

PETROVIETNAM JOURNAL



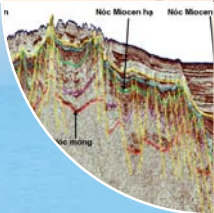
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Exploration and appraisal activities in 2006 - 2012,

**PLAN FOR 2015 AND STRATEGY FOR
FUTURE UPSTREAM ACTIVITIES**





Hanoi, 22 - 23 May, 2013

SCIENCE - TECHNOLOGY CONFERENCE

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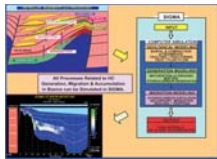
Designed by

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Cover photo: Dai Hung 02 platform from above (the silver prize, photo contest "PVEP - the journey to find oil"). Photo: Hoang Quang Ha



SCIENTIFIC & TECHNOLOGICAL PAPERS

PETROVIETNAM	
Modeling of petroleum generation in Phu Khanh Basin by Sigma-2D software	
<p>Nguyen Hoa Trung, Trinh Xuan Cuong, Nguyen Thi Tuyet Lan, Do Manh Tuan, Nguyen Ngoc Minh, Nguyen Trung Quan Vietnam Petroleum Institute Akihiko Ohai Idemitsu Oil and Gas Co., Ltd</p>	
Abstract	<p>The Phu Khanh Basin is a narrow, elongated basin extending from 11.5 to 14°N off the coast of central Vietnam. It is bounded to the west by the narrow Da Nang shelf and separated from the Quang Ngai Graben to the North by the Da Nang shear zone, and from the Cui Long Basin to the South by the Tay Hoa shear zone.</p> <p>The purpose of this paper is to understand, by 2D modeling, the generation, migration and accumulation histories for oil and gas from source rocks in the Phu Khanh Basin. Several regional sections covering shallow to deep-water areas were modeled by SIGMA-2D software. In the sedimentary basin, Oligocene lacustrine source rock has generated oil since the Middle Miocene time and is in gas window in almost the entire area of the basin, with the main part in the deep water area at the present time. The Lower Miocene fluvio-deltaic source rock has generated oil since the Late Miocene time and is in gas window in the central part of the basin at the present time.</p> <p>Oil and gas generated both in the Oligocene and Lower Miocene source rocks in deep water areas migrated along a regional carrier system in Lower Miocene (both sandstone and porous carbonates) after vertical migration of the Oligocene oil and gas by cap rock leakage and through faults. The oil and gas accumulated in structural highs in both deep water and in shallow water areas. Some were already found as oil seeps from onshore outcrops (T1) and were encountered in exploration wells such as 124-CMT-12.</p>
1. Introduction	<p>The Phu Khanh Basin is one of Vietnam's large offshore Cenozoic Basins located along the Western and Southern margins of the East Vietnam Sea. It is located at latitudes from 11 - 15°N offshore central Vietnam, as a narrow North - South trending basin approximately 250km long and 50 - 75km wide (Lee and Watkins, 1998). These basins have attracted increasing interest from the national and international oil and gas industry as significant hydrocarbon resources have been identified. While the Vietnamese sedimentary basins have generally been explored to some extent with an open seismic coverage acquired over a period of 20 years from 1974 - 1993 (2). In 2009, crude oil was</p>
 <p>discovered only at well 124-CMT in carbonate reservoir, while the other well was dry in block 127.</p>	
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PETROLEUM EXPLORATION & PRODUCTION

Exploration and appraisal activities in 2006 - 2012, plan for 2015 and strategy for future upstream activities

Pham Thanh Lile
Vietnam Oil and Gas Group

Abstract

One of the most important activities to the technical staff in general and petroleum geologists in particular is to ensure the exploration activities, to evaluate the potential hydrocarbon reserves then to conduct its production logically. The first issue of this paper is to introduce to the readers and to colleagues (in and out of the petroleum domain), a summary of the exploration and appraisal activities of Petrovietnam in Vietnam as well as overseas during the period of 2006 - 2012 with the sudden changes reflecting, especially of the world economic crisis that has occurred. Several petroleum contracts have been signed, the 2D and