-	-	[15]
BioD-28	-	-	0.0002	0.0007	0.0641	0.0009	0.0423	0.2393	0.6425	0.0012	-	0.0003	0.0077	0.0008	-	[15]
BioD-29	-	0.0001	0.0004	0.0007	0.0526	0.0020	0.0163	0.6249	0.2094	0.0699	0.0060	0.0123	0.0135	0.0019	-	[15]
BioD-30	-	0.0003	0.0025	0.0057	0.4252	0.0013	0.0403	0.4199	0.0981	0.0009	0.0036	0.0015	0.0009	-	-	[15]
BioD-31	-	-	0.0002	0.0013	0.1057	0.0013	0.0266	0.4105	0.3667	0.0710	0.0044	0.0067	0.0045	0.0012	-	[15]
BioD-32	-	0.0001	0.0004	0.0007	0.1076	0.0007	0.0394	0.2296	0.5353	0.0702	0.0038	0.0023	0.0080	0.0024	0.0022	[16]
BioD-33	-	-	0.0003	0.0007	0.0522	0.0020	0.0162	0.6211	0.2107	0.0695	0.0060	0.0135	0.0035	0.0019	-	[16]
BioD-34	-	-	-	0.0009	0.0890	0.0015	0.0276	0.4182	0.3751	0.0702	0.0046	0.0068	0.0046	0.0012	-	[16]
BioD-35	0.0750	0.0600	0.5330	0.1710	0.0730	-	0.0190	0.0550	0.0140	-	0.0020	-	-	-	-	[17]
BioD-36	-	-	-	-	0.1050	0.0040	0.0270	0.4660	0.3010	0.0100	0.0130	0.0140	0.0240	-	0.0350	[17]
BioD-37	-	-	-	-	0.0580	0.0080	0.0170	0.6000	0.1990	0.0960	0.0070	0.0160	-	-	-	[17]
BioD-38	-	-	0.0040	0.0130	0.4810	0.0030	0.0400	0.3730	0.0800	0.0020	0.0030	0.0010	-	-	-	[17]
BioD-39	-	-	-	-	0.0420	0.0040	0.0200	0.5740	0.2130	0.1120	0.0120	0.0210	0.0010	-	-	[17]
BioD-40	-	-	-	-	0.0580	0.0080	0.0160	0.6000	0.1990	0.0960	0.0070	0.0160	-	-	-	[17]
BioD-41	0.0750	0.0600	0.5330	0.1710	0.0730	-	0.0190	0.0550	0.0140	-	-	-	-	-	-	[17]
BioD-42	-	-	0.0040	0.0130	0.4810	0.0030	0.0400	0.3730	0.0800	0.0020	0.0030	0.0010	-	-	-	[17]
BioD-43	-	-	-	-	0.0420	0.0040	0.0200	0.5740	0.2130	0.1120	0.0120	0.0210	0.0010	-	-	[17]

Table 3. Composition of the biodiesel studied, FAEE in mass fraction

	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	Ref data
BioD-44	-	-	-	0.0840	0.0303	0.4933	0.3329	0.0595	-	[18]
BioD-45	-	-	-	0.1162	0.0290	0.2695	0.5274	0.0579	-	[18]
BioD-46	-	0.0066	0.0087	0.4029	0.0457	0.4361	0.1000	-	-	[18]
BioD-47	-	-	-	0.4260	0.0470	0.3930	0.1340	-	-	[18]

Table 4. Dynamic viscosity prediction of 47 biodiesel mixtures at different temperatures. Comparison between experimental data reported in literatures and predicted values of this work

Mixture	Npt	T range (K)	OAAD (%)	Ref data	Mixture	Npt	T range (K)	OAAD (%)	Ref data
BioD-1	5	293 - 373	10.19%	[12]	BioD-25	18	278 - 363	1.04%	[15]
BioD-2	14	293 - 358	5.40%	[13]	BioD-26	18	278 - 363	2.26%	[15]
BioD-3	14	293 - 358	7.38%	[13]	BioD-27	18	278 - 363	1.80%	[15]
BioD-4	5	293 - 373	5.53%	[12]	BioD-28	18	278 - 363	1.46%	[15]
BioD-5	5	293 - 373	2.06%	[12]	BioD-29	18	278 - 363	1.57%	[15]
BioD-6	5	293 - 373	1.34%	[12]	BioD-30	18	278 - 363	1.48%	[15]
BioD-7	5	293 - 373	2.23%	[12]	BioD-31	18	278 - 363	2.21%	[15]
BioD-8	5	293 - 373	3.46%	[12]	BioD-32	6	278 - 363	12.59%	[16]
BioD-9	5	293 - 373	7.01%	[12]	BioD-33	6	278 - 363	14.89%	[16]
BioD-10	5	293 - 373	8.73%	[12]	BioD-34	6	278 - 363	18.22%	[16]
BioD-11	5	293 - 373	6.16%	[12]	BioD-35	1	313	0.96%	[17]
BioD-12	5	293 - 373	5.96%	[12]	BioD-36	1	313	9.48%	[17]
BioD-13	5	293 - 373	5.10%	[12]	BioD-37	1	313	6.50%	[17]
BioD-14	5	293 - 373	1.56%	[12]	BioD-38	1	313	3.41%	[17]
BioD-15	5	293 - 373	2.02%	[12]	BioD-39	1	313	5.34%	[17]
BioD-16	5	293 - 373	1.37%	[12]	BioD-40	1	313	6.33%	[17]
BioD-17	5	293 - 373	1.07%	[12]	BioD-41	1	313	0.58%	[17]
BioD-18	5	293 - 373	7.27%	[12]	BioD-42	1	313	3.41%	[17]
BioD-19	5	293 - 373	1.79%	[14]	BioD-43	1	313	5.34%	[17]
BioD-20	5	293 - 373	2.97%	[14]	BioD-44	9	283 - 363	5.32%	[18]
BioD-21	5	293 - 373	1.38%	[14]	BioD-45	9	283 - 363	0.83%	[18]
BioD-22	5	293 - 373	2.45%	[14]	BioD-46	9	283 - 363	3.98%	[18]
BioD-23	5	293 - 373	1.05%	[14]	BioD-47	14	283 - 363	6.18%	[18]
BioD-24	5	293 - 373	1.25%	[12]					

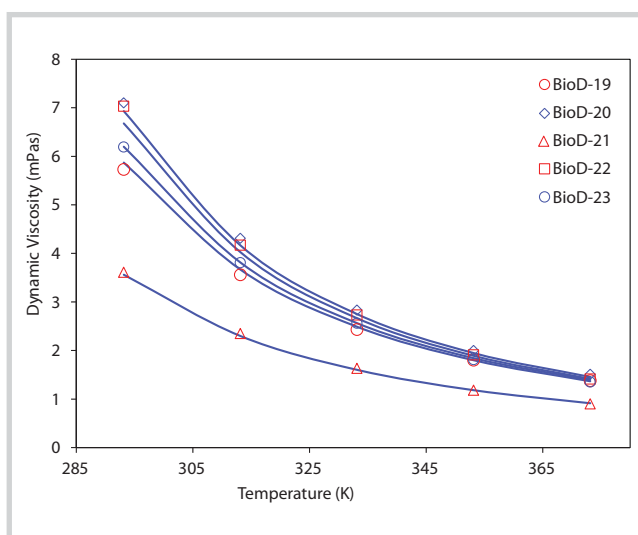


Figure 4. Temperature effects on dynamic viscosity for biodiesel mixtures, symbols are experimental data, line are calculated results in this work

biodiesel was investigated and corresponding models were proposed.

Different empirical correlations have been developed, such as Chavarria-Hernandez [47], do Carmo [48], Yuan [14, 46], Ramirez-Verduzco [27], and Ceriani [26], which relate various performance parameters with viscosity of biodiesel, and compared to deviation obtained

in this work, in most of the cases, the maximum deviation obtained in this work is lower than other models published.

Although only 47 actual biodiesel fuels were tested, the method presented in this study can be extended to any type of methyl ester biodiesel fuel with known ester composition. For the ethyl ester biodiesel fuel, more experimental data is needed to validate the model. The applicable temperature of this method can be extended up to the temperature of 373K of the fuels because of the limitation of the Vogel equation. Below 278K, this method should be used with caution when the temperature is reduced down to the cloud point of the fuel, depending on the components.

4. Conclusions

Viscosity is one of the most significant properties of biodiesel, because of its major effect on the engine performance. For this reason, reliable mathematical models that accurately describe the dynamic viscosity of biodiesel as a function of temperature are of great interest for the development of combustion models as well as for the design of process equipment. Based on these requirements, this work has been performed to:

Table 5. Comparison of AADs obtained by using equations of this work as well as 7 other different models applied to the same data bank of biodiesel mixtures

Mixture	Npt	T range (K)	Chavarria-Hernandez [47]	do Carmo [48]	Yuan [46]	Ramirez-Verduzco [27]	do Carmo [48]	Yuan [14]	Ceriani [26]	This work	Ref data
BioD-41	1	[313,15]	3.32	0.00	7.49	2.50	6.99	9.65	9.21	0.58	[17]
BioD-36	1	[313,15]	3.44	0.09	2.48	4.54	2.14	0.92	3.67	9.48	[17]
BioD-37	1	[313,15]	0.51	3.13	0.21	2.57	4.59	1.40	2.38	6.50	[17]
BioD-38	1	[313,15]	2.30	9.89	1.95	3.00	11.63	2.84	1.01	3.41	[17]
BioD-39	1	[313,15]	0.79	2.73	0.22	1.42	4.46	1.94	3.23	5.34	[17]
BioD-19	5	[293,373]	2.55	5.43	1.57	2.86	5.67	2.21	11.08	1.79	[14]
BioD-20	5	[293,373]	5.45	12.96	6.79	8.57	13.19	7.92	8.12	2.97	[14]
BioD-21	5	[293,373]	4.22	1.82	7.14	7.42	6.22	9.10	10.62	1.38	[14]
BioD-22	5	[293,373]	5.97	11.47	5.97	7.91	12.50	6.26	7.70	2.45	[14]
BioD-23	5	[293,373]	5.32	2.80	3.67	3.66	2.83	4.68	12.17	1.05	[14]
BioD-18	5	[293,373]	5.45	1.48	0.37	3.01	4.07	1.43	3.56	7.27	[12]
BioD-1	5	[293,373]	12.45	0.40	4.44	13.43	0.65	4.69	11.78	10.19	[12]
BioD-24	5	[293,373]	12.87	6.28	13.52	4.86	6.21	14.01	22.36	1.25	[12]
BioD-25	15	[283,353]	5.71	0.18	4.59	4.71	0.39	5.24	7.78	1.04	[45]
BioD-26	18	[278,363]	2.59	5.38	2.37	2.45	5.78	2.98	8.74	2.26	[45]
BioD-27	15	[283,353]	4.71	10.53	7.30	6.91	9.71	8.08	5.27	1.80	[45]
BioD-28	17	[283,363]	5.29	2.52	5.41	4.03	3.28	6.19	11.29	1.46	[45]
BioD-29	18	[278,363]	3.69	9.72	5.92	5.50	10.77	6.03	6.65	1.57	[45]
BioD-30	16	[288,363]	4.89	11.89	5.48	7.03	13.12	5.94	4.79	1.48	[45]
BioD-31	18	[278,363]	2.50	1.56	2.63	2.72	2.06	3.38	7.27	2.21	[45]
BioD4-BioD10	35	[293,373]	5.16	4.06	7.74	6.98	6.18	8.72	13.39	4.34	[12]
BioD11-BioD17	35	[293,373]	2.88	0.48	2.59	3.03	2.76	3.48	7.40	3.32	[12]

Table 6. Comparison of AADs obtained by using model proposed in this work and other models applied to the same data bank of biodiesel mixtures

Mixture/ Ref data [18]	BioD-44	BioD-45	BioD-46
Model	AAD (%)	AAD (%)	AAD (%)
Ceriani et al. [8]	12.91	6.00	1.30
SRA [49]	16.31	9.16	4.44
NAK model [9]	14.72	8.12	2.18
Restricted NAK model [44]	12.10	6.89	0.81
This work	5.32	0.83	3.98

- Correlate the parameters of the Vogel equation for dynamic viscosity to the “best” experimental data collected in this study; applied to pure fatty acid methyl esters and fatty acid ethyl esters that are commonly present in biodiesel fuels. The maximum average absolute deviation of correlated dynamic viscosities for the alkyl esters was 0.73%, indicating that the Vogel equation closely represented the relationship between dynamic viscosity and the temperature of the alkyl esters;

- Propose modified mixing equation to predict biodiesel dynamic viscosity from their saturated and unsaturated esters composition, and therefore it can be extended to any type of alkyl ester biodiesel fuel with

known ester composition. However, impurities were not considered in the model developed in this study since the model was for mixtures of fatty acid methyl esters mainly.

- Suggest a simple correction factor, independent of temperature incorporated in a simple modified mixing equation that can be applied to all cases in predicting viscosity of variation biodiesel mixtures. The proposed method was used to predict viscosities of 47 biodiesel mixtures, compared with experimentally measured viscosities in the range of 278 - 393K and prediction overall average errors were less than 3.25%. If the considered temperature is outside of regression data, the model would have generated higher prediction errors.

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CATALYTIC PYROLYSIS OF WASTE TIRE USING NOBLE METALS-SUPPORTED HMOR CATALYSTS

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Summary

The catalytic pyrolysis of waste tire over bifunctional catalysts, based on noble metals (Pt, Ru, Re, Rh) supported on HMOR zeolite, was investigated in a semi-batch reactor. The prepared catalysts were characterised by H_2 -chemisorption, TPR, TPD of H_2 and NH_3 , XRD, N_2 -adsorption/desorption and ICP, whereas the spent catalysts were analysed by TPO and XRF. The pyrolysis results indicated an important increase in the yield of gaseous product at the expense of liquid yield when the bifunctional catalysts were introduced. Moreover, the contents of polycyclic and polar-aromatics decreased drastically for all prepared catalysts; and, the reduction of aromatics was more pronounced for poly- and polar-aromatics than for di-aromatics. As a consequence, the derived oils were much lighter and contained high concentration of saturates. The catalytic activity of the studied catalysts for light oil production as well as aromatic reduction can be summarised as followed: $Ru/HMOR > Rh/HMOR > Pt/HMOR >> Re/HMOR$. Additionally, the catalytic activity under the studied conditions for the current catalysts was independent on the metal dispersion as well as the total concentration of acid sites, but dependent on the intrinsic nature of the metal used. The best performance of Ru catalyst was found to relate to its highest sulfur tolerance and coke resistance.

Key words: Pyrolysis, waste tire, bifunctional catalyst, Ru, Re, Rh, Pt, MOR.

1. Introduction

Tire pyrolysis essentially produces a carbonised char, condensable oil and a gas fraction. Gas fraction has been reported to have high calorific value [1], and high hydrogen content [2 - 4], whereas the tire-derived oil was shown to be similar, to a certain extent, to the commercial petroleum naphtha [5]. However, the high concentration of aromatic hydrocarbons (HCs) [5 - 7], especially polycyclic HCs (PAHs), has limited its application as a fuel since a higher smoke, hydrocarbon (HC) and CO emissions were recorded when pyrolysis oil was used in an engine [8]. Our previous study [9], a first step in the attempts to study the possibility of fuel production from waste tire, has shown that the mordenite-catalysed pyrolysis of waste tire produced the oil having high selectivity toward gasoline, kerosene and gas oil fractions. However, a relatively high amount of polycyclic aromatics and polar-aromatics still existed in the oil.

Bifunctional catalysts with both metal and acid functions are extensively studied for the reduction of aromatics in fuels [10 - 13]. Castano et al. studied the aromatics reduction of pyrolysis gasoline over HY-supported catalysts using Pt, Pd, Ir and Ni, and reported that Ir-catalyst was the most effective among the studied catalysts due to its greater metal dispersion, stronger acidity, hydrogen adsorption capacity and metal surface exposure [14]... Meanwhile, Albertazzi et al. investigated the hydrogenation of naphthalene of various metals (Rh, Pd, Pt, Ru, Ir)-supported catalysts and found that the catalytic activity of Rh and Pd-catalysts is higher than that of Ir, Ru, Pt-based catalysts [15].

The aim of this work is to investigate the catalytic activity of noble metals (Ru, Pt, Re, Rh) supported on HMOR catalysts for waste tire pyrolysis. The influences of various noble metal-based catalysts on the nature and yield of products, particularly the pyrolytic oil will be discussed in relation with the catalyst characterisation results.

2. Experiments

2.1. Catalyst preparation

Mordenite (MOR, H-form, SiO_2/Al_2O_3 mole ratio = 19, surface area (BET) = $380\text{m}^2/\text{g}$) zeolite (TOSOH, Singapore) was first calcined in air at 500°C for 3 hours. Then, it was loaded with noble metals, Ru ($RuCl_3$, FLUKA), Rh ($Rh(NO_3)_3$, ALDRICH), Re ($ReCl_3$, FLUKA), Pt ($Pt(NO_3)_3$, FLUKA), using the incipient wetness impregnation technique to obtain 1%wt noble metal-supported catalysts. Then, the samples were dried in the oven at 110°C for 3 hours followed by calcination in a flow of air at 500°C for 3 hours. Next, they were pelletised, ground, and then sieved to specific particle sizes of 400 - $425\mu\text{m}$. Prior to the catalytic activity measurement, the catalysts were reduced at 400°C by H_2 for 3 hours.

2.2. Catalyst characterisation

The composition of the prepared catalysts was determined by Inductively Coupled Plasma (ICP) technique using a Perkin Elmer Optima 4300 PV machine after the dissolution of the catalysts using HF solution. The surface area (BET) and pore volume (B.J.H) of the prepared

samples were characterised by N_2 physical adsorption using the Sorptomatic 2900 equipment. XRD patterns were obtained using the Rigaku D/Max 2200H using $CuK\alpha$ small radiation, and operated at 40KV and 30mA. The catalyst samples were scanned from 5 to 60 degrees ($2\theta/\theta$) with a scanning speed of $5^\circ/\text{min}$.

Hydrogen chemisorption was carried out using a conventional laboratory made-up system equipped with a TCD detector. Prior to performing the chemisorption at room temperature, an approximate 50mg of reduced sample was pretreated in helium at 150°C for 0.5 hour. Dispersion data was calculated by assuming a stoichiometry $H/Ru = 1$ [13]. Temperature-programmed desorption (TPD) using NH_3 was conducted in a TPD/TPR Micromeritics 2900 apparatus. Approximately 0.1g of sample was first pretreated in He at 150°C for 30 minutes. Then, the system was cooled to 100°C , and the NH_3 adsorption was performed using NH_3/N_2 for 1.5 hours followed by the introduction of He to remove the physically adsorbed NH_3 for 30 minutes at 100°C . Finally, the system was cooled to 50°C , and then the temperature program desorption was started from 50°C to 600°C with a heating rate of $5^\circ\text{C}.\text{min}^{-1}$. For Temperature-programmed reduction (TPR) using hydrogen, the calcined sample was heated to 150°C and kept at this temperature for 1 hour under the flow of helium to remove water and other contaminants. TPR profiles were recorded with a temperature program from room temperature to 700°C ($10^\circ\text{C}/\text{min}$). TPD- H_2 was conducted using the same Micromeritics apparatus. The reduced sample was pretreated by helium flow at 150°C and then cooled to room temperature. H_2 adsorption was performed at room temperature for 0.5 hour using UHP H_2 followed by flushing with helium at the same temperature for another 0.5 hour. The TPD- H_2 was performed from room temperature to 600°C at a rate of $10^\circ\text{C}/\text{min}$ under helium flow. The amount of desorbed hydrogen was monitored by a TCD. Temperature-programmed oxidation (TPO) was performed using the apparatus for TPR from room temperature to 900°C ($10^\circ\text{C}.\text{min}^{-1}$), and the final temperature was held for 30 minutes. The amount of coke was then determined from the area under the curve and calculated by the software equipped with the machine. The sulfur contents in the spent catalysts were determined by X-ray fluorescence (XRF) spectrometer, Philips PW2400. The catalyst characterisation was done in the Lab at the Petroleum and Petrochemical College, Chulalongkorn University.

2.3. Pyrolysis of waste tire

A used passenger car tire for pyrolysis has a lifetime of 50,000km. The tire was shredded and crumbed to produce a size range of 0.5 - 1.4mm. The granulated sample was sieved, and the portion with 0.5 - 0.6mm size (30 mesh) was selected for testing.

The detail of pyrolysis process was described elsewhere [9]. Briefly, a tire sample was pyrolysed in the lower zone of the reactor (500°C), and then the evolved product was carried to the upper zone packed with a catalyst (350°C). The obtained product was next passed through a condensing system to separate incondensable compounds from the liquid product. The gas product was stored in a gas bag. The solid and liquid products were weighed to determine the product distribution. The amount of gas was then determined by mass balance. The gaseous product was analysed by a GC equipped with an FID. Prior to being analysed, the liquid product was dissolved in n-pentane to precipitate asphaltenes. The obtained maltenes was analysed by liquid adsorption chromatography [16]. As a consequence, saturated hydrocarbons, mono-, di-, poly- and polar-aromatics in the maltenes were fractionated. Finally, a SIMDIST GC was used to analyse the obtained maltene and hydrocarbon fractions according to the ASTM D2887 method to determine the simulated true boiling point curves. The petroleum fractions were then cut based on their boiling point, including naphtha ($< 200^\circ\text{C}$), kerosene (200°C - 250°C), gas oil (250°C - 370°C) and residue ($> 370^\circ\text{C}$).

3. Results and discussion

3.1. Catalyst Characterisation

The amounts of metal loaded on each sample determined by ICP are presented in Table 1. Accordingly, the true numbers were very close to the targeted values. Figure 1 shows the diffraction patterns of the reduced catalysts and HMOR support. Compared to the bare HMOR zeolite, the bifunctional catalysts showed a slight decrease in crystallinity, as deduced from the intensity of peaks at 2θ of 19.76° , 22.46° , 25.76° . However, the peaks corresponding to the metal species were hard to detect, possibly because of the amount of metal loaded was below the detectable range of the machine.

Several structure properties of the prepared catalysts obtained from N_2 adsorption/desorption analysis are also shown in Table 1. The incorporation of noble metal decreased both surface area and pore volume of the

parent zeolite support. And, all the prepared catalysts had comparable surface area and pore volumes.

Metal dispersion determined by H_2 -chemisorption is also given in Table 1. It can be seen that there existed small difference between the metal dispersion among all the prepared samples. However, the order of metal dispersion can be summarised as followed: Pt/HMOR > Re/HMOR > Ru/HMOR > Rh/HMOR. In addition, the average metallic particle size in all catalysts was in the range of 2.5nm to 4nm, which was much larger than the pore diameter of the main channel of HMOR zeolite. This, together with the decrease in both surface area and pore volume of the parent zeolite after incorporation of metal, suggested the occurrence of pore blockage and/or the diffusion of noble metal into the zeolite channels.

The acid site strength and concentration in the reduced M/HMOR were revealed by TPD of ammonia and the obtained results are presented in Figure 2. In a good agreement with the TPD- NH_3 study by [17], the ammonia desorption curve of HMOR showed two desorption peaks. The first one located at around 200°C, and the second one peaked at around 540°C, which corresponded to the weak and strong acid sites, respectively. And one should be noted that the weaker acid sites were located closer to the surface, whereas the strong acid sites were

located in the deepest part of the zeolite structure [14]. From the figure, obviously the incorporation of noble metals led to a reduction in the intensity of desorption peaks, particularly the peak corresponding to the strong acid sites for all sample. This effect is because a fraction of -OH groups was eliminated by reaction with the metal salt precursors during catalyst preparation and/or the blockage of metal particle decreasing the accessible acid sites, particularly the ones inside the zeolite channels. And the order of total acid site concentration for noble metal-supported catalysts was as follow: Ru/HMOR > Pt/HMOR > Re/HMOR > Rh/HMOR. In the TPD- NH_3 spectra of Rh and Pt catalysts, the number of strong acid sites decreased drastically, suggesting the diffusion of these metal into the zeolite channels, or in other words, higher metal dispersion, which was in good agreement with H_2 -chemisorption and N_2 -adsorption/desorption results. Surprising us was the TPD- NH_3 profile of the Ru/HMOR, in which a new peak at around 280°C was observed at the temperature in the range corresponding to weak acid sites (Figure 2). This new peak can be attributed to ruthenium clusters since this metal was reported to have high tendency to adsorb ammonia [12] and/or the interaction between metal and support for Ru-based catalyst [18].

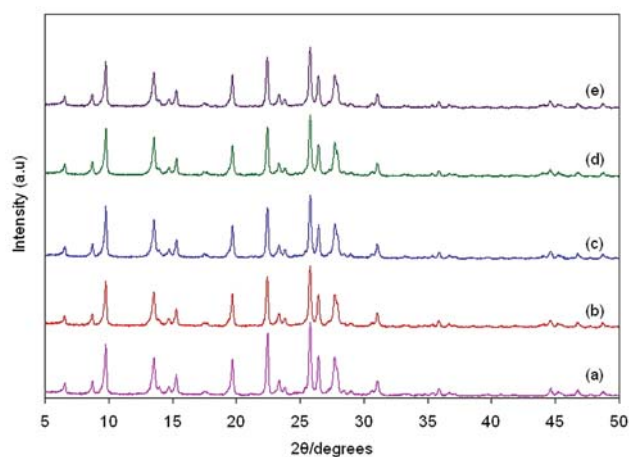


Figure 1. XRD patterns of (a) HMOR, (b) Ru/HMOR, (c) Rh/HMOR, (d) Re/HMOR, and (e) Pt/HMOR

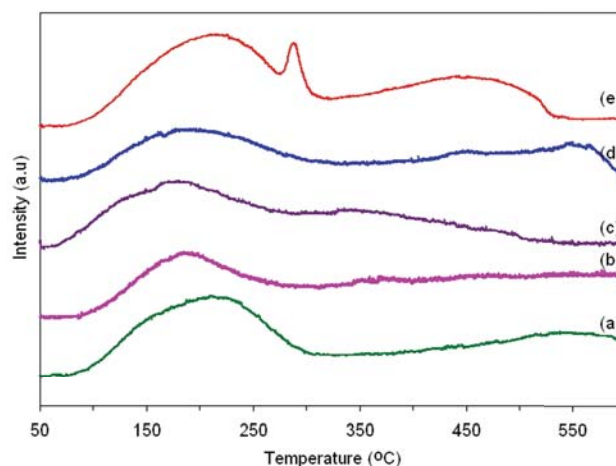


Figure 2. TPD- NH_3 profiles of (a) HMOR, (b) Pt/HMOR, (c) Rh/HMOR, (d) Re/HMOR, and (e) Ru/HMOR

Table 1. Physical and chemical properties of the studied catalysts

Catalyst	M ¹ %wt	Dispersion (%)	Surface area (m ² .g ⁻¹)	Pore volume (cm ³ .g ⁻¹)	Asphaltenes (g.g ⁻¹ oil)	Coke (% wt)
HMOR	-	-	372.5 ± 9.3	0.231		14.7
Pt/HMOR	0.94	30.8	359.8	0.208	0.000494	21.3
Re/HMOR	0.97	35.4	350.5	0.212	0.000654	29.7
Rh/HMOR	1.02	27.3	352.7	0.217	0.000387	20.8
Ru/HMOR	0.98	21.1	354.9	0.204	0.000309	16.4

¹Metal content in % weight (%wt) in the prepared catalyst

Temperature-programmed reduction is a powerful technique to study the reduction behavior of oxide phases or salts, as well as providing information regarding the degree of interaction between metal and support. Mordenite is comprised of two channel types: (i) larger channel, also called main channel, accessible through twelve member oxygen rings with an opening of $7.0 \text{ \AA} \times 6.5 \text{ \AA}$, and (ii) smaller channels, often referred to as side-pockets, which include eight member oxygen rings with $3.4 \text{ \AA} \times 4.8 \text{ \AA}$ [19]. Thus, hydrogen with a kinetic diameter of 0.24 nm can enter the inner zeolite structure and the reduction of metal oxides/salts may occur somewhere on the zeolite surface, in the zeolite channels or in the side-pockets [10]. Another important outcome of TPR analysis, therefore, is the location of species in the zeolite. The TPR profiles of all prepared catalysts are shown in Figure 3.

As expected, the TPR profile of the HMOR zeolite showed no peaks. The profile of Rh catalyst showed the two overlapping peaks, maxima at 110°C and 135°C

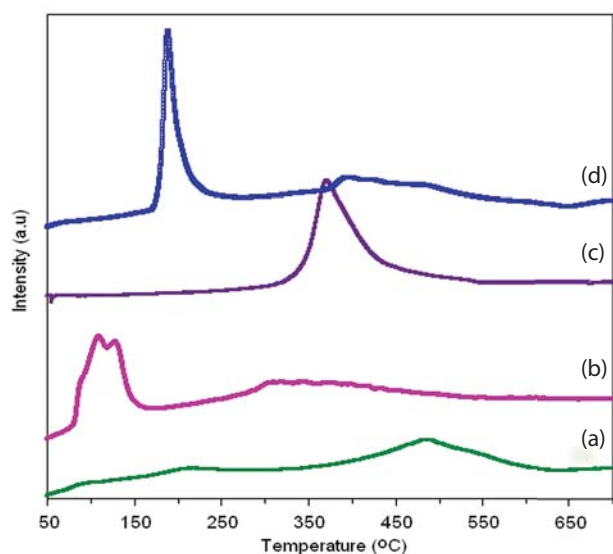


Figure 3. TPR- H_2 profiles of (a) Pt/HMOR, (b) Rh/HMOR, (c) Re/HMOR, and (d) Ru/HMOR

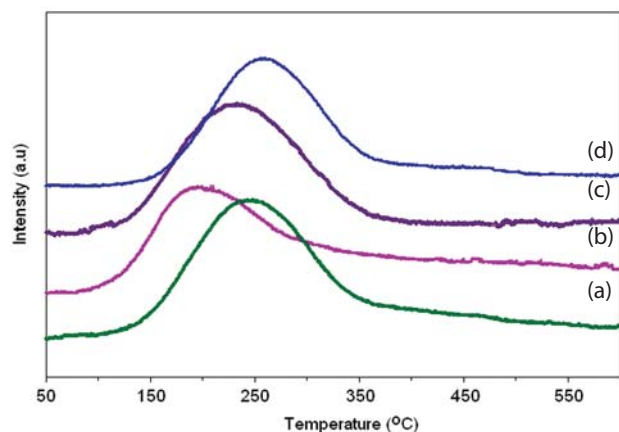


Figure 4. TPD- H_2 profiles of (a) Pt/HMOR, (b) Rh/HMOR, (c) Re/HMOR, and (d) Ru/HMOR

that can be attributed to the reduction of Rh(3) in two different environment [20]. These might not be necessary two different electronic states but possibly by Rh_2O_3 with different metal particle sizes, which interact in a different way with the support [20]. Another very broad and low intense peak was also observed at around 350°C in the H_2 -consumption curve of Rh-catalyst, suggesting the presence of rhodium species in a more difficult for reduction environment. The TPR result of Pt/HMOR catalyst showed a unique, very broad peak with a maximum occurring at around 498°C . The broad peak suggested the reduction of platinum species located at different environments. Taking into account XRD measurements (Figure 1) and the study of Castano et al. [14], this peak can be ascribed to the reduction of Pt(2) located in the main channel and/or the side-pockets in the zeolite. The hydrogen consumption curve of Re catalyst showed a unique, fairly broad peak at approximate 370°C . The widening of the peak was possibly due to the reduction of rhenium species located in different environments. The Ru/HMOR exhibited a main peak centered at about 198°C . The very intense peak was possibly due to the reduction of Ru(3) poorly dispersed on the surface of the zeolite [21]. The profile also showed a small and ill-defined band of hydrogen consumption between 350°C and 450°C which could correspond to a small amount of ruthenium oxide or oxychloride formed by the exposition and drying in air during catalyst preparation [12].

Figure 4 depicts the TPD- H_2 profiles of all prepared catalysts. Accordingly, TPD profile of the bared zeolite support showed no peak. And all profiles exhibited a unique peak located at temperatures lower than 350°C corresponding to the desorption of hydrogen that chemically adsorbed on the surface of the metallic particles. Considering the intensity of the peak, which is the indication of the hydrogen adsorption on the metallic sites, the observed trend was: $\text{Re} > \text{Pt} > \text{Ru} > \text{Rh}$. This result was in a good agreement with the H_2 -chemisorption analysis.

All TPO profiles of the spent catalysts had two peaks (not shown here). The first one located at around 350°C is most likely due to the oxidation of adsorbed hydrocarbon species, which could be formed from condensed polycyclic compounds [22]. And the peak at basically $500 - 600^\circ\text{C}$ might be attributed to the oxidation of deposited carbon species [23]. The quantitative analysis calculated the temperatures of $250^\circ\text{C} - 800^\circ\text{C}$ is shown in Table 1. Generally, the order of the amount of coke on the spent catalysts is $\text{Re} > \text{Rh} > \text{Pt} > \text{Ru}$.

3.2. Pyrolysis products

3.2.1. Product yields

Figure 5 shows the product distribution, i.e. yield of gas, liquid and solid product, with all catalysts prepared. It can be seen that in the non-catalytic pyrolysis, the yields (%wt) of solid, liquid and gas were approximate 47, 42 and 11, respectively. The solid product was mainly carbonaceous material and therefore, as expected, the yield of solid obtained from all runs was similar. This is attributed to the fact that the pyrolysis conditions were kept constant and the tire was reported to be completely decomposed at 500°C [9].

The presence of catalysts strongly influenced the yield of gas and liquid products. Generally, the use of noble metal supported catalysts increased the gas yield, and the order of gas production was Ru > Pt > Rh > Re > none. It is well known that the products obtained from waste tire pyrolysis contain high concentration of aromatics [5 - 7]. In addition, the catalytic cracking of aromatics should require in a first step the hydrogenation of the aromatic ring over metallic clusters, producing (partial) hydrogenated compounds, which rapidly undergo cracking and/or ring-opening on the acid sites. Meanwhile, all the noble metals used in this study have been reported to exhibit good hydrogenation activity, particularly for the hydrogenation of aromatics and/or desulfurisation [14, 15]. Therefore, a higher conversion of hydrocarbons, especially the aromatics can be achieved with noble metal-supported catalysts. Consequently, the yield of gaseous product increased, whereas that of oil fell off in this paper, when noble metal-supported catalysts were used. The high activity of the noble metal-supported catalysts also led to a drastic asphaltene reduction, as shown in Table 1.

3.2.2. Petroleum fractions

The influences of various noble metal-based catalysts on the petroleum fractions of the derived oils were illustrated in Figure 6. It can be seen that the bifunctional catalysts strongly influenced the contents of petroleum fractions in the oils. And different noble metal-supported catalysts produced oil with different petroleum cuts.

In the non-catalytic oil, although the content of naphtha was the highest (~30%), but there existed a high portion of hydrocarbons distributed in the heavy fractions like residues, gas oil. The treatment of noble metal-supported catalyst led to a shift of hydrocarbons from heavy fractions toward lighter fractions, particularly naphtha, indicating that lighter oils were produced.

The high activity of noble metal-supported catalysts for light oil production, again, can be attributed to their bifunctionalities, as mentioned earlier. In general, the order of naphtha production (Figure 6) for different metals was as follow: Ru > Pt > Rh > Re. This order was similar to the order of catalytic activity for conversion of waste tire to gaseous product (Figure 5). However, it should be noted that the activity for naphtha production of Re/HMOR was lower than that of only the zeolite support, HMOR.

3.2.3. Composition of the obtained oil

The oil obtained from non-catalytic pyrolysis contained high concentration of aromatic hydrocarbons, particularly high content of polar-aromatics (~12%wt). Noble metal-supported catalysts significantly affected the compositions of the derived oils, as shown in Figure 7. It can be seen that the contents of saturates and single-ring aromatics increased in accordance with the reduction in both multi-ring aromatic compounds, i.e. di- and poly-aromatics, and polar-aromatics. Moreover, the reduction in poly- and polar-aromatics was more pronounced as compared to the reduction in di-aromatics for all studied catalysts. And the highest activity for aromatic reduction was observed over Ru-based catalyst, meaning that its oil has the highest concentration of saturates, whereas the oil

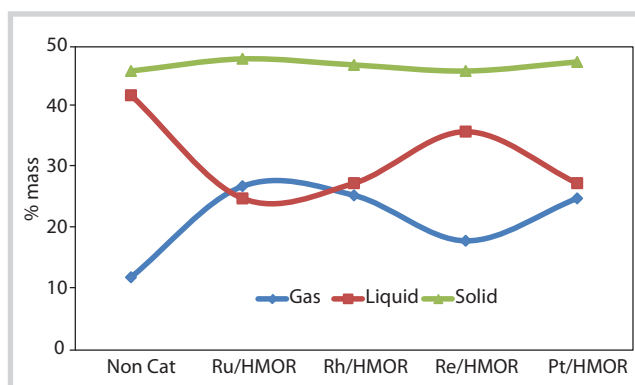


Figure 5. Yield of pyrolysis products (%wt)

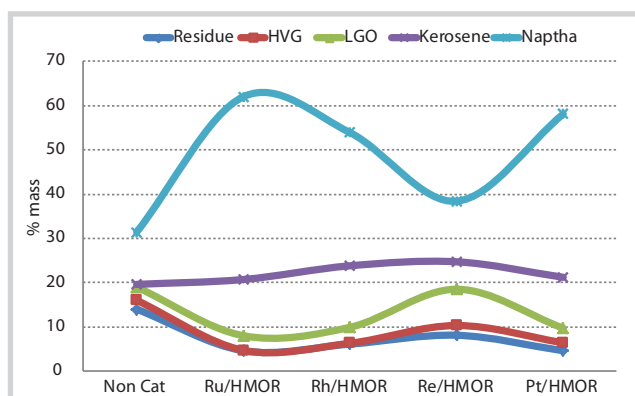


Figure 6. Petroleum fractions of pyrolysis oils obtained from using various catalysts

produced over Re/HMOR had the highest concentration of aromatic hydrocarbons. The content of different types of hydrocarbon in oils generated over Rh- and Pt-based catalysts can be comparable. However, Pt-based catalyst produced slightly higher saturates and lower di-aromatics as compared to Rh-supported catalyst.

3.4. Discussion

The complex structure of tire makes it difficult to understand the multi-reactions occurring during pyrolysis. And aromatics are produced and consumed during catalytic pyrolysis of waste tire through different reactions, such as Diels-Alders reaction, aromatisation, condensation, dealkylation, hydrogenation, and cracking, etc [4, 9, 24]. As reported in our previous paper, the use of HMOR decreased the poly- and polar-aromatics content in the derived oil [9]. And compared to the bare zeolite support, the incorporation of noble metal to the zeolite led to a further reduction in the concentration of multi-ring aromatic compounds as well as polar-aromatics, except for Re/HMOR (Figure 7).

Table 2 summarises the kinetic diameters of several aromatics [25]. As such, the main channel of the zeolite support is not accessible for the poly-aromatics but for di-aromatics, to a small extent. Meanwhile, from H₂-chemisorption analysis and TPR profiles, a considerable amount of noble metal particles locates outside the zeolite structure. Moreover, for HMOR zeolite, the weak acid sites

were mainly located at the outer surface of the zeolite, as revealed from TPD-NH₃ analysis. And the amount of weak acid sites accounted for a high portion of the total acid sites in the prepared bifunctional catalysts. Therefore, on the outer surface of the zeolite support there was a high concentration of both metallic and acidic sites that were accessible for the di-, poly- and polar-aromatics trying to enter the zeolite channels. Accordingly, the multi-ring aromatics might be hydrogenated over metallic sites, producing (partial) hydrogenated compounds, which rapidly undergo cracking and/or ring-opening on the acid sites [26]. The presence of noble metal had another advantage in that it can prevent the formation of the polar- and poly-aromatics by converting their precursors followed by cracking over acidic sites [24]. As a consequence, the presence of noble metal promoted the conversion of the heavy compounds like multi-ring aromatic and polar-aromatics to the lighters, thus, producing lighter oil and the oil contains higher concentration of saturates (Figure 6 and Figure 7). The higher reduction of poly-aromatics than di-aromatics can be ascribed to the higher reactive for hydrogenation of the former [27]. However, the high amount of coke (Table 1) that might be generated by the condensation of the polycyclic aromatics [9] and polar-aromatics [24] should not be excluded for the reduction of these compounds in the oil after catalysis treatment.

TPR analysis revealed that the reduction temperatures of Re and Pt supported on HMOR catalysts were, to a certain extent, higher than that used for catalyst reduction during preparation. Therefore, the reduced samples were subjected to analysis by TPR. The complete reduction of all prepared samples was confirmed since the reduced samples did not consume any hydrogen. This effect might be explained by the long reaction time of reduction employed (3 hours, 500°C).

On the other hand, it is well accepted that the metal dispersion strongly influences the catalytic activity of a metal-supported catalyst. And the hydrogenation activity of noble metal-supported catalysts increased with increasing metal dispersion [28]. In this paper, the order of metal dispersion for the prepared catalysts as revealed from H₂-chemisorption analysis was: Pt > Re > Ru > Rh. Besides, it has been reported that the cracking reactions over acid sites are dominant compared with hydrogenolysis over metal sites [14]. For the prepared catalysts, the order of total concentration of acid sites as revealed from TPD-NH₃ analysis was: Ru > Pt > Re > Rh.

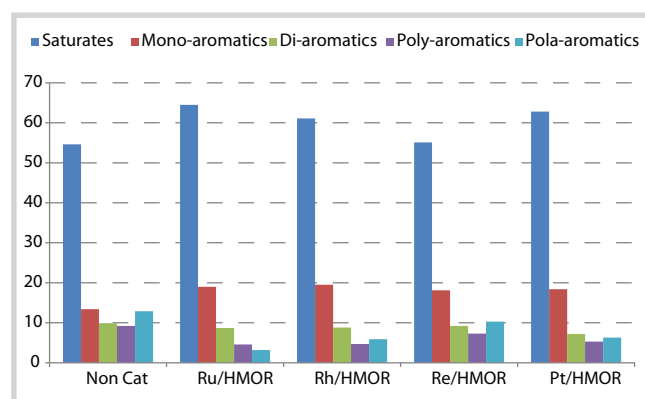


Figure 7. Compositions of pyrolysis oils obtained from using various catalysts

Table 2. The kinetic diameters of several aromatics [23]

Compound	H/C atomic ratio	Boiling point (°C)	Molecular size (Å)
Alkylbenzenes	1.0 - 1.4	200 - 250	5.0 x 6.8
Naphthalene	1.26	218	6.0 x 7.0
Tetrahydronaphthalene	1.38	206	6.0 x 7.0
Anthracene	0.94	340	6.0 x 9.5
Pyrene	0.63	404	8.5 x 8.5

Considering the catalytic activity for the reduction of multi-ring and polar-aromatics and simultaneously the production of light oil of the prepared catalysts, the order can be summarised as followed: Ru > Pt > Rh > Re. One can see that this order did not match the accessible number of metal or acid sites. Therefore, it is safe to conclude that the metallic nature strongly influences the catalytic activity of the noble metal supported on HMOR catalysts.

As revealed from TPO analysis, the lowest amount of coke was detected on the spent ruthenium catalyst, whereas Re catalyst produced the highest amount of coke [Table 1]. Meanwhile, liquid analysis revealed a considerable amount of polar-aromatics, which were mainly sulfur-containing aromatics [24]. Furthermore, due to the intrinsic structure of HMOR zeolite that has one main channel, once one segment of the channel is block, the whole channel is rendered inactive. Therefore, it is proposed that Re/HMOR displayed the lowest sulfur tolerance, resulting in a very quick deactivation, explaining its poorest catalytic activity performance. In contrast, Ru catalyst showed the best catalytic activity due to its intrinsic nature that gives high sulfur tolerance. Rodriguez-Castellon et al. reported that Ru exhibited a better sulfur tolerance than Pt, Pd or Pd-Pt catalysts due to the low density of states at the Fermi level of this metal [20]. Consequently, the spent catalysts were subject to analysis for their sulfur contents using XRF. Accordingly, the sulfur (%wt) in the Ru, Rh, Pt, Re spent catalysts were 0.78, 1.21, 1.35 and 2.51, respectively. This result confirmed the highest sulfur tolerance of the ruthenium catalyst among the studied samples. Furthermore, sulfur-containing compounds might deactivate the metal-supported catalysts [12] by the strong bonding between the sulfur atoms and metal atoms [23], making the metal sites inactive. It is appreciable that when the metallic function has no proper hydrogenation activity, the unsaturated bonds can not react quickly enough. Moreover, the acid sites generate alkenes and aromatics from β -scission and aromatisation (cyclisation and subsequent hydride transfer), respectively [14]. Furthermore, the high temperature used in this study was, to a certain extent, responsible for favourable aromatisation. That explained the high concentration of aromatics generated over this Re catalyst than over other metal-supported catalysts.

4. Conclusions

The uses of noble metals (Rh, Re, Ru, Pt) supported on HMOR catalysts produced an important increase in

the yield of gaseous product at the expense of the oil yield. This effect was attributed to the high activity of the bifunctional catalysts for the conversion of polycyclic and polar-aromatic hydrocarbons into lighter compounds. And the aromatic reduction was more pronounced for poly- and polar-aromatics than for di-aromatics. The polycyclic and polar-aromatic reduction and simultaneously light oil production activities for the current catalysts can be summarised in the order: Ru/HMOR > Rh/HMOR > Pt/HMOR >> Re/HMOR. We found that these activities were independent on the metal dispersion as well as the total acid concentration, but the intrinsic nature of the noble metal used. The best catalytic performance of ruthenium catalyst was ascribed to its metallic nature that exhibited the highest sulfur tolerance, resulting in the least coke formation.

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A STUDY ON APPLICATION OF VOLATILE CORROSION INHIBITORS FOR EQUIPMENT PROTECTION IN THE PETROLEUM INDUSTRY

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Summary

While usage of volatile corrosion inhibitors (VCI) is one of the effective methods in corrosion protection for rough, complicated and multi sub-component equipment, traditional protecting methods show no obvious efficiency. The results of an applied research at Ca Mau Power Plant and Dung Quat Refinery showed that volatile corrosion inhibitors have an ability to absorb on metal surface to prevent corrosion with high efficiency of above 80% for copper coupons, above 85% for steel coupons in electrical boxes and up to over 90% for steel coupons attached to flanges of air exposed pipeline.

Key words: Corrosion, protection of metal, volatile corrosion inhibitor.

1. Introduction

In the petroleum industry, equipment works under an aggressive environment, especially at seaside locations where a high percentage of Cl^- ions and a high humidity are the strong corrosive factors. If there is no appropriate protection, the equipment and machines would be vulnerable to corrosion leading to failure after a short time in operation.

Using metal, organic or composite coating or spreading grease to keep metal surface from exposing to the surroundings are possible and widely used methods.

However, the traditional methods prove ineffective for rough, complicated equipment and multi sub-component machines which make it difficult to reach their small details such as electrical panels of onsite monitoring systems, flanges of pipelines and other apparatus and air exposed parts of distillation towers, separators, and heat exchangers during maintenance duration.

Volatile corrosion inhibitors have, therefore, been studied and applied by many scientists for corrosion protection at these locations [1 - 5].

Volatile corrosion inhibitor is a chemical substance with an ability to vaporise and absorb on every position on a metal surface, protecting it by either creating a molecular sized thin film attached to the metal surface to prevent moisture and other corrosive factors from directly contacting the surface or reacting with the metal surface to have it passive to inhibit corrosion process.

In Vietnam, studies on manufacturing and applying volatile corrosion inhibitors are still limited, most of

them were experimented at laboratories for weapon storage [5].

Study, development and application of volatile corrosion inhibitors would increase the effectiveness of equipment protection. In addition, volatile corrosion inhibitors may be used as a useful tool to ensure asset integrity in oil and gas plants.

This paper showed the preliminary results of applying volatile corrosion inhibitor for electrical panels of onsite monitoring systems and flanges of pipelines and other apparatus at Ca Mau Power Plant and Dung Quat Refinery.

2. Experiments

The volatile corrosion inhibitors used in our research were products of Cortec Corporation – USA in the form of plastic bags or granules.

In this research, VCI impregnated plastic bags were used to wrap flanges while VCI granules were attached directly to an appropriate position in electrical box.

To evaluate corrosion rate, coupons were placed in the vicinity of experimental locations. At each plant, 4 flanges and 4 electrical boxes were chosen for our research.

To evaluate VCI efficiency, 3 shelves of coupons placed in 3 electrical boxes with VCI protection were compared to 1 shelf of coupons placed in 1 electrical box without VCI.

Similarly, 3 shelves of coupons placed in 3 VCI impregnated plastic bags were compared to 01 shelf of coupons placed in normal plastic bag.

Coupons were taken three times: after 3 months, after 6 months and after 9 months of experiment. Surface

analysis and corrosion rate evaluation using weight loss method were carried out after that.

2.1. Analysis of corrosive factors in atmosphere

Tempet 100 (USA) and HS-1050, HN-1050 (France) were used to identify such corrosive factors in the atmosphere as SO_2 , H_2S , NO_2 , NH_3 , CO , and CO_2 with high accuracy (error $\leq \pm 1\%$). Detector Tube was used to reaffirm these results.

2.2. Coupon preparation

Copper coupons were made from pure copper with clarity of 99% equivalent to materials for fabricating electrical circuit panel. Steel coupons were made from steel equivalent to materials of pipeline flanges.

Coupons fabricated in the form of flat specimen with dimensions of $10 \times 40 \times 2$ (mm x mm x mm) were ground and polished using silicon carbide grinding paper ranging from coarse (600, 800 grit sizes) to fine (1000, 1200 grit sizes). The coupons were then degreased, cleaned, dried, weighted and kept in anti-humidity container according to ASTM G1-03 - Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens. The prepared coupons were attached to shelves with 6 copper coupons and 6 steel coupons for each shelf.

2.3. Surface analysis

The volatile corrosion inhibitor and coupons (copper and steel) after experiment were analysed morphologically and chemically using *Scanning Electron Microscopy (SEM)* with *Energy Dispersive X-Ray Analysis (EDX)*.

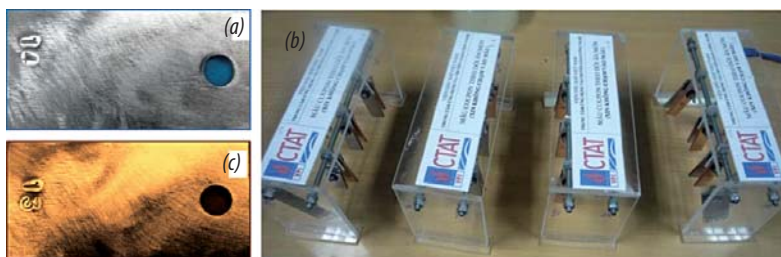


Figure 1. Steel coupons (a), Copper coupons (b) and Shelves of coupons (c)



Figure 2. Coupons are experimented at field
(a) Coupons placed in electrical box
(b) Coupons placed at flange

2.4. Corrosion rate calculation

The resistance method and the weight-loss method were used to identify the corrosion rate and the protection efficiency of inhibitors. The resistance method allows measuring corrosion rate by inserting of an electrical resistance probe into any corrosive environment to be studied. Because of corrosion, any changes in dimensions would result in changes in probes' resistances.

After experiment, probes were connected to CK – 3 Portable Corrosometer to calculate corrosion rates.

Protection efficiency was calculated using the following formula:

$$\eta = 100\% \frac{V_{kuc} - V_{uc}}{V_{kuc}} \quad (1)$$

Where: V_{kuc} : Corrosion rate in case of not using corrosion inhibitor (mm/year)

V_{uc} : Corrosion rate in case of using corrosion inhibitor (mm/year)

The weight-loss method is one of the common practices. In the method, weighed coupons were exposed for a fixed duration and then retrieved and reweighed; corrosion rate (CR) can be determined by the following Eq.:

$$CR = (8.76 \times 10^4 \cdot W) / (A \cdot T \cdot D) \text{ [mm/y]}$$

Where: $K = 8.76 \times 10^4$

T is time of exposure in hours;

A is area in cm^2 ;

W is weight loss in gram;

D is density in g/cm^3

3. Results and discussion

3.1. Analysis results in atmosphere at Dung Quat Refinery and Ca Mau Power Plant

Analysis results of corrosive factors in the atmosphere at Dung Quat Refinery and Ca Mau Power Plant were shown in Tables 1 and 2.

Both Dung Quat Refinery and Ca Mau

Table 1. Concentration of corrosive factors in atmosphere at Dung Quat Refinery

Sampling date	SO ₂ (ppm)	NO ₂ (ppm)	CO (ppm)	CO ₂ (ppm)	H ₂ S (ppm)	NH ₃ (ppm)	Salinity (mg/m ³)
Before experiment (16/10/2011)	1.5	<1	<1	380	<1	<1	69
15/1/2012	1.5	<1	<1	379	<1	<1	71
21/4/2012	1.5	<1	<1	379	<1	<1	68
22/7/2012	1.5	<1	<1	378	<1	<1	69

Table 2. Concentration of corrosive factors in atmosphere at Ca Mau Power Plant

Sampling date	SO ₂ (ppm)	NO ₂ (ppm)	CO (ppm)	CO ₂ (ppm)	H ₂ S (ppm)	NH ₃ (ppm)	Salinity (mg/m ³)
Before experiment (23/10/2011)	2	<1	<1	382	<1	<1	79
22/1/2012	2	<1	<1	382	<1	<1	76
28/4/2012	2	<1	<1	381	<1	<1	78
29/7/2012	2	<1	<1	382	<1	<1	78

Table 3. Steel coupons in electrical boxes at Ca Mau Power Plant

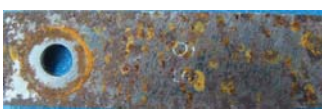
Steel coupons in electrical boxes	After 3 months	After 6 months	After 9 months
Fe-TĐ-CM 1 (Without VCI)			
Fe-TĐ-CM 2 (With VCI)			
Fe-TĐ-CM 3 (With VCI)			
Fe-TĐ-CM 4 (With VCI)			

Table 4. Steel coupons at flanges at Ca Mau Power Plant

Steel coupons at flanges	After 3 months	After 6 months	After 9 months
Fe-MB-CM 1 (Without VCI)			
Fe-MB-CM 2 (With VCI)			
Fe-MB-CM 3 (With VCI)			
Fe-MB-CM 4 (With VCI)			

Table 5. Steel coupons in electrical boxes at Dung Quat Refinery

Steel coupons in electrical boxes	After 3 months	After 6 months	After 9 months
Fe-TĐ-DQ 1 (Without VCI)			
Fe-TĐ-DQ 2 (With VCI)			
Fe-TĐ-DQ 3 (With VCI)			
Fe-TĐ-DQ 4 (With VCI)			

Table 6. Steel coupons at flanges at Dung Quat Refinery

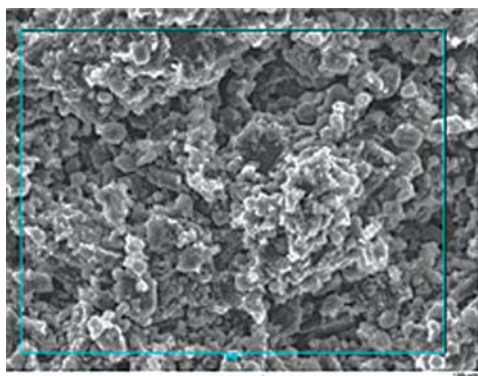
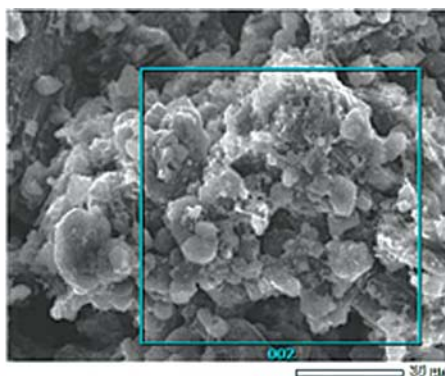
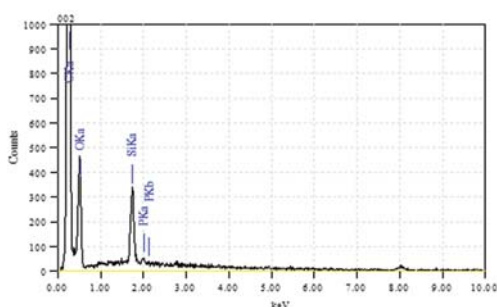
Steel coupons at flanges	After 3 months	After 6 months	After 9 months
Fe-MB-DQ 1 (Without VCI)			
Fe-MB-DQ 2 (With VCI)			
Fe-MB-DQ 3 (With VCI)			
Fe-MB-DQ 4 (With VCI)			

Table 7. Copper coupons in electrical boxes at Ca Mau Power Plant

Copper coupons in electrical boxes	After 3 months	After 6 months	After 9 months
Cu-TĐ-CM 1 (Without VCI)			
Cu-TĐ-CM 2 (With VCI)			
Cu-TĐ-CM 3 (With VCI)			
Cu-TĐ-CM 4 (With VCI)			

Table 8. Copper coupons in electrical boxes at Dung Quat Refinery

Copper coupons at flanges	After 3 months	After 6 months	After 9 months
Cu-TĐ-DQ 1 (Without VCI)			
Cu-TĐ-DQ 2 (With VCI)			
Cu-TĐ-DQ 3 (With VCI)			
Cu-TĐ-DQ 4 (With VCI)			

**Figure 3.** SEM images of VCI**Figure 4.** EDX pattern of VCI

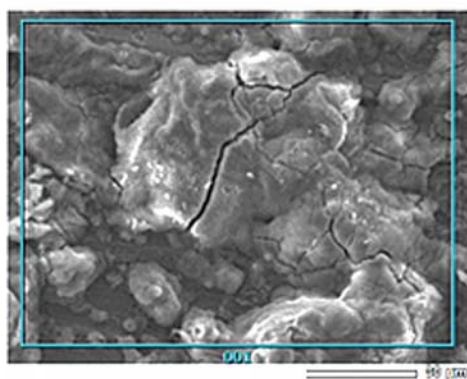
Elements	(keV)	Mass , %	Atom , %
C K	0.277	60.14	67.77
O K	0.525	35.81	30.29
Si K	1.739	3.81	1.84
P K*	2.013	0.24	0.10

Power Plant are located at the seaside. Due to the effects of a tropical monsoon climate with relatively high average temperature of 25 - 28°C (according to data from the National Centre for Hydro-Meteorological Forecasting), high concentration of Cl⁻ ion and high temperature are the main factors promoting corrosion. Besides, oxygen and CO₂ in the atmosphere are additional factors accelerating corrosion. Salt content and CO₂ concentration are stable in all samples.

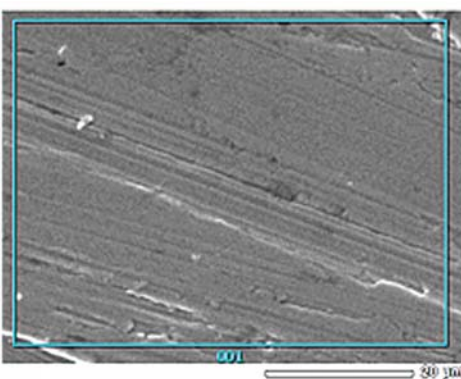
3.2. Surface analysis of coupons before and after on-site experiments

3.2.1. Images of coupons after on-site experiments

In general, when volatile corrosion inhibitors were not used, some traces of rust occurred with the increase of exposing time (after 9 months > after 6 months > after 3 months). As compared to coupons placed in closed

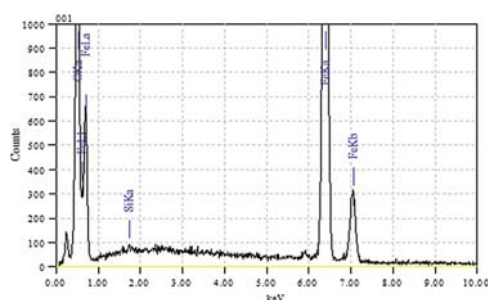


(a) Without VCI



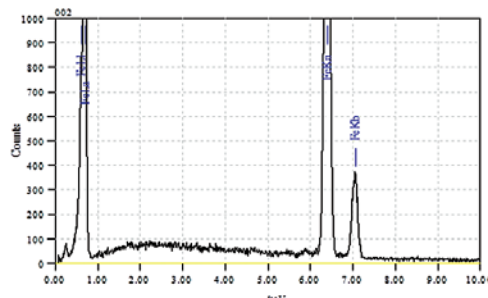
(b) With VCI

Figure 5. SEM images of steel coupons in electrical boxes in Ca Mau Power Plant



Elements	(keV)	Mass, %	Atom, %
O K	0.525	30.97	60.85
Na K*	1.041	0.27	0.38
Si K*	1.739	0.11	0.12
Fe K	6.398	68.65	38.65

(a) Without VCI



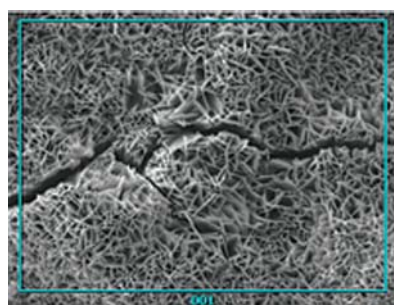
Elements	(keV)	Mass, %	Atom, %
Si K*	1.739	0.09	0.18
Fe K	6.398	99.91	99.82

(b) With VCI

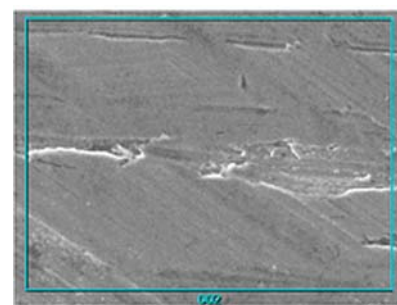
Figure 6. EDX pattern of steel coupons in electrical boxes in Ca Mau Power Plant

boxes which lacked contact with the atmosphere, coupons placed at flanges had more rust spots of deeper and wider size demonstrating more extreme corrosion. In the same conditions, the coupons with volatile corrosion inhibitors had negligible spots (Tables 3 - 6).

As compared to the steel specimens, the copper specimens were more stable to the atmosphere, thus the copper coupons had less rust in spite of some visible rust spots and stains on the surfaces of coupons without VCI. When the copper coupons were placed in electrical boxes with VCI, there was almost no sign of corrosion after 9 month experiment (Tables 7 and 8).

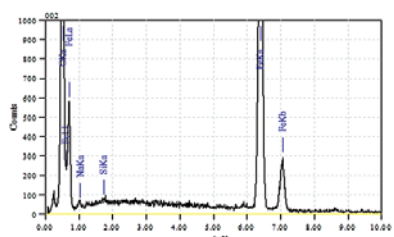


(a) Without VCI

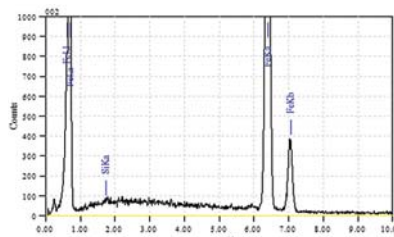


(b) With VCI

Figure 7. SEM images of steel coupons at flanges in Ca Mau Power Plant



(a) Without VCI

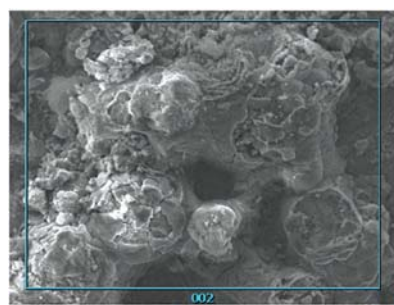


(b) With VCI

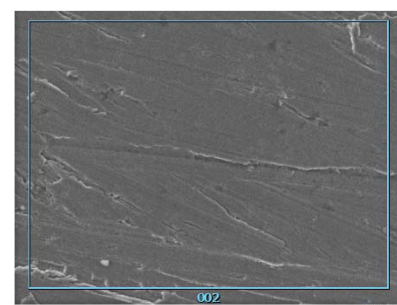
Elements	(keV)	Mass, %	Atom, %
O K	0.525	30.97	60.85
Na K*	1.041	0.27	0.38
Si K*	1.739	0.11	0.12
Fe K	6.398	68.65	38.65

Elements	(keV)	Mass, %	Atom, %
Si K*	1.739	0.08	0.17
Fe K	6.398	99.92	99.83

Figure 8. EDX patterns of steel coupons at flanges in Ca Mau Power Plant



(a) Without VCI



(b) With VCI

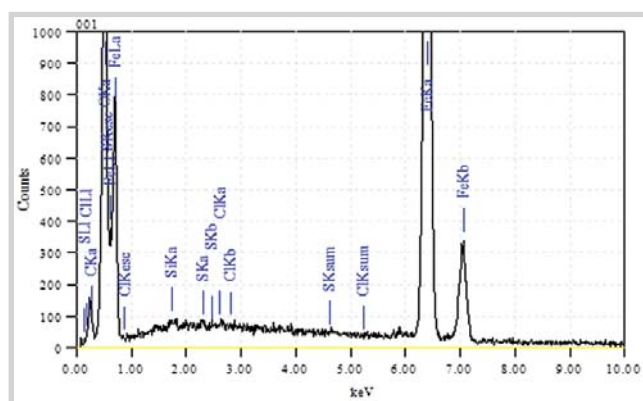
Figure 9. SEM images of steel coupons in electrical boxes in Dung Quat Refinery

3.2.2. Morphological characteristic and chemical components of VCI, coupon surfaces and corrosion products

Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX) was used to identify morphological characteristic and chemical components of VCI, coupon surfaces and corrosion products.

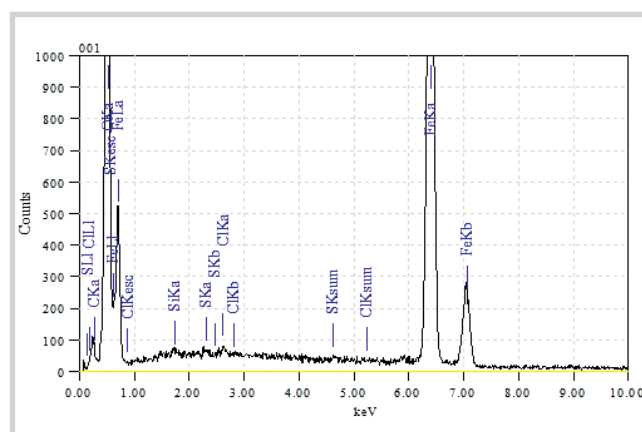
- Volatile corrosion inhibitor

As can be seen from Figures.3 and 4, the structure of VCI is relatively porous with about 60% (w/w) C and above 35% (w/w) O. There could be a small amount of Silicon (3.8%) and Hydrogen (out of detectable range of EDX). These results demonstrate that VCI is a silicon compound.



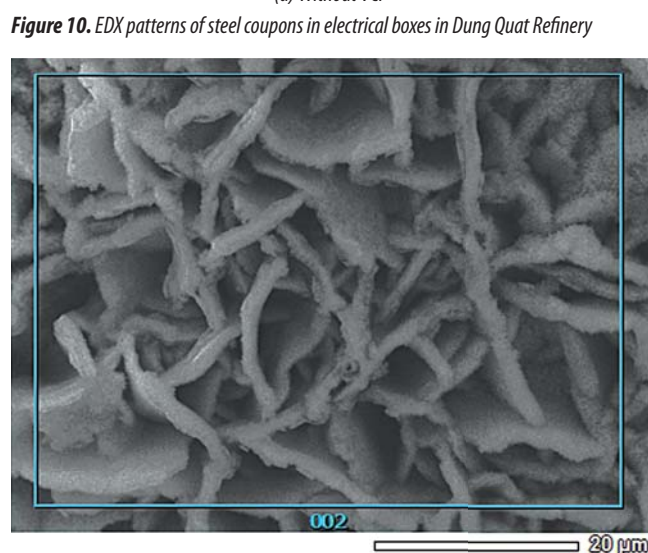
Elements	(keV)	Mass, %	Atom, %
C K*	0.277	2.97	8.38
O K	0.525	21.42	45.47
Si K*	1.739	0.04	0.05
S K*	2.307	0.23	0.24
Cl K*	2.621	0.13	0.13
Fe K	6.398	75.21	45.73

(a) Without VCI

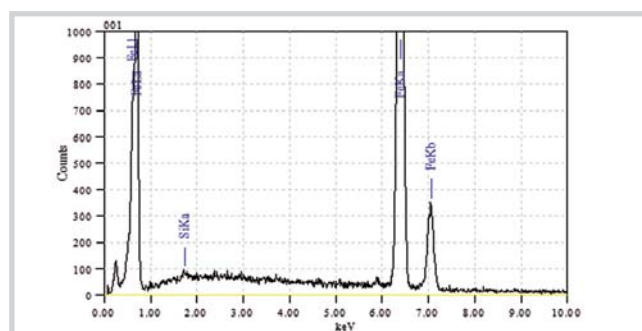


Elements	(keV)	Mass, %	Atom, %
Si K*	1.739	0.23	0.46
Fe K	6.398	99.77	99.54

(b) With VCI

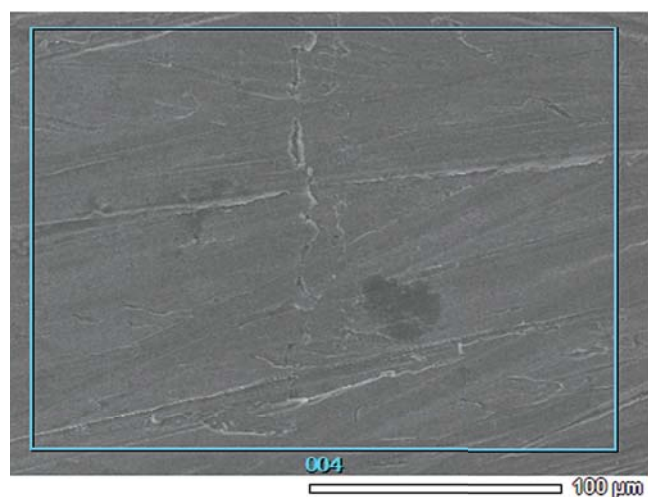


(a) Without VCI

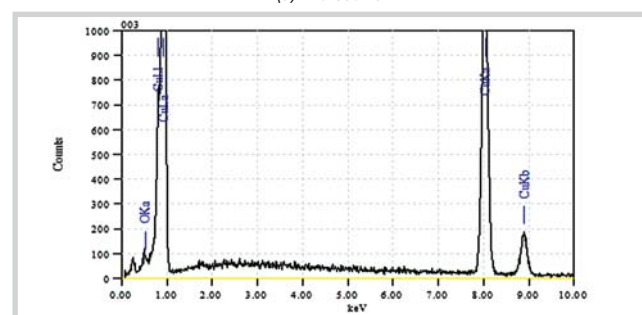


Elements	(keV)	Mass, %	Atom, %
C K*	0.277	2.13	5.42
O K	0.525	29.69	56.93
Si K*	1.739	0.13	0.15
S K*	2.307	0.18	0.17
Cl K*	2.621	0.19	0.17
Fe K	6.398	67.68	37.16

(a) Without VCI



(b) With VCI



Elements	(keV)	Mass, %	Atom, %
Si K*	1.739	0.15	0.30
Fe K	6.398	99.85	99.70

(b) With VCI

Figure 11. SEM images of steel coupons at flanges in Dung Quat Refinery

Figure 12. EDX patterns of steel coupons at flanges in Dung Quat Refinery

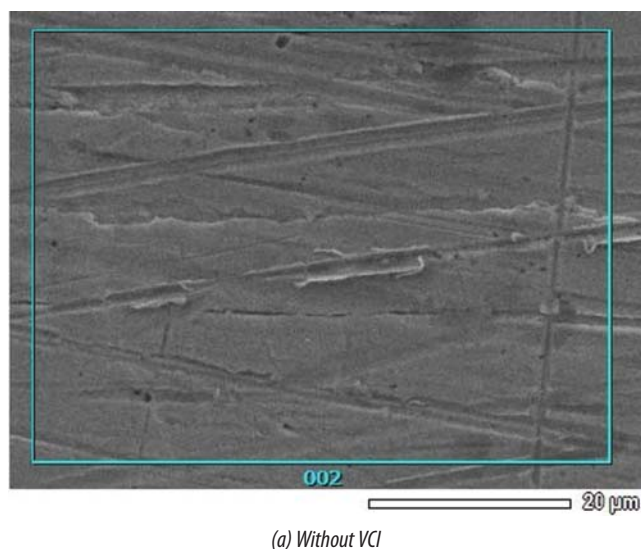
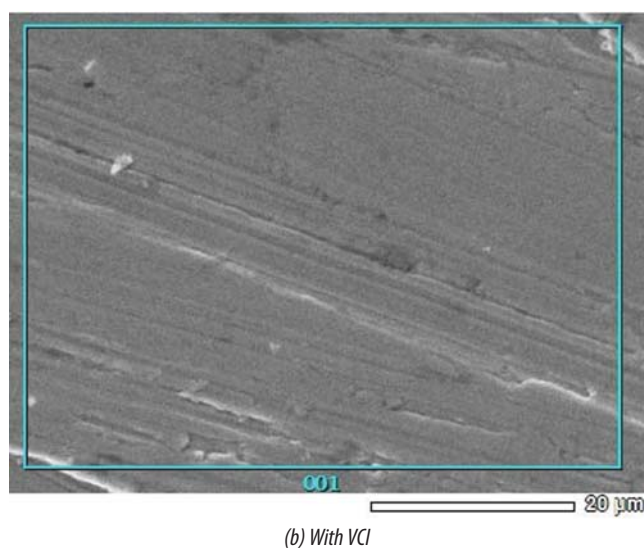


Figure 13. SEM images of copper coupons in electrical boxes in Ca Mau Power Plant

- Steel coupons

Images of corrosion products on steel surface placed in electrical boxes and flanges at Ca Mau Power Plant and Dung Quat Refinery were shown in Figures 5 and 8.

For steel coupons placed in electrical boxes without VCI, the layers of corrosion products were thick and porous. In addition to the main component of Fe, oxygen content accounts for 20%. It indicates that corrosion products were in the form of ferrous oxides (Figures 5 and 6). Similarly, for steel coupons placed at flanges without VCI, corrosion products created a thick and cracked layer of rust with oxygen accounting for up to 30% and a small amount of sodium due to accumulation of salt from the atmosphere (Figures 7 and 8). When using the VCI, there is no sign of corrosion (flat surface and absence of corrosion products) on the coupons' surface in both locations (electrical boxes and flanges). A higher percentage of silicon (as compared to coupons without VCI) combining with the main component of Fe demonstrates that there was an absorption of silicon contained VCI into metal surface to prevent corrosion.

Steel coupons placed at Dung Quat Refinery with and without VCI showed the same tendency as those placed at Ca Mau Power Plant. In case of not using VCI, there was an appearance of Cl⁻ ion which is the corrosive factor in the atmosphere accumulating in corrosion products.

- Copper coupons

Different from steel coupons, copper coupons were stable to marine environment. After 9 months of

experiment, corrosion products did not visibly appear in both two experimental cases with and without VCI (Figures 13 and 14).

3.3. Determination of VCI protection efficiency

3.3.1. Determination of VCI protection efficiency by resistance method

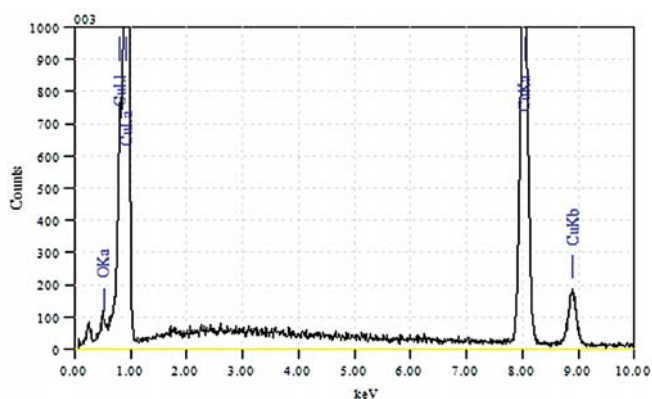
Protection efficiencies of volatile corrosion inhibitor were calculated from results of resistance method by formula (1) and shown in Figure 11.

In case of using VCI, at both plants, because the electrical boxes were closed, limiting contact between the metal surface and the surroundings, the corrosion rates measured in the electrical boxes were lower than the ones measured at flanges. With VCI, the corrosion rates decreased significantly and the protection efficiency reached 85 - 90% for the coupons in the electrical boxes and about 90% for the coupons at flanges. In general, the corrosion rates measured at Ca Mau Power Plant were higher than at Dung Quat Refinery.

3.3.2. Determination of VCI protection efficiency by weight loss method

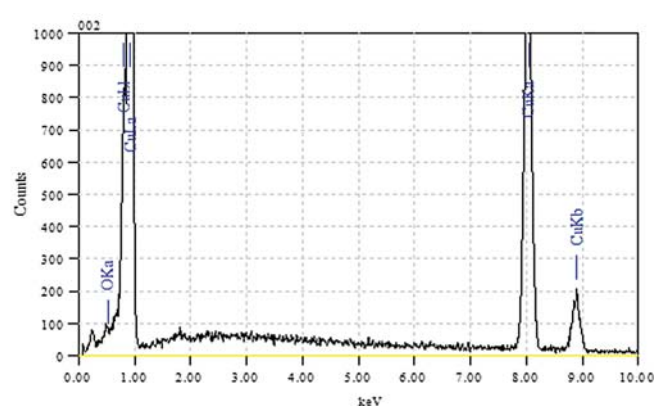
After the on-site experiment period, the coupons were cleaned and dried to constant weight to calculate corrosion rates by formula (2). Protection efficiencies were identified from the corrosion rates. Protection efficiencies of steel and copper coupons from Ca Mau Power Plant and Dung Quat Refinery were shown in Figure 12.

Weight-loss method showed similar results to resistance method. At Ca Mau Power Plant, the VCI



Elements	(keV)	Mass, %	Atom, %
O K	0.525	0.81	3.16
Cu K	8.040	99.19	96.84

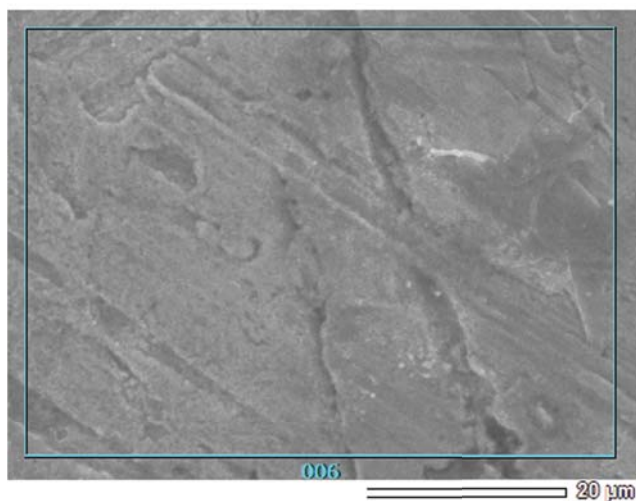
(a) Without VCI



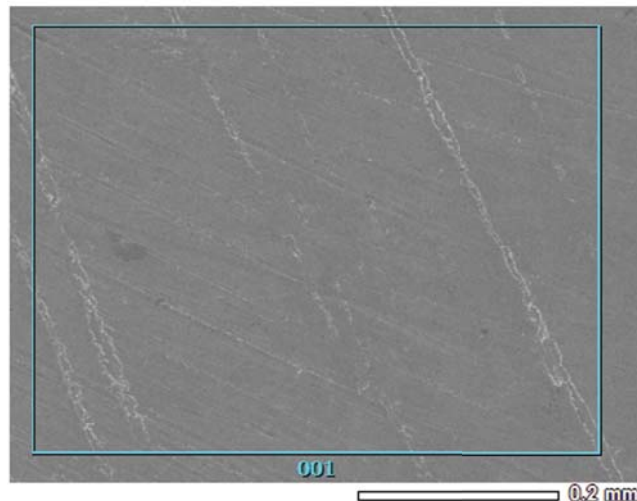
Elements	(keV)	Mass, %	Atom, %
O K	0.525	0.06	0.25
Cu K	8.040	99.94	99.75

(b) With VCI

Figure 14. EDX patterns of copper coupons in electrical boxes in Ca Mau Power Plant

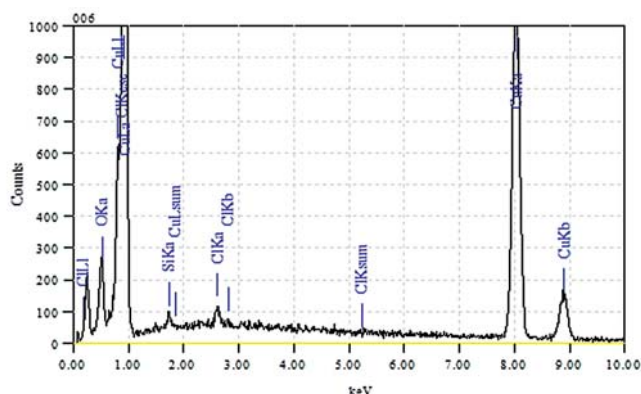


(a) Without VCI



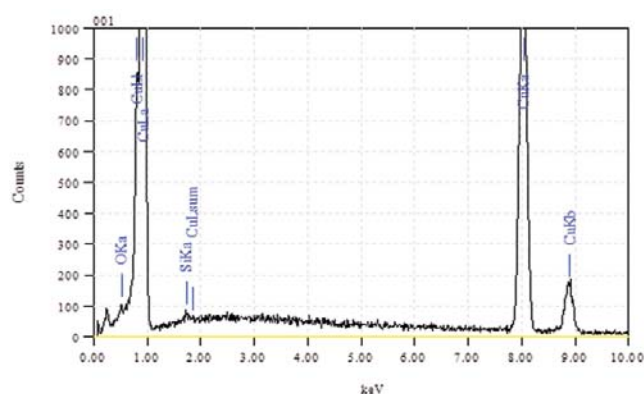
(b) With VCI

Figure 15. SEM images of copper coupons at flanges in Dung Quat Refinery



Elements	(keV)	Mass, %	Atom, %
O K*	0.525	4.71	16.21
Si K*	1.739	0.65	1.27
Cl K	2.621	0.69	1.08
Cu K	8.040	93.95	81.44

(a) Without VCI



Elements	(keV)	Mass, %	Atom, %
O K*	0.525	0.32	1.27
Si K*	1.739	0.26	0.58
Cu K	8.040	99.42	98.15

(b) With VCI

Figure 16. EDX patterns of copper coupons at flanges in Dung Quat Refinery

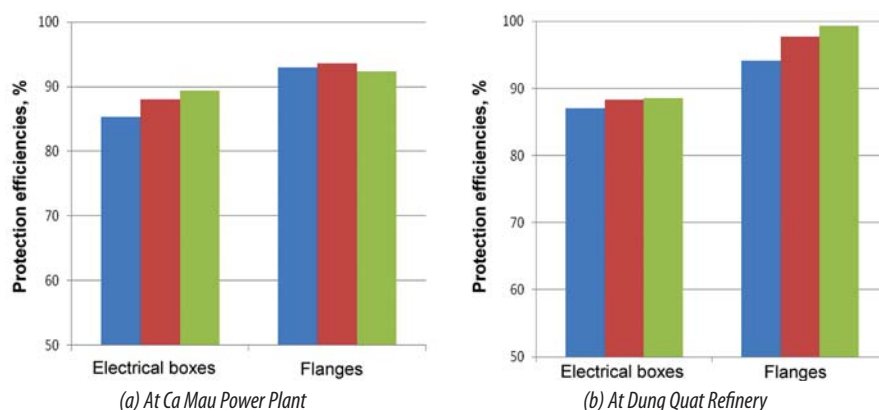


Figure 17. Protection efficiencies of VCI by resistance method

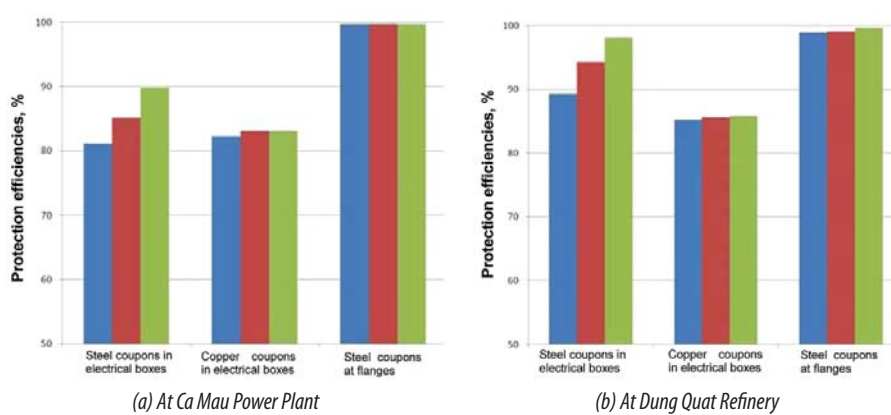


Figure 18. Protection efficiencies of VCI

exhibited an effective protection of 83% for copper specimens and up to 85 - 99% for steel specimens placed in electrical boxes and at flanges. At Dung Quat Refinery, the efficiencies reached 85% for copper coupons, 94% for steel coupons in electrical boxes and 99% for steel coupons at flanges.

4. Conclusions

From the results of applying volatile corrosion inhibitors to electrical panels and flanges of pipeline and apparatuses on field at Ca Mau Power Plant and Dung Quat Refinery, it can be concluded

that volatile corrosion inhibitor have high protection efficiency. At Ca Mau Power Plant, the VCI exhibited an effective protection of 83% for copper specimens and up to 85 - 99% for steel specimens placed in electrical boxes and at flanges. At Dung Quat Refinery, the efficiencies reached 85% for copper coupons, 94% for steel coupons in electrical boxes and 99% for steel coupons at flanges. Because of its ease of use without any disturbance to normal operation, the method of protection was acknowledged and appreciated by leaders from Ca Mau Power Plant and Dung Quat Refinery.

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SYNTHESIS AND STRUCTURE SOLUTION OF SMALL PORE ALUMINOPHOSPHATES

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Summary

By utilising template molecules known to produce Zeotype framework materials, two new synthesis routes leading to the production of DAF-4 and DAF-5 were presented. To reproduce the microporous material DAF-4 the template molecule successful in the synthesis of the pure SiO_2 structural analogue, LEV, was used and produced the phase pure material DAF-4. To reproduce the DAF-5 microporous material, the template used was chosen for its shape, which closely matched that used previously, differing only in the nitrogen atom positions. A phase pure sample of DAF-5 was produced.

Key words: Small pore aluminophosphates, structure solution.

1. Introduction

Zeolite analogues containing transition metals are highly desirable for industrial processes. As a result of this, hetero-atom substituted small pore aluminophosphates have attracted considerable attention in recent years due to their wide range of substitution chemistry, leading to the production of solid catalysts with a range of functionality [1 - 3].

Alongside efforts to produce zeolite analogues utilising the template molecule used in the formation of high-silica zeolites, the search for new microporous AIPO materials has led to many interesting developments. The useful properties of these materials have directed research efforts into their development and template role in synthesis and especially the rational design of new structures. One such design used the molecule 4-piperidinopiperidine as predicted by the computer methodology ZEBEDDE [3] as the template to produce a microporous framework with a structure analogous to that of the mineral Chabazite. This template was used for the synthesis of a cobalt-substituted aluminophosphate, [5] which was shown to have a chabazite-type structure containing one 4-piperidinopiperidine molecule per cage fully occupying the cage. The material produced was designated DAF-5.

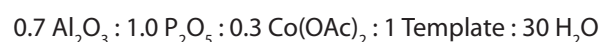
Knowing that this template produces a Chabazite-type framework, it was decided that a template would be used with a slightly different structure, by keeping the same overall structure shape but moving one of the nitrogen atoms to the 4th positions to make 4,4-bipiperidine. With this we aimed to produce a second synthetic route to the material DAF-5.

The structure of the pure siliceous zeolite Levyne was reported in the early nineties by McCusker [6], using the organic molecule adamantanamine as the templating species. Both the aluminosilicate and pure siliceous forms have been reported [7] but only the structurally analogous aluminophosphate DAF-4 has been reported utilising 2-methylcyclohexane as the structure-directing template [1]. Knowing that the pure SiO_2 form was produced with the adamantanamine template, a cobalt-substituted AIPO was synthesised with the Levyne-type structure.

2. Synthesis and methods

A cobalt-substituted aluminophosphate (CoAlPO) was prepared using 4,4-bipiperidine as the template molecule. Cobalt was chosen as the substituting heteroatom for reasons previously stated.

An aqueous gel was prepared using aluminium hydroxide, cobalt acetate tetrahydrate, 85% phosphoric acid, the template and distilled water. A small amount of water was added to the cobalt acetate until it dissolved. The remainder of the water was added to the phosphoric acid. The aluminium hydroxide was added to the acid/water mix, followed by the cobalt acetate solution, and the template was added last. The gel was stirred vigorously after each addition to ensure thorough mixing. The resultant gel was then placed in a PTFE liner and heated hydrothermally in a stainless steel autoclave at 195°C for 20 hours. The initial gel composition for the synthesis was



Phase purity was checked by powder diffraction,

recorded with a Siemens D500 diffractometer at University College London.

The same initial gel composition was again used for the adamantanamine synthesis, but the hydrothermal synthesis conditions were optimised at 170°C for 4 days.

The samples produced were blue crystals with dimensions up to approximately 40x20x20µm. The crystals used for the diffraction experiment were too small for a conventional laboratory X-ray source and therefore the single-crystal studies were performed at station 9.8 of Daresbury SRS, using a Bruker SMART CCD diffractometer. The structure was then solved and refined using the SHELX-97 suite of programmes [8].

3. Results and discussion

The diffraction patterns for the two as-prepared samples are shown in Figures 3 and 4. It is clear in both cases that the prepared sample patterns match closely with those of their respective framework standard, type. The bipiperidine material matches the Chabazite standard and the adamantanamine material matches the simulated pattern generated from the single-crystal solution by the programme PowderCell 2.3.

Both the powder X-ray patterns obtained show the single crystal data to be representative of the bulk sample.

3.1. Bipiperidine templated material

The structure was found to be analogous to that of the chabasitic DAF-5 structure and was solved and refined in the space group R $\bar{3}$. The crystallographic details are given in Table 1.

The substituted cobalt content refines to 35%, giving a much higher cobalt substitution to that previously obtained in the original DAF-5 synthesis where optimum conditions produced a 20% Co substitution.

The atom positions and selected bond lengths are shown in Tables 2 and 3 respectively. All the values obtained from the refinement are chemically reasonable. The position of the template is clearly visible within the framework structure, despite the obvious 3-fold disorder due

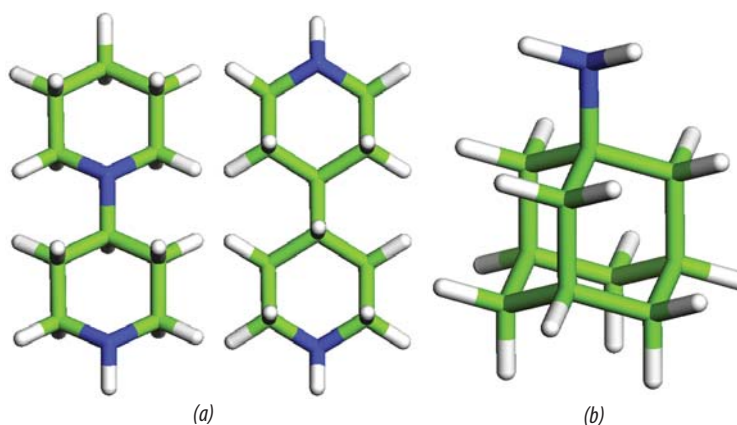


Figure 1. Structure of 4-piperidinopiperidine (a) Structure of 4,4-bipiperidine (b). Carbon atoms shown in green and nitrogen in blue

Figure 2. Structure of adamantanamine. Carbon atoms are shown in green and nitrogen in blue

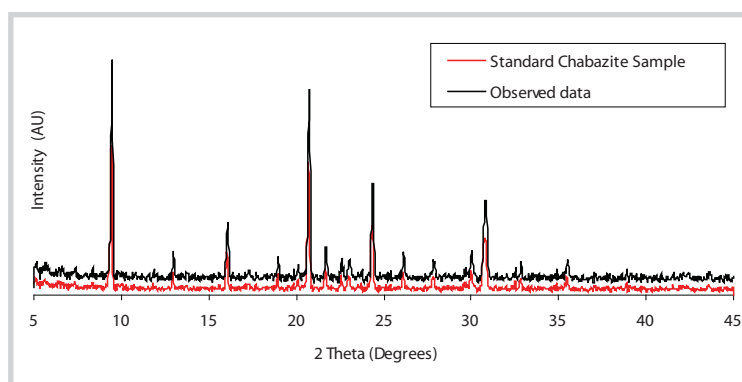


Figure 3. Powder X-ray diffraction patterns for the as-prepared Bipiperidine-templated sample (Black) and a standard Chabazite sample. Intensities are arbitrary and the patterns have been offset for clarity

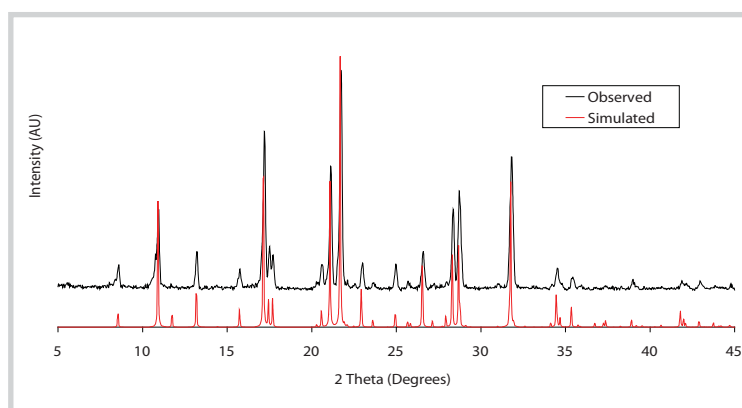


Figure 4. Powder X-ray diffraction patterns for the as-prepared adamantanamine-templated sample (Black) and the simulated powder pattern. Intensities are arbitrary and the patterns have been offset for clarity

to its position in the centre of the cage, where it occupies a position similar to that found with the 4-piperidinopiperidine structure as reported by G.Sankar et al [5]. Again we see only a single template molecule present within the cage. The template location is shown in Figure 5, the hydrogen atoms have been omitted for clarity.

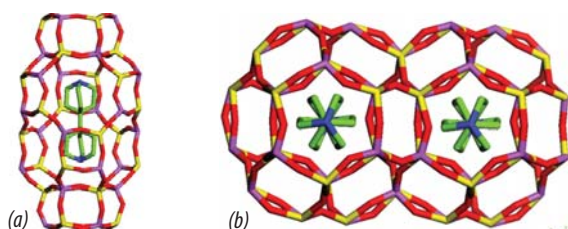
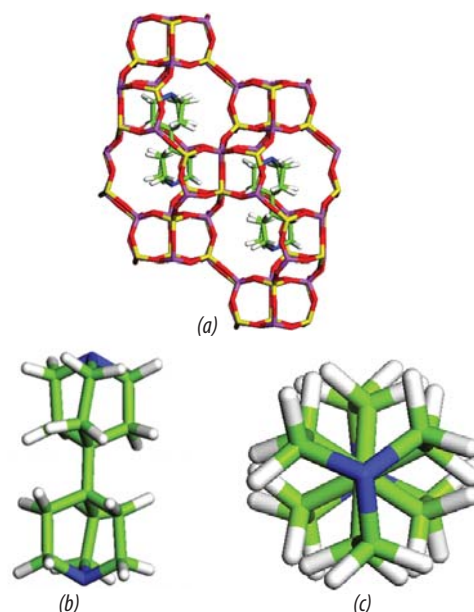
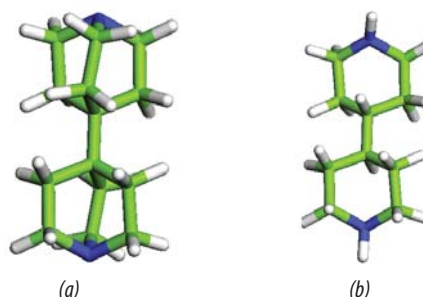
The disorder at the template location is clearly visible in Figure 6, where the orientation of the template molecule is shown. The

Table 1. Crystallographic details for the CoAlPO CHA (Bipiperidine template) structure

Chemical formula	Al _{0.65} Co _{0.35} PO ₄ N _{0.33} C _{1.667} H _{3.33}
Formula weight	135.29
Temperature	150(2)K
Radiation, wavelength	Synchrotron, 0.6929Å
Crystal system, space group	Trigonal, R $\bar{3}$
Unit cell parameters	a = 13.5732(2) Å α = 90° b = 13.5732(2) Å β = 90° c = 15.4406(4) Å γ = 120°
Cell volume	2463.54(8) Å ³
Z	21
Calculated density	1.915g/cm ³
Absorption coefficient μ	1.520mm ⁻¹
F(000)	1394
Diffraction meter	ω rotation with narrow frames
θ range for data collection	3.1 to 29.4°
Index ranges	h-17 to 19, k-19 to 12, l-18 to 21
Completeness to $\theta = 29.4^\circ$	91.6%
Reflections collected	5,566
Independent reflections	1,494 ($R_{int} = 0.0199$)
Reflections with $F^2 > 2\sigma$	1,406
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0996, 20.4589
Data/restraints/parameters	1,494/30/81
Final R indices [$F^2 > 2\sigma$]	$R_1 = 0.0693$, $wR_2 = 0.1959$
R indices (all data)	$R_1 = 0.0723$, $wR_2 = 0.1985$
Goodness-of-fit on F^2	1.135
Largest and mean shift/su	0.001 and 0.000
Largest diff. peak and hole	0.88 and -0.88eÅ ⁻³

Table 2. Fractional coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for CoAlPO CHA, (Bipiperidine template)

Atom	x	y	z	U _{iso}
Al1	0.67309(7)	0.57063(7)	0.73932(5)	0.0282(3)
Co1	0.67309(7)	0.57063(7)	0.73932(5)	0.0282(3)
P1	0.43880(8)	0.34057(8)	0.72732(6)	0.0288(4)
O1	0.5419(4)	0.4538(4)	0.7089(3)	0.0762(16)
O2	0.3940(4)	0.3399(4)	0.8169(2)	0.0543(10)
O3	0.3501(4)	0.3254(4)	0.6615(3)	0.0649(13)
O4	0.4704(4)	0.2494(4)	0.7176(3)	0.0605(11)
N1	0.6667	0.3333	0.5620(8)	0.147(6)
C1	0.621(2)	0.4077(19)	0.5226(7)	0.159(6)
C2	0.604(2)	0.390(2)	0.4231(6)	0.178(6)
C3	0.6667	0.3333	0.3837(4)	0.190(7)

**Figure 5.** Structure of CoAlPO CHA determined from single-crystal X-ray diffraction. The location and disorder of the template are clearly shown in (a) and (b). The hydrogen atoms have been omitted for clarity**Figure 6.** The template disorder determined from single-crystal X-ray diffraction. The location and disorder of the template are clearly shown in (a), (b) and (c). The hydrogen atoms have been omitted for clarity**Figure 7.** The template disorder determined from single-crystal X-ray diffraction: The 3-fold disorder present at the template location (a) and one of the three contributing orientations (b)**Table 3.** Selected bond lengths and angles for the CoAlPO CHA (Bipiperidine template). The Co partially occupies the Al T sites

Atom pair	Bond length (Å)	Bond angle	Degrees
Al1-O1	1.756(4)	O1-Al1-O2A	112.3(2)
Al1-O3B	1.764(4)	O1-Al1-O4C	106.0(3)
Al1-O2A	1.797(4)	O2A-Al1-O4C	113.4(2)
Al1-O4C	1.814(4)	O1-Al1-O3B	105.4(2)
P1-O1	1.500(4)	O2A-Al1-O3B	108.0(2)
P1-O3	1.509(4)	O3B-Al1-O4C	111.6(2)
P1-O2	1.509(3)		
P1-O4	1.506(4)	O1-P1-O2	110.3(3)
		O1-P1-O4	108.7(3)
N1-C1	1.547(12)	O2-P1-O4	111.4(2)
N1-C1F	1.547(13)	O1-P1-O3	106.5(3)
N1-C1C	1.547(12)	O2-P1-O3	109.0(3)
C1-C2	1.553(12)	O3-P1-O4	110.9(3)
C2-C3	1.527(13)		
C3-C2F	1.527(13)		
C3-C2C	1.527(13)		
C3-C3G	1.557(12)		

Table 4. Crystallographic details for the CoAlPO LEV (adamantanamine template) structure

Chemical formula	Al _{0.78} Co _{0.22} PO ₄ N _{0.22} C ₂₂₂ H ₃₃₃
Formula weight	162.88
Temperature	150(2)K
Radiation, wavelength	Synchrotron, 0.6843Å
Crystal system, space group	Hexagonal, R $\bar{3}c$
Unit cell parameters	a = 13.4256(6) Å $\alpha = 90^\circ$
	b = 13.4256(6) Å $\beta = 90^\circ$
	c = 45.184(3) Å $\gamma = 120^\circ$
Cell volume	7053.1(6) Å ³
Z	54
Calculated density	2.071g/cm ³
Absorption coefficient μ	1.257mm ⁻¹
F(000)	4,428
θ range for data collection	1.90 to 29.22°
Index ranges	H - 19 to 10, k - 15 to 19, l - 60 to 62
Completeness to $\theta = 25^\circ$	99%
Reflections collected	15,623
Independent reflections	2,300 ($R_{int} = 0.0461$)
Reflections with $F^2 > 2\sigma$	2,008
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0744, 65.4886
Data/restraints/parameters	2,300/31/108
Final R indices [$F^2 > 2\sigma$]	$R_1 = 0.0667$, $wR_2 = 0.1778$
R indices (all data)	$R_1 = 0.0735$, $wR_2 = 0.1816$
Goodness-of-fit on F^2	1.155
Largest and mean shift/su	0.000 and 0.000
Largest diff. peak and hole	0.949 and -0.914eÅ ⁻³

Table 5. Fractional coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for CoAlPO, LEV (adamantanamine template)

Atom	x	y	z	U _{iso}
Al1	0.90620(7)	0.3333	0.0833	0.0163(3)
Co1	0.90620(7)	0.3333	0.0833	0.0163(3)
Al2	0.77118(7)	0.00432(6)	0.035179(17)	0.0176(2)
Co2	0.77118(7)	0.00432(6)	0.035179(17)	0.0176(2)
P1	0.6667	0.09653(8)	0.0833	0.0161(3)
P2	1.00567(6)	0.23703(7)	0.035059(18)	0.0175(2)
O1	0.7701(2)	0.2129(2)	0.08934(8)	0.0414(8)
O2	0.9740(3)	0.3142(3)	0.05193(7)	0.0397(7)
O3	0.9185(2)	0.1114(2)	0.04049(7)	0.0371(7)
O4	0.6848(3)	0.0410(3)	0.05588(6)	0.0367(7)
O5	1.0076(2)	0.2690(3)	0.00272(6)	0.0367(7)
O6	1.1222(2)	0.2565(3)	0.04492(6)	0.0319(6)
N1	1.0000	0.0000	0.07964(10)	0.081(9)
N1'	0.8754	-0.2369	0.17026(10)	0.063(5)
C1	1.0000	0.0000	0.11229(10)	0.059(2)
C2	0.9408	-0.1220	0.12369(10)	0.0749(18)
C3	0.9363	-0.1225	0.15770(10)	0.0673(16)
C4	0.8763	-0.0604	0.16772(10)	0.081(2)

three different orientations of the template can be clearly seen, with the rotation through the long axis of the molecule about the nitrogen positions.

Although only one third occupied in any of the positions shown in a) of Figure 7, the molecule has a shape as shown in b).

3.2. Adamantanamine-templated material

As the original microporous synthesis using adamantanamine was a pure silica form, we expected the space group for the CoAlPO system to differ, and this was true, as the structure was solved and refined by direct methods in Rc compared to the previous Rm . The unit cell dimension of the c axis is double that found for the pure siliceous material and similar to that for DAF-4. The substituted cobalt content refines to 22%. The crystallographic details are given in Table 4.

Despite the template disorder within the system, a good final refined model was obtained, with a low R-factor of 7.35% and clearly showing the presence of only one template molecule occluded within the cage

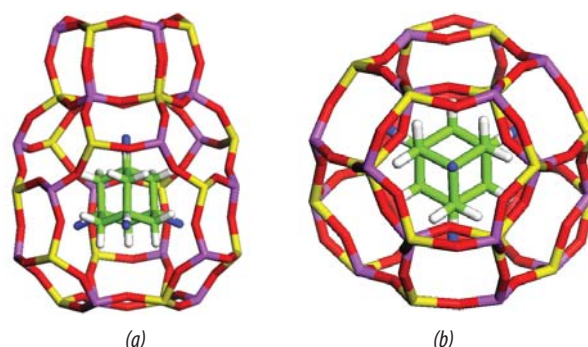


Figure 8. Views of the CoAlPO structure refined from data collected at 150K. The template location and orientation are clearly shown in (a) and (b). Note only one template species per cage; the substituted cobalt has been omitted for clarity but partially occupies some of the aluminium sites

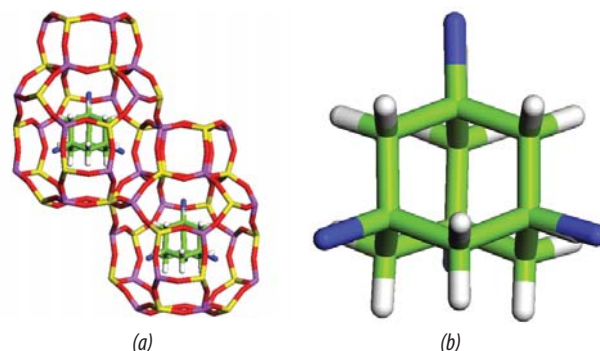


Figure 9. Schematic views of the location of the template molecules (a) highlighting the presence of a single molecule per cage (b). The enlarged template shows the disorder present within the system

Table 6. Selected bond lengths and angles for the CoAlPO LEV (adamantanamine template). The Co partially occupies the Al T sites. The average bond lengths for the N-C and C-C bonds are given, as the variation was small

Atom pair	Bond length (Å)	Bond angle	Degrees
P1 - O1	1.507(3)	O1-P1-O1a	109.7(3)
P1 - O1a	1.507(3)	O1a-P1-O4a	111.27(17)
P1 - O4	1.527(3)	O1-P1-O4	111.26(17)
P1 - O4a	1.527(3)	O1-P1-O4a	106.87(19)
P2 - O2	1.508(3)	O1a-P1-O4	106.86(19)
P2 - O3	1.517(3)	O4-P1-O4a	110.9(2)
P2 - O5	1.519(3)		
P2 - O6	1.518(2)		
Al1 - O1	1.753(3)	O1-Al1-O1b	109.0(2)
Al1 - O2	1.773(3)	O1-Al1-O2	111.36(15)
Al1 - O1b	1.753(3)	O1-Al1-O2b	108.47(16)
Al1 - O2b	1.787(3)	O1b-Al1-O2b	111.37(15)
Al2 - O3	1.787(3)	O1b-Al1-O2	108.47(16)
Al2 - O4	1.742(3)	O2-Al1-O2b	108.2(2)
Al2 - O5c	1.773(3)		
Al2 - O6d	1.762(3)		
N - C	1.475		
C - C	1.501		

structure although the disorder does suggest it is freely rotating within the confines of the cage. The refined structure and the location of the disordered template are shown in Figure 8.

With the final structure refined in the space group $R\bar{3}c$, it is not possible to identify any cobalt ordering within the system. Attempts were made to lower the symmetry in order to resolve this but no satisfactory solutions could be found. Therefore, the Co Occupancy was refined on both the aluminium T sites with the Co+Al occupancies = 1 for each T atom position.

The disordered template location is clearly shown in Figure 9 and shows how the single template molecule is located within the cage. The result obtained does suggest that the template can freely rotate within the confines of this position but suggests that the nitrogen group points into the double six-ring.

Analysis of the bond lengths and angles for the DAF-4 type material does not give clear indication of an aluminium site preference within the structure, but does hint that slightly more has substituted on the Al2 site, as shown by the slightly longer bond lengths for this site.

4. Conclusion

In this work two framework analogues of known structures have been presented, showing new synthetic routes to the known aluminophosphate materials DAF-4 and DAF-5. In both cases single-crystal structure solution

was used to provide the clearest possible insight into the framework structure obtained and the number and location of the structure-directing template molecules within the cages of the material. The structure of the adamantanamine-templated material is analogous to the pure SiO_2 Levyne structure and matches closely the crystallographic data obtained for the original DAF-4 synthesis, both space group and cell dimensions. A quicker synthesis was achieved than for the pure microporous material, 4 days as opposed to 7 [1].

As seen with the DAF-5 synthesis by Sankar et al. [5] in this synthesis a single but bulky bipiperidine template molecule was found, emphasising the importance of template shape upon the synthesis of materials alongside the charge-balancing effects.

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MOTIVATING ENHANCED OIL RECOVERY (EOR) PROJECTS IN VIETNAM - A REGULATORY APPROACH

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Summary

While new oil fields are becoming difficult and expensive to explore, countries and companies have started to look at other unconventional sources to secure hydrocarbon reserves. One of such unconventional sources is oil itself left stranded in the reservoir, which can be recovered by enhanced oil recovery (EOR) methods. Vietnam is now in a similar position as it sees EOR the opportunity to increase the country's oil reserves apart from new projects abroad, where commercial potential might be limited amid a number of technical, economic and regulatory constraints. This paper therefore will look at EOR issues in Vietnam, starting with a discussion about EOR activities, followed by examining the features of an EOR project: which techniques can be used and which economic consequences might prevail. The paper will present the modelling results for a typical project in Vietnam to assess the impact of various policy factors on the project's profitability. Then three steps to improve the fiscal terms for EOR projects are proposed, including both the short-term quick fixes as well as the long-term changes in policies and regulations.

Key words: Enhanced oil recovery, tertiary recovery, petroleum contracts, oil and gas policy.

1. Introduction

A young and rising population and rapid economic growth in recent decades mean Vietnam needs enormous energy in general and oil in particular for development. The average GDP growth rate was 7.4% for the period 1990 - 2010, and though slowing down in recent years, is currently at more than 5.5% annually. Energy demand is therefore expected to hit 140 Mtoe in 2035, more than double that of 2010 [1]. Other forecast figures also show rapid increase in oil demand in Vietnam, reaching 64 Mtoe in 2030 [4], nearly four times that of 2012 [2]. The projection for oil production however does not show comparable growth figures. Currently, there are 22 oil fields under production by Vietnam and another 12 fields are being developed. As seen in Figure 1, oil production from discovered domestic fields starts to decline quickly after 2015. Adding output from other new domestic fields can not change the downtrend, only to delay the production peak for another one year to 2016. Then, total oil production in 2025 is around half of that in 2015 [6]. To keep up with the growing local demand, it is important that Vietnam needs to find more oil from other unconventional sources. And EOR is one of the options that Vietnam can consider.

Actually EOR has been high on the agenda for other countries as well as oil and gas majors. This comes from the fact that petroleum is still the dominating fuel - with oil expected to be at 27 - 30% of global energy mix in 2030 [3]. While access to new exploration acreage is difficult and expensive, largest producing fields (which started in the 1970s) are approaching the end of their life time. Oil and gas companies have, therefore, invested significantly in new technologies to get more oil out of current fields, given the recovery factor for petroleum remains just around 35% [5]. Others estimate that if oil recovery factor (Oil recovery factor - ORF or percent of the technically-recoverable out of in-place oil) improves by 1%, the world conventional oil reserves would increase by 88 billion barrels - or three times the current annual production [3]. EOR projects were highest at about 500 during the 1980s, but fell

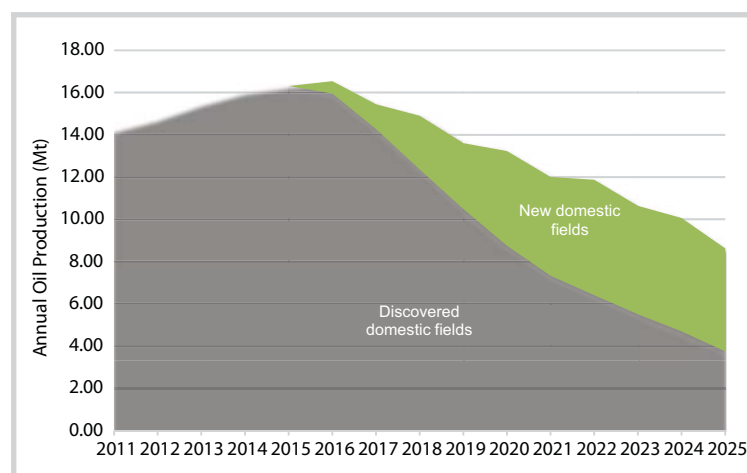


Figure 1. Vietnam annual oil production projections (2011 - 2025) [6]

gradually to less than 200 in early 2000s, before picking up after 2005. Currently, EOR contributes around 3 million barrels per day (mmbpd) out of 85 mmbpd world daily production [5].

In Vietnam, EOR programmes are currently limited and mostly tested at lab scale. In 2013, there were only two pilot tests for Bach Ho and Rang Dong fields. How to motivate more EOR activities at commercial scale in Vietnam is the purpose of this paper, which will look at the issue from a regulatory perspective. The paper will start with the common definition of EOR to identify which particular exploration and production activities are entitled to the Government's support. Then a brief discussion of the various EOR technologies is mentioned, before the key economic features of an EOR project are analysed. The next section will look at various Government tools, specifically the Petroleum Contract terms, which are used to adjust the incentives for the Contractor(s). A model to calculate an EOR's profitability will be presented, with various cases to assess the impacts of different terms set by the Government. Based on these simulation results, we will identify the key policy levers to incentivise foreign Contractor(s) and propose a long-term pathway to adjust the fiscal regimes so that EOR programmes will become a needed and beneficial activity for both the Contractor(s) and the host Government.

2. EOR definitions and project characteristics

2.1. EOR definitions

To understand and agree on a definition for EOR, it is useful to divide the production process into three phases, based on the nature of energy used to produce oil (Figure 2). Each phase has a unique technical requirement: what and how energy is used to produce oil - from energy within the formation to external sources. This will be the key criteria to define different production phases and in particular EOR. Each phase also has unique economic and business implications - what costs and benefits are there for the Contractor(s), which will influence the decisions of various stakeholders in an EOR project. The timing of these phases are not fixed, with some project (extra heavy oil in Venezuela for example) can move straight into later parts from the beginning. So while this paper will describe each phase in sequence, it should be noted that the nature of extraction energy will decide when and whether EOR is carried out.

The first phase of production - primary recovery, crude oil can be produced by its natural flow or by artificial lift. Natural flow means elastic energy, dissolved gas drive, edge water drive, gas cap drive or potential gravity - all of which normally brings out 5 - 10% of oil in place. As output can drop quickly under natural flow, artificial lift such as gas lift, piston pumping, can be used to recover

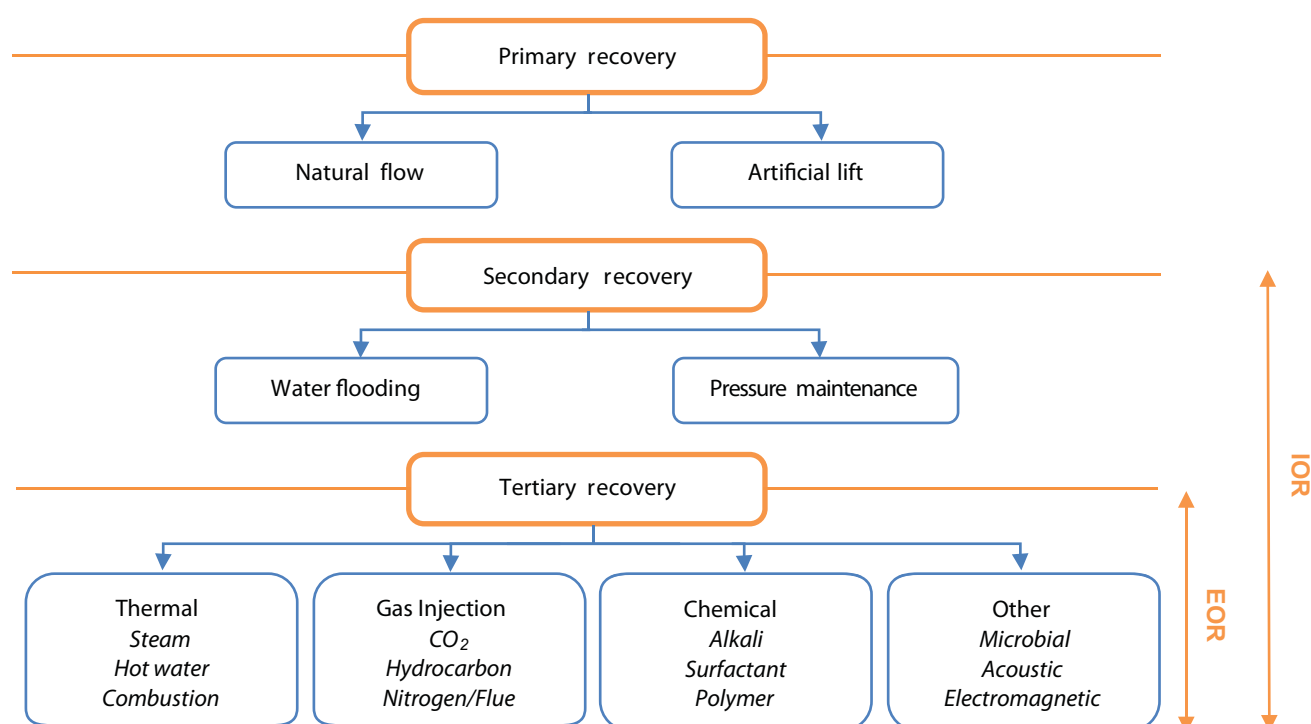


Figure 2. Production phases and EOR [9]

more surface oil, pushing the total oil recovery of the Primary Recovery phase up to 15%.

The second phase or secondary recovery involves reservoir pressure maintenance techniques to move oil to producing wellbores. In particular, water or gas (immiscible) flooding and hydrodynamic methods are applied to push oil recovery to 20 - 60%. These methods however can only affect the mobile oil within the reservoir, and there will be a limit to the recovery factor, which depends on the technical details of the field development plan. The field operator will, therefore, try to optimise this second phase to increase the production rate, improve the secondary recovery and consequently the economic efficiency. Both the first and the second phases however only use the energy of the reservoir or external sources without changing the chemical and physical nature of the oil and fluids. Such methods are called conventional oil recovery, and also lead to the third phase or the topic of this paper.

The third phase or tertiary recovery employs more advanced techniques, altering the oil and fluid's indicators such as surface tension, viscosity, and mobility ratio to get more immobile oil out of the reservoir. Techniques including thermal, gas (miscible) injection, chemical and other solutions like microbial or electromagnetic, are expected to push oil recovery rate to 50 - 80%. It should be noted that techniques for the second phase are also used in conjunction with more advanced methods in this tertiary recovery phase.

As shown in Figure 2, EOR are advanced techniques that must be employed in the tertiary recovery phase to produce the immobile oil by changing the chemical and physical characteristics of oil and fluids, which the primary and secondary recovery phases fail to bring out. Improved oil recovery (IOR), another frequently used term, means both methods used in the second and third phases, which involve energy from external sources rather than from the reservoir only. IOR therefore includes EOR, though only EOR methods are the subject of this paper.

Some EOR techniques have actually been deployed in early years, such as steam trials in 1930s or gas injection in 1940s; while on the other hand, latest methods are looking into low-salinity water flooding, unconventional heavy oil or offshore EOR [8]. In general, the oil and gas industry sees the following techniques as modern EOR:

- Gas methods: Carbon dioxide (CO_2), nitrogen (air) or gas injection;

- Thermal methods: Steam injection;
- Chemical and physicochemical methods: Alkali, surfactant, polymer;
- Others: Horizontal drilling with multi-stage hydro fracturing [3].

Thermal and gas are the two dominant methods, accounting for 50% and 45% of global EOR's hydrocarbon production respectively, while chemical techniques contribute the rest 5%. One important reason for this trend is the effects on incremental outputs, with thermal and gas methods can raise oil recovery factor by 15 - 20% and 5 - 10% respectively, while thermal techniques can only push the factor up by 3 - 8% [3]. In practice, choosing which particular EOR methods to use will require considering a number of technical and economic factors for a given field. For example, two major technical factors are the reservoir depth and oil viscosity and the applicability of various EOR methods is shown in Figure 3. High-viscosity oil in North America or the Middle East can be better recovered by the injection of steam to thin the oil, or polymer to thicken the water and improve sweep. Or in oilfields with low viscosity and increasing depth, carbon dioxide can be miscible with oil to reduce residual oil saturation, and therefore improve the recovery rate.

2.2. Project characteristics

Implementing an EOR project is a long and complex process given the advanced nature of the techniques as well as the uncertain nature of the tertiary production

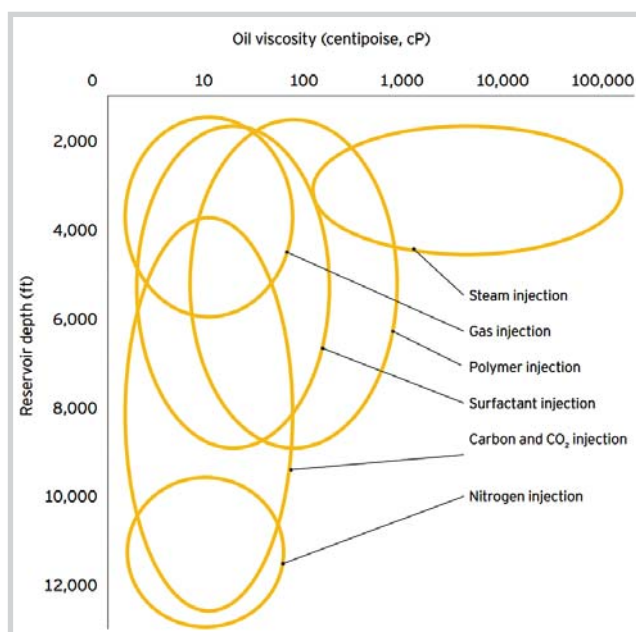


Figure 3. EOR methods and related technical factors [3]

phase. The preparation time of an EOR project can be as long as 6 - 10 years before field-scale production begins, with 3 major steps. Firstly, the laboratory testing and design step (1 - 2 years) will involve field screening study, EOR technique selection, reservoir modelling together with geological studies, and importantly the design parameters. Secondly, a pilot test (2 - 4 years) will apply the chosen techniques on a pilot well or field, where reservoir simulation is fine-tuned, while detailed economic models are analysed. Thirdly, a full scale deployment (3 - 5 years) is implemented on selected reservoirs, where the initial response is examined and used to decide later production potential (to be as long as 30 years) [7].

So an EOR project can have a very long lead time before production starts. This implies significant uncertainty and risk in testing and pilot, which might not lead to any large-scale production after a period as long as 6 years. Besides, this means the project's cash flow will concentrate at project-end, so the Contractor(s) might face some financial stress given the high investments needed. On the other hand, EOR project cost is driven by operating costs as shown in Figure 4. So the management and procurement of EOR agents or fluids will be the key in keeping

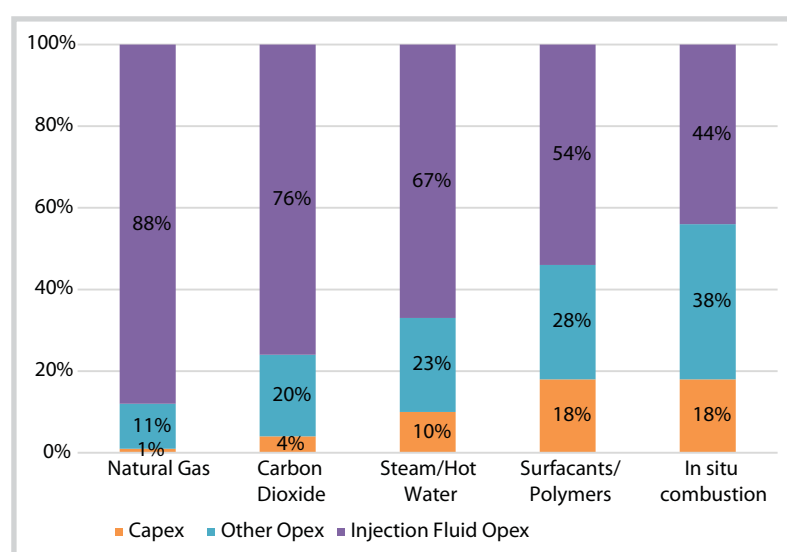


Figure 4. EOR cost components [7]

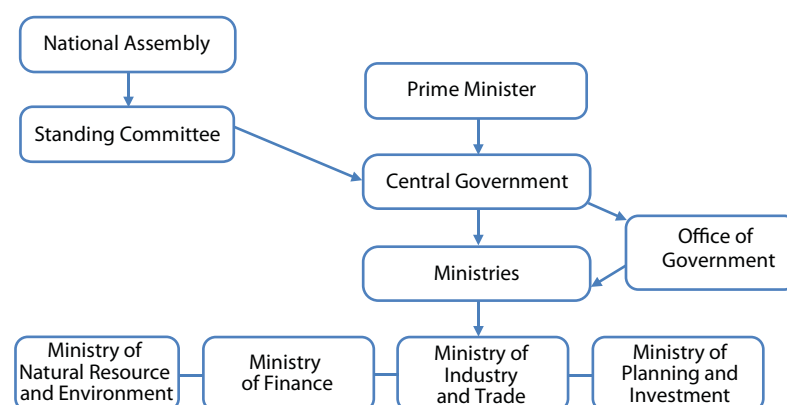


Figure 5. The regulatory framework and related institutions for oil and gas industry in Vietnam

the project running smoothly and its costs under control, given possibilities of demand-supply mismatch, constraints from local content requirements, and environmental regulations [7]. As seen on Figure 4, natural gas and carbon dioxide themselves can take up to 88% and 76% respectively of the total cost in related EOR projects. For in situ combustion for example, injection fluids are only 44%, but adding other items, total operation costs still take about 82% of the total costs.

Summing up, the unit production cost for EOR sees a wide range from 20 to 80USD/barrel. EOR projects therefore can be quite costly compared to conventional oil projects whose cost ranges from less than 20USD/barrel to highest at more than 40USD/barrel. EOR can be even more expensive than offshore deepwater, which has maximum production cost around 70USD/barrel. Looking at the higher range for production cost, EOR only ranks after heavy oil bitumen, oil shales and Arctic oil [3].

3. Motivating EOR projects

Given the economic and financial challenges, the Government's support is vital to bring EOR projects forward, for the benefits of both the host country and the Contractor(s). Such support can be in a variety of forms under the petroleum regime, which might require considerable time and effort to implement by different institutions. An overview of the regulatory framework for petroleum projects in Vietnam is presented in Figure 5.

Apart from the Constitution which is the highest-level legal document, the key document is the Petroleum Law, which is detailed in a number of related Decrees, and ultimately influences other measures of the host country. Then, there will be various regulations, either by the Ministries or the National Oil Company (NOC), affecting both the technical and economic sides of the projects. Finally, there is the contract between the host government

and the Contractor(s) - the Petroleum Contracts (PC), including terms, conditions, and all the details that are key to the operation and profitability of standard project and subsequent EOR schemes. Therefore, the PC and related tools are important and short-term measures for the Government to motivate EOR projects.

Under the PC, and after royalty, the Contractor(s) will recover project costs from petroleum revenue, with the remaining income to be shared between two parties. However, there will be in fact much more factors, or tools that the Government can use to fine-tune a project's attractiveness (Figure 6).

To assess the current incentives for oil and gas projects in Vietnam, and possible effects on an EOR schemes, this paper will present the simulation results using a financial model of a specific project in Vietnam. The model is constructed in Excel, with inputs including operation and financial assumptions for the projects such as production profile, CAPEX and OPEX, decommissioning cost, ownership structure, oil and gas price (subject to various scenarios of medium and long-term price movements), as well as PC terms; and outputs including Net Present Value (NPV) and Internal Rate of Return (IRR). Basically, the model will show the effects of varying inputs, especially the PC terms, on the project's profitability.

The modelled project (Project A refers to the original project, and Project A(EOR) refers to the EOR scheme) replicates the technical profile of a producing and EOR-potential field in Vietnam. Project A is assumed to start exploration in 1993 and production activities in 1999. The Contractor(s) agrees to move into EOR in 2012 and first incremental output begins in 2015. Detailed assumptions for Project A are presented in Table 1.

The purpose is to measure the attractiveness of current Vietnam's PC: how it is compared to other EOR incentives in neighbouring countries in terms of NPV for the Contractor(s) (using the same project's technical datasets), and how it changes when other factors change. We will then use the findings to propose several policy options and steps to motivate EOR projects in Vietnam.

We start with looking at Vietnam's Petroleum Laws and comparing these with the Malaysian

and Indonesian terms for the original project without EOR (Project A). The results show that without investment incentive conditions, the Vietnam's PC under the Petroleum Laws (1993, 2000 and 2008) - though better than that of Malaysia, generates lower NPV for the Contractor(s) compared with the Indonesian. But when investment incentive terms are applied, Project A's NPV is the highest under the case of Vietnam's Petroleum Law 2000 at USD 6,225 million, compared with USD 4,663 million for Malaysia (above-1,000-m-depth incentives) and USD 4,972 million for Indonesia (GR79/2010 regulations).

We then examine how these petroleum contract terms affect the NPV for an EOR project - Project A(EOR) as in our calculation. The results show that Vietnam Petroleum Law 2000 again gives the highest NPV at USD 119.7 million, which is the profit for the foreign Contractor(s) on the EOR programme only. This is slightly higher than the outcome for the Petroleum Law 1993 and that of Indonesia's EOR policies.



Figure 6. Factors influencing the project's attractiveness for the Contractor(s)

Table 1. Model inputs for Project A

Items	Project A	Project A (EOR)
Petroleum production (MMboe)	249.74	7.59
- Oil	239.20	7.59
- Gas	10.54	0.00
Total costs (USD million)	4,070.95	141.13
- Sunk costs	674.45	0.00
- CAPEX	1,232.59	125.53
- OPEX	2,011.88	8.10
- Decommissioning costs	152.03	7.5

Therefore, this paper will use the Vietnam Petroleum Law 2000 as the baseline regulation to first construct an EOR incentive schemes for Vietnam and then to assess the impact of various factors on the incentive's attractiveness. Specifically, we refer to the Vietnam Petroleum Law 2000 when constructing the base case for EOR incentive scheme, with key terms as followed:

- Natural resource tax: 4%;
- Export tax: 4%;
- Corporate income tax: 32%;
- Cost recovery rate: 70%;
- Profit share for the Contractor(s): 70%.

We alter several terms to access the impact on project's profitability, in order to come up with a proposed PC structure that is robust to attract an EOR project. The results are presented on Figure 7. It should be noted that the figure is to assess the impact on the project's NPV when altering specific terms in the PC, and the figure will not reflect the relative importance of each term. First, raising the natural resource tax rate will lower the project's profitability but by a small amount. In particular, the project NPV falls 3.6% and 5.4% as natural resource tax rate is up from 4% to 6% and 7% respectively. Similarly, crude oil export tax rate has a negative effect on the project's NPV: pushing NPV down by 12.6% as the tax rate hits 10%. Raising tax rates for EOR activities is not a recommended option but these results can help to calculate the impact of such option, especially when it can be employed with other supporting measures.

The simulation also looks at cost recovery rate, which allows the Contractor(s) to quickly get back money for the amount spent on CAPEX and OPEX. However, the results show that project's NPV only improves slightly, by 0.9% and 1.5%, when cost recovery is lifted from 70% to 80% and 90% respectively. For corporate income

tax, we consider two other cases: 32% but with 100% tax waiver for the first profitable year and 50% waiver for the second year; and 28%. The results show that NPV is up by only 1.9% if tax waiver policy is used, but jumps to 7.7% at 28% corporate income tax. The final measure being examined is the profit oil and gas rate for the foreign Contractor(s), which obviously is the direct share among the parties and will considerably influence the project's profitability. The simulation shows that NPV jumps by 9.6% when the Contractor's share is raised from 70% to 75%, and NPV reaches 19.2% when the Contractor(s) receives 80% of profit oil/gas. So apart from policy adjustments, changing profit oil rate is still the direct and powerful measure to determine the profitability of a project from a Contractor's perspective.

4. Conclusion and policy recommendations

The above sections on project economics and fiscal regime simulation show that effective Government policies to motivate EOR activities must address two important issues: long-term commitment of the Contractor(s), and the specific risks for individual projects. First, the Government should design its policies and related petroleum regulations so that the foreign Contractor(s) will focus on the ultimate recovery rate of the field, rather than on the immediate targets or short-term profits. This will help to achieve optimal exploitation of hydrocarbon resources and bring long-term financial rewards to the host Government and foreign Contractor(s). The solutions can include direct measures, such as compulsory life-cycle planning which requires the foreign Contractor(s) to consider and propose EOR programmes. Early planning leads to early assessment and R&D studies, which is not only cost-effective but also provide more and better results for the Contractor(s) when implementing the EOR programmes later in the project. Encouraging long-term commitment in EOR also relates to other indirect measures by the Government. For example, promoting energy security will direct more attention to the indigenous oil and gas resources, where EOR can help to fully recover. Also, emphasising environmental issues

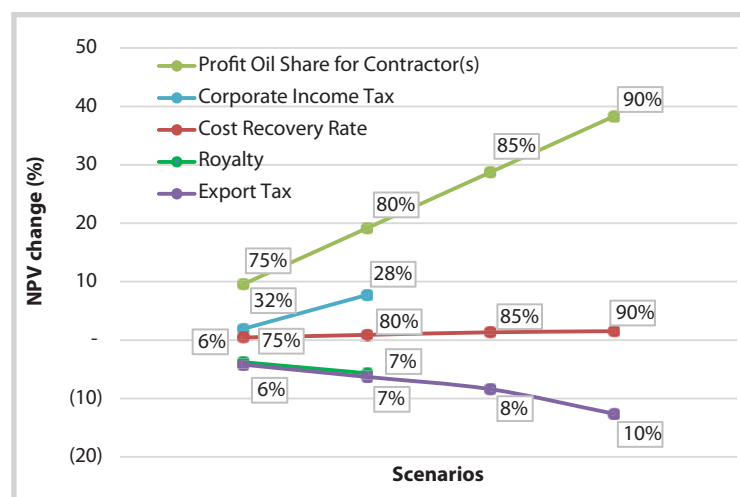


Figure 7. Sensitivity analysis for Project A (EOR)'s NPV

requires sustainable treatment of CO₂, where EOR again can be helpful by capturing CO₂ for the long-term storage. Besides these high-level policies, the Government also needs to employ flexible tools at lower levels to adjust the incentives for various projects due to their respective technical and economic risks.

The paper therefore proposes a 3-step strategy to motivate EOR projects in Vietnam, starting from the short-term measures and ready tools that the Government can use to quickly encourage EOR programmes, to longer-term measures that require lengthy political process but will also be the key to the attractiveness and viability of EOR projects in Vietnam.

Step 1: The Government first adjusts the profit oil and gas rate for EOR projects, to the range of 70 - 90% for the foreign Contractor(s). Besides, Petrovietnam will propose the Government (subject to the Prime Minister's approval) to extend the PC duration as an incentive for the Contractor(s) to continue to strive for more production from the existing fields.

Step 2: The Government then amends the cost recovery and windfall tax for projects signed after 1 Jan 2010. In particular, cost recovery rate is advised to be raised to 75 - 90% while windfall tax will be the same as for investment incentive projects regulated under Decree 100/2009/ND-CP dated 3 November 2009.

Step 3: The Government will seek approval from the National Assembly to amend related tax policies. Specifically, natural resource tax for the incremental production will be at 4 - 7%. Export duty will be at 4 - 10%, again for the incremental production by the EOR project. And finally, the corporate income tax should be adjusted down to 28% for the profit attached to EOR production, and this tax rate will be lifted to 32% once the EOR project has recovered the CAPEX costs.

These adjustments can be made to the current PC Model, or applied to a newly-created EOR PC which is based on but separated from the original PC. The EOR PC then can be designed to fit with the unique technical and economic characteristics of EOR practice. This will have the flexibility advantage for the Government and the Contractor(s) to strike a deal that brings a win-win outcome in a type of programme that is usually costly, risky, and time consuming.

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PETROVIETNAM NEWS

EPC contracts signed for Phu My NH₃ (revamping) - NPK complex



PVFCCo signed the EPC contract with the contractor consortium of ThyssenKrupp Industrial Solutions and PTSC. Photo: Dinh Khoi

Petrovietnam Fertilizer and Chemicals Corporation (PVFCCo) together with the contractor consortium of Technip Group, ThyssenKrupp Industrial Solutions and Petrovietnam Technical Services Corporation (PTSC) signed the EPC Contract for Phu My NH₃ (revamping) - NPK Complex.

Phu My NH₃ (revamping) - NPK Complex covers an area of over 15 hectares, on the land of Phu My Fertilizer Plant. The total invested capital of this complex project is nearly VND 5,000 billion (equivalent to USD 237 million), with 70% financed by bank loan and 30% by the Owner's equity, consisting of two parts: NH₃ Workshop (revamping) and Phu My NPK Plant.

The NH₃ Workshop (revamping) will increase the current NH₃ output at Phu My Fertilizer Plant by 90,000 tons/year (from the current 450,000 tons/year to 540,000 tons/year), using the technology from Haldor Topsoe A/S (Denmark). The EPC contractor consortium consists of

Technip Group (previously also the Contractor for Phu My Fertilizer Plant) and PTSC. A part of the additional NH₃ produced will be used as direct feedstock for Phu My NPK Plant while the other part will satisfy the domestic demand for NH₃, which is still in great shortage.

The projected Phu My NPK Plant with capacity of 250,000 tons/year is the first in Vietnam to apply the chemical technology of Incro SA (Spain), the most advanced technology in the world at present to produce high-quality NPK fertilizer with guaranteed content of all necessary elements that are suitable to crops at different growth periods and under different soil conditions. The contractor consortium consists of ThyssenKrupp Industrial Solutions and PTSC. Reportedly, Vietnam demands around 4 million tons of NPK every year, of which high quality NPK fertilizer products can only meet 5 - 10%. The products of Phu My NPK Plant will replace most of currently imported NPK.

Mr. Cao Hoai Duong, PVFCCo's President & CEO said: "The fact that PVFCCo selects the world's most advanced technologies, the equipments of European origin and a contractor consortium of reputable Group and companies experienced in large global projects will ensure timely and safe project completion with high-quality products of international standard. After 26 months of implementation, the Project is expected to be brought into operation in the second quarter of 2017, raising PVFCCo to a new height of development. In addition, this project is a typical demonstration for the use of internal resources within the oil and gas industry to support the agriculture sector of our country with high-quality fertilizers".

Vu Dinh

Petrovietnam - 40 years of integration and development

The Vietnam Oil and Gas Group (Petrovietnam) informed that in conjunction with its 40th Anniversary, a Conference and Exhibition with the theme "Petrovietnam - 40 years of integration and development" will be scheduled for October 2015 in Ho Chi Minh city. This is an important event to mark significant milestones through four decades of development - its emergence and contribution to Vietnam's economy in general as well as to Vietnam's oil and gas industry in particular.

Along with the international exhibition, the Science and Technology Conference is one of the most important events within the framework of this anniversary. The aim of the conference is to introduce and promote scientific achievements, confirming the impact of modern technology on the petroleum industry.

This conference also motivates co-operation in science and technology transfer in the oil and gas industry with a view to satisfying the requirements of national industrialisation and modernisation. The conference will create a forum for oil and gas companies to discuss current hot topics in the petroleum industry in both regional and international perspectives, as well as the impacts for the coming years..

In the new stage of development, Petrovietnam affirms that development of science and technology is the foundation, motivation and one of the three breakthrough solutions for Vietnam's oil and gas industry in order to achieve rapid and sustainable development.

Manh Chung

Experience in implementation and management of refinery upgrading and expansion projects



Dung Quat refinery. Photo: BSR

From 17 - 18 June 2015 in Quang Ngai province, Binh Son Refining and Petrochemical Company Limited (BSR) and UOP (USA) held a workshop on experience in implementing and managing refinery upgrading and expansion projects in the world.

At the workshop, experts from UOP introduced and share experience in deploying and managing multiple projects to upgrade and expand refineries in the world

that UOP has been involved so that they can be applied to the project to upgrade and expand the Dung Quat refinery. On that basis, UOP raises issues such as the project's objectives, implementation plan and schedule, history of BSR major projects, policies and procedures for the project, capital and experience of BSR in the project implementation process, and BSR's ability to organise the project. The workshop analysed and discussed the challenges in the process of upgrading and expanding the refinery, the organisation of the project implementation, experience, ability and capacity of BSR, and environmental safety issues.

Earlier, the Management Board of Dung Quat Economic Zone granted the investment certificate for the project to upgrade and expand Dung Quat refinery on 24 December 2014. Accordingly, the USD 1.82 billion project will boost crude oil processing capacity at the refinery to 8.5 million tons/year from its current 6.5 million tons/year.

Tran Minh

Successful load-out of jacket for BK Thien Ung



Jacket for BK Thien Ung. Photo: VSP

On 29 June 2015, Vietsovpetro successfully loaded out the jacket of BK Thien Ung on the launching barge by stand-jack skidding system. The jacket, weighing 6,600 tons, has the length of 130m and will be transported and installed in Thien Ung field of Block 04-3 in the Nam Con Son basin, on the Southern continental shelf of Vietnam.

Mr. Tu Thanh Nghia, President & CEO of Vietsovpetro, confirmed after 30 years of exploration

and production in Block 09-1, the construction of BK Thien Ung in Block 04-3 marks a new development step of Vietsovpetro. This project will help stabilise Vietsovpetro's production in the following years. This is also the first time Vietsovpetro assumed the role of general contractor for the construction of gas production rig in deep water areas, with a high proportion of local content in the design, procurement and fabrication.

Minh Phuong

SCIENTIFIC CONFERENCE ON DUNG QUAT REFINERY UPGRADING AND EXPANSION PROJECT

On 19 June 2015, a scientific conference on "Promoting internal resources to participate in the upgrading and expansion of Dung Quat refinery project" was held and chaired by the Vietnam Petroleum Association (VPA) in Vung Tau city. The conference concentrated on assessing the capability and experience of the local contractors involved in the construction of Dung Quat Refinery, and on that basis evaluating the capacity to implement work items in the refinery upgrading and expansion project.

Khoi Nguyen

PTSC INVESTS IN PURCHASING A 7,080 BHP AHTS VESSEL

On 17 June 2015, Greatship (India) Limited officially signed the protocol to handover M/V Greatship Akhila to Petrovietnam Technical Services Corporation (PTSC). The vessel is 63m in length and 15m in breadth, with a deadweight of 1,639 tons, capacity of 7,080 BHP, and is equipped with a dynamic positioning system DP-2 with high mobility, meeting all requirements for exploration and production activities. After being handed over to PTSC, the vessel's name will be changed to "PTSC Tien Phong". PTSC currently has a fleet of 23 service vessels.

Le Anh

PVFCCo excellently completes the periodic overall maintenance of Phu My Fertilizer plant



The overall maintenance was carried out at Phu My Fertiliser Plant. Photo: PVFCCo

Petrovietnam Fertilizer and Chemicals Corporation (PVFCCo) announces that the periodic overall maintenance of Phu My Fertilizer Plant has been successfully completed ahead of schedule. The overall maintenance of Phu My Fertilizer Plant is carried out once every 2 years. This year, it started on 26 May 2015 and has satisfied

all 4 criteria of safety, quality, progress and cost. The plant officially released the urea product with 100% capacity at 23:55 hours on 20 June 2015, which meant 2 days ahead of schedule. This progress brought benefit worth tens of billions VND to PVFCCo and contributed to the timely supply of fertilizers for the next summer-autumn crop.

Although the domestic fertilizer market has met with many difficulties but in the first 6 months of 2015, PVFCCo has produced 370,762 tons of Phu My fertilizer (equal to 48% of the yearly plan) and sold 430,000 tons of Phu My fertilizer (equal to 54% of yearly plan). PVFCCo estimated its first-half revenues will reach 4.945 trillion VND (equal to 53% of the yearly plan), and its profits amount to 63% of the yearly plan. According to Nielsen Vietnam's assessment, Phu My Fertilizer continues to be the leading brand in Vietnam's fertilizer market with 40% of the market share.

Thuy Nguyen

DMC-VTS puts barite production plant in Laos into operation



Barite products manufactured by DMC-VTS Joint Venture. Photo: DMC

On 19 June 2015, at Savannakhet province (Lao People's Democratic Republic), the Joint Venture of DMC-VTS organised the ceremony for inauguration and official operation of barite production plant. It is the result of co-operation between Petrovietnam Drilling Mud Corporation (DMC) and VTS Group.

With a total investment of over 3.5 million USD, the plant is built in an area of 3ha. The plant is equipped with a modern system of equipment and production line

of 15 - 17 tons/hour capacity, meeting the API standard for stable quality of products and the international standards for warehouses. It is estimated that the plant can supply 50,000 tons of products annually to meet the demand for barite of the oil and gas industry of Laos and Vietnam, facilitate export and bring stable revenue for the joint venture.

Dr. Dinh Van Son, member of the Board of Directors of Petrovietnam emphasised the plant shall bring the barite manufacturing industry in Laos to a new, professional and modern level. The Petrovietnam's leader also requested that DMC should ensure sustainable environmental development and improvement of life quality together with production. He hoped that the Lao Government would continue to create conditions for the investment activities of the oil and gas industry in general and of DMC in particular to be effectively implemented in the coming period.

Cung Duy

SEMINAR ON UTILISATION OF STANDARD OFFSHORE FACILITIES



Mr. Raymond Poh, senior principle surveyor of DNV.GL, presented at the seminar. Photo: NWL

On 23 June 2015, many companies and petroleum contractors in Vietnam attended the seminar on the benefits of using DNV certified containers, reefers and modules held by Ferguson Group (Singapore), DNV.GL and New World Logistics JSC in Vung Tau city.

At the seminar, senior principle surveyor of DNV.GL (Singapore) Raymond Poh presented the safety standards of DNV2.7-1 certificate, the approval and certification procedures, the regulations and standards for offshore containers, the benefits of using certified DNV2.7-1 offshore facilities (especially offshore containers, reefers and modules) and the risks of using substandard equipment offshore.

Son Hai



GLOBAL MARKET

Supply and demand

Although oil price collapse continues its trend in the first quarter 2015, the worldwide oil and gas production was quasi stable and supply would be higher than demand in the remaining time of the year (Table 1). EIA expects that OPEC members will continue to produce more than 30 million barrels/day of oil over the next quarter and the non-OPEC countries will take the same orientation. An exception of this trend is the contraction in US shale due to the high cost compared to the conventional crude oil prices in the market. EIA predicts that the major shale regions of the country will see oil production fall by 91,000 barrels in July. The Eagle Ford in South Texas will account for more than half of that drop off with a fall of 49,000 barrels/day. At the same time, the fall in rig counts seems to be levelling off. Because there is a significant lag

between the decline in the number of rigs in operation and a resulting fall in production, it is possible that production levels will continue to dip even as rig counts stabilise.

Meanwhile, China has seen its oil imports seesaw back and forth in recent months. In April, China imported a record 7.37 million barrels/day. In May, China only imported 5.47 million barrels/day, as an unusually large volume of refining capacity was offline for maintenance.

In the OPEC production quota unchanged context, analysts predict that by the end of this year (2015) global supply will outstrip demand by an estimated 1.5 - 2 million barrels/day. Although this scenario could take place, prices began to increase at a low rate in May and June with some fluctuations in short duration due to the global and regional political tension (Table 2; Figure 1).

Table 1. Worldwide crude oil and gas production

	March 2015		February 2015		Average crude production	Cum. first quarter of 2015
	Crude (1,000 barrels/day)	Gas (bcf)	Crude (1,000 barrels/day)	Gas (bcf)	(1,000 barrels/day)	Gas (bcf)
Argentina	531	103.1	529	103.1	531	298.87
Bolivia	49	63.0	49	63.0	49	189.00
Brazil	2,300	81.0	2,300	81.0	2,300	244.00
Canada	3,870	495.0	3,899	495.0	3,876	1,436.01
Columbia	980	30.0	980	30.0	980	90.00
Ecuador	550	1.0	530	1.0	547	3.00
Mexico	2,319	142.9	2,678	142.9	2,533	533.95
Peru	62	38.8	63	38.8	62	117.05
Trinidad	81	122.6	84	122.6	83	363.16
United States	9,531	2,373.9	9,405	2,373.9	9,434	6,883.98
Venezuela	2,400	63.0	2,380	63.0	2,393	189.00
Other Latin America	89	4.2	89	4.2	89	12.72
Western Hemisphere	22,762	3,518.5	22,985	3,518.5	22,877	10,361.73
Austria	17	4.0	17	4.0	17	11.02
Denmark	153	12.7	161	12.7	157	39.08
France	17	0.1	16	0.1	16	0.26
Germany	47	26.0	50	26.0	47	79.70
Italy	102	20.3	82	20.3	93	58.76
Netherlands	29	229.9	32	229.9	30	916.36
Norway	1,563	384.9	1,617	384.9	1,589	1,105.33
Turkey	46	1.2	47	1.2	47	3.50

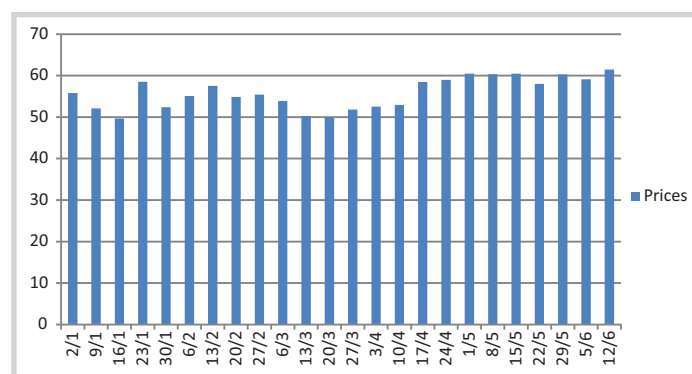
	March 2015		February 2015		Average crude production	Cum. first quarter of 2015
	Crude (1,000 barrels/day)	Gas (bcf)	Crude (1,000 barrels/day)	Gas (bcf)	(1,000 barrels/day)	Gas (bcf)
United Kingdom	857	115.7	821	115.7	852	327.61
Other Western Europe	8	1.0	9	1.0	8	3.11
Western Europe	2,839	795.8	2,851	795.8	2,856	2,544.73
Azerbaijan	830	62.9	811	62.9	820	184.45
Croatia	12	5.0	12	5.0	12	15.00
Hungaria	12	5.0	12	5.0	12	15.00
Kazakhstan	1,397	130.0	1,417	130.0	1,394	390.00
Romania	81	34.0	81	34.0	80	102.00
Russia	10,086	1,957.3	10,167	1,957.3	10,121	6,027.82
Other FSU	370	520.0	370	520.0	370	1,560.00
Other Eastern Europe	8	23.4	9	23.4	8	70.24
Eastern Europe & FSU	12,847	2,737.5	12,929	2,737.5	12,868	8,364.50
Algeria	1,120	230.0	1,100	230.0	1,107	690.00
Angola	1,760	4.0	1,790	4.0	1,773	12.00
Cameroon	82	2.0	82	2.0	82	6.00
Congo (Zaire)	28	-	28	-	28	-
Congo (Brazzaville)	290	-	290	-	290	-
Egypt	690	105.0	690	105.0	690	315.00
Equatorial Guinea	248	0.1	248	0.1	248	0.18
Gabon	260	0.3	260	0.3	260	0.90
Libya	480	25.0	270	25.0	363	75.00
Nigeria	1,740	70.0	1,860	70.0	1,830	210.00
Sudan	258	-	258	-	258	-
Tunisia	50	8.1	50	8.1	51	24.15
Other Africa	285	9.1	285	9.1	285	27.30
Africa	7,291	453.5	7,211	453.5	7,266	1,360.53
Bahrain	49	32.0	48	32.0	49	96.00
Iran	2,790	465.0	2,840	465.0	2,817	1,395.00
Iraq	3,700	28.0	3,320	28.0	3,487	84.00
Kuwait	2,800	43.3	2,800	43.3	2,800	129.87
Oman	982	86.0	963	86.0	970	258.00
Qatar	680	600.0	670	600.0	673	1,800.00
Saudi Arabia	10,190	250.0	9,710	250.0	9,863	750.00
Syria	30	14.0	30	14.0	30	42.00
United Arab Emirates	2,840	165.0	2,840	165.0	2,840	495.00
Yemen	160	-	160	-	160	-
Other Middle East	1	26.5	1	26.5	1	79.50
Middle East	24,222	1,709.8	23,382	1,709.8	23,690	5,129.37
Australia	249	149.7	311	149.7	296	447.25
Brunei	114	37.5	117	37.5	113	109.12
China	4,266	412.8	4,237	412.8	4,254	1,243.41
India	774	100.2	764	100.2	768	291.11
Indonesia	795	213.0	790	213.0	794	639.00
Japan	11	16.5	11	16.5	11	48.77
Malaysia	506	197.0	665	197.0	600	596.33
New Zealand	35	15.0	34	15.0	35	39.34
Pakistan	95	110.0	96	110.0	95	345.26
Papua New Guinea	30	0.5	30	0.5	30	1.49
Thailand	254	129.8	233	129.8	240	360.41
Vietnam	300	33.0	300	33.0	300	99.00
Other Asia-Pacific	38	107.4	43	107.4	40	332.51
Asia-Pacific	7,467	1,522.4	7,630	1,522.4	7,575	4,553.00
Total world	77,428	10,737.4	76,988	10,737.4	77,131	32,313.86
OPEC	31,050	1,944.3	30,110	1,944.3	30,493	5,832.87

Source: Oil and Gas Journal, June 8, 2015

Table 2. World crude prices (USD/barrel)

	15 March 2015	15 April 2015	15 May 2015
OPEC reference basket	52.46	57.30	62.16
Arab light - Saudi Arabia	52.20	57.73	62.62
Basrah light - Iraq	50.53	55.61	60.40
Bonny light 37° - Nigeria	56.75	60.65	65.30
Es Sider - Libya	54.78	58.40	63.22
Girassol - Angola	56.86	61.12	65.51
Iran heavy - Iran	51.27	56.26	61.38
Kuwait export - Kuwait	50.52	55.96	60.92
Marine - Qatar	54.27	58.51	63.26
Merey - Venezuela	45.79	49.49	55.09
Murban - UAE	57.41	61.66	66.18
Oriente - Ecuador	45.79	52.73	58.04
Saharan blend 44° - Algeria	56.93	59.75	64.12
Minas 34° - Indonesia	54.11	58.55	62.98
Fateh 32° - Dubai	54.66	58.55	63.54
Isthmus 33° - Mexico	51.41	59.10	63.78
Brent 38° - UK	55.93	59.50	64.32
Urals - Russia	55.07	59.70	64.33
WTI/Brent	-6.43	-5.07	-5.04
Brent/Dubai	1.27	0.95	0.78

Sources: Oil and Gas Journal, 29 June 2015

**Figure 1.** WTI prices in the first 6 months of 2015 (USD/barrel)

According to www.marketwatch.com, on 9 June 2015 oil futures rallied by more than 3% as signs of an overall slowdown in US crude production expected later in the year helped lift prices for the US crude benchmark back above 60 USD/barrel.

US oil production averaged 9.6 million barrels a day in May, the highest monthly level since 1972, according to the EIA report. Output, however, is expected to decline from June through early 2016. The EIA also forecast 2016 output to average 9.27 million barrels a day - below its 9.43 million forecast for 2015.

Later Tuesday, the American Petroleum Institute released its weekly US oil inventory data, followed by the EIA Wednesday. Analysts polled by Platts forecast a decline of 1.6 million barrels. Media reports in recent days have also played up talk among analysts and politicians over lifting the 40-year-old ban on US oil exports.

The oil markets can deal with an off month, but there are growing signs that China may not live up to its hype as an insatiable consumer of petroleum products. Tepid economic growth is cutting into demand growth scenarios for Chinese oil consumption, a worrying sign for those that are long on oil prices. Softer Chinese demand in the months ahead will mean there will be a whole lot more oil sloshing around than there otherwise would have been, potentially prolonging the period of weak oil prices.

Oil is not the only energy source that is seeing a glut. Growing supplies of natural gas could soon result in a similar phenomenon. It was only a year and a half ago that the US saw supplies dwindle to exceptionally low levels, forcing prices to temporarily spike. In 2014, the US produced a record level of natural gas and production continued to rise in the first half of 2015. As inventories rise, gas prices fall. While that is good for consumers, shale gas drillers are beginning to worry. In July 2014, the US average consumer price of natural gas was over 15USD/Mcf for residential, and 5USD/Mcf for industrial/electric power clients, but at the present time these prices come down, remaining only about 9USD/Mcf and 4USD/Mcf respectively.

Merger and assets transaction activities

Enterprise Products Partners (EPP) has executed agreements to acquire all of the member interests in EFS Midstream LLC from affiliates of Pioneer Natural Resources Co., Irving, Texas, and Reliance Industries Ltd., Mumbai, for USD 2.15 billion. The companies announced last year their desire to divest EFS Midstream. Payment will take place in two instalments, with the first amount of USD 1.15 billion being paid at closing and the final payment of USD 1 billion being paid by the first anniversary of the closing. The company said completion of the transaction is subject to customary regulatory approvals and closing conditions. EPP expects the closing in the third quarter of 2015.

Under the agreement's terms, the Pioneer and Reliance joint development will dedicate its Eagle Ford shale acreage to EPP under a 20-year, fixed-fee gathering agreement that includes a minimum volume requirement for the first 7 years. Pioneer and Reliance will also dedicate their Eagle Ford shale acreage under related 20-year fee-based agreements

with EPP for gas processing, NGL transportation and fractionation, and for natural gas, processed condensate, and crude oil transportation services.

EFS Midstream provides gas gathering, treating, compression, and condensate processing in the Eagle Ford shale and includes about 460 miles of natural gas gathering pipelines, 10 central gathering plants, 780MMcfd gas treating capacity, and 119,000 barrels/day of condensate stabilisation capacity.

Hibiscus Petroleum Berhad has terminated its USD 18 million purchase of Talisman Energy Inc.'s 25% interest in Kitan oil field in the Timor Sea. The purchase deal was struck in June 2014, but Hibiscus told the Malaysian stock exchange this week that conditions precedent to the share sale agreement had not been fully satisfied by the May 31 cut-off date.

Kitan field, which lies in the Joint Petroleum Development Area between Australia and Timor Leste 550km northeast of Darwin, was discovered in 2008.

It is operated by Italy's Eni S.p.A with 40% interest. Japan's Inpex Corp. holds 35% and Talisman holds 25%. The field was brought on stream in 2011 via three subsea wells connected to the Glas Dowl floating production, storage, and offloading vessel. Production is running at about 10,000 barrels/day.

Statoil has been awarded four licenses covering 16,000km² in the largely unexplored Sandino basin of the Nicaraguan Pacific. Statoil will operate the licenses with 85% interest, partnering with Empresa Nicaraguense de Petroleo (Petrico), which will hold the remaining interest. Initial work commitments during the 2.5 year first exploration phase include reprocessing of 2D seismic, acquisition of new seismic data, and geologic and geophysical studies. Information obtained from the initial studies and seismic survey will form the basis for Statoil's next steps in the licenses. "Offshore the Nicaraguan Pacific is virtually untested and the awards of new acreage in this frontier area are in line with our exploration strategy of access at scale", commented Nick Maden, senior vice-president for Statoil's exploration activities in the Western Hemisphere.

Woodside Petroleum Ltd. has chosen not to take up its option to proceed to phase 2 of the Lake Tanganyika South production-sharing agreement in Tanzania with Beach Petroleum Ltd. Woodside farmed into Beach's permit last year. The terms remain confidential, but in general Woodside agreed to refund Beach's past costs,

including its early seismic survey programme, and then fund another seismic programme that was carried out during 2014 - 2015. Beach serves as operator with 30% interest while Woodside held the remaining interest. Phase 2 included Woodside providing a capped carry for Beach through the cost of the first exploration well. Woodside would have also taken the operatorship.

Now, however, with Woodside's exit, Beach has resumed 100% interest in the PSA. The company says it has preserved its rights to go ahead with the drilling phase, but has yet to decide whether to bring in another farm-in company or sell out of the block.

Beach secured the onshore-offshore block that encompasses the southern end of 600km Lake Tanganyika in 2008, keen to explore the potential of the Albertine Rift, the western branch of the East African Rift play that has been successfully explored to the north in Lake Albert in Uganda.

The Beach block included natural oil seeps that indicate a working petroleum system beneath the lake. Early work suggested a potential for traps containing 200 million barrels or more.

The practical problem though is that exploration drilling requires transport inland, followed by assembly of an offshore drilling rig to work in the deepest part of the lake. There has been some thought given to first drilling a land-based deviated well under the lake to check for a valid petroleum system before commitment to the offshore drilling.

Woodside has decided that the low oil price environment does not satisfy the risk-reward equation.

Z Energy Ltd. the downstream petroleum entity headquartered in Wellington, has acquired Chevron New Zealand for NZD 785 million. The purchase provides Z Energy with ownership of the Caltex business in New Zealand that includes 147 retail outlets and 73 diesel outlets. The deal comes on the heels of Chevron's separate sale of its 11.4 % interest in New Zealand Refining Co. Ltd., which operates the 107,000 barrels/day Marsden Point refinery of Northland on the North Island's east coast last week. Z Energy holds a 15% interest in the refinery.

Z Energy says its deal with Chevron excludes Chevron's upstream interests, but adds that it was in the best position and a logical buyer of Chevron's retail and distribution chain.

The company has now vastly increased its market share in New Zealand. Formed 5 years ago, Z Energy

says this latest acquisition will bring to 350 its number of retail outlets. The company bought 210 outlets from Royal Dutch Shell PLC in 2010. Z Energy will raise NZD 185 million in synergies from 2017 and give an immediate boost to the company's earning.

Tidewater Midstream & Infrastructure Ltd. will pay CAD 190 million to unspecified "private company vendors" to purchase their 63% operated working interest in an unnamed 185-MMcf/d natural gas processing plant in West Pembina along with related pipelines in central Alberta, Canada. The purchase price consists of CAD 170 million cash and CAD 10 million in Tidewater common shares (at CAD 1.35/share).

Tidewater Midstream & Infrastructure said the plant has current throughput of about 140MMcf/d and can process sweet and sour natural gas and has "area leading" deep cut gas processing capability. In addition, the plant connects to producers through about 240 miles of gas gathering and NGL takeaway and crude systems.

Blaze Energy's website says it conducts most of its operations in the "Brazeau River and West Pembina" areas of Alberta. Its Brazeau River complex possesses large deep cut sour gas capacity and, last year, was "operated and 63%-owned" by Blaze, which also operated gas gathering of about 220 miles.

The US Department of Energy has issued a conditional authorisation for Alaska LNG Project, LLC to export as much as 2.55bcfd of US-produced natural gas for a 30-year period to countries with no free-trade agreement with the US. Earlier this year, Alaska LNG project partners filed resource reports with the US Federal Energy Regulator Commission for the project. Alaska LNG is in the Nikiski area of Alaska's Kenai Peninsula. Federal law generally requires approval of gas exports to countries that have an FTA with the US. For countries that do not have an FTA with the US, the Natural Gas Act directs DOE to grant export authorisations unless it finds that the proposed exports "will not be consistent with the public interest", DOE said.

Timor-Leste has let a USD 3.8-million pre-front-end engineering design contract to Amec Foster Wheeler for the proposed Beaco LNG plant.

Amec Foster Wheeler's scope for the contract includes concept selection studies, development of technical design, development of procurement and construction strategies, project implementation plans, capital cost estimate and schedule for overall project.

Amec Foster Wheeler says work will be performed in close consultation with Timor-Leste's state-owned Timor GAP EP, which is managing the implementation of the Tasi Mane project comprising three clusters of development - the Suai supply base, Betano refinery, and Beaco LNG plant-situated along 155km of Timor-Leste's southern coast.

DEA Deutsch Erdoel AG has farmed out its stake in the West Nile Delta project in Egypt to its joint venture partner and operator BP PLC "in order to better balance its portfolio", the company reported. The deal includes the sale of a portion of DEA's stake in the ongoing Phase 1 development of 5tcf of gas resources. The USD 12 billion West Nile Delta project, which is planned to start production in 2017, is expected to produce 1.2bcfd, or about 25% of Egypt's current gas production. "With the remaining interest of 17.25% in both concessions, West Nile Delta will remain the largest project in DEA's portfolio", the company said.

BP Exploration & production Inc. has let a contract to Technip covering pipeline systems for a southern expansion of ultra-deepwater Thunder Horse oil and gas field on Mississippi Canyon Blocks 778 and 822 in the Gulf of Mexico. The project includes a new drill centre 2 miles from the Thunder Horse semi-submersible production, drilling, and quarters platform in 6,050ft of water, 150m southeast of New Orleans. Four wells will tie in to the drill centre. BP expects production from the project to start in 2017 and peak at 42,000 barrels of oil equivalent/day.

Anadarko Petroleum Corp. has let a contract to CB&I, Chiyoda Corp., and Saipem SPA-together forming the CCS joint venture - for the initial development of a LNG project in Mozambique.

The scope of work includes two LNG trains, each with capacity of 6 million tons/year, an increase of 1million tons/year for each train over the original plan while maintaining an estimated cost that is consistent with the co-venturers' original projection, Anadarko says. The scope also includes two 180,000 m³ LNG storage tanks, condensate storage, multi-berth marine jetty, and associated utilities and infrastructure.

The co-venturers have secured more than 8 million tons/year in nonbinding long-term off-take agreements that are now progressing toward binding sales and purchase agreements, and obtained letters of intent from lenders for project financing at a very material level.

Ha Phong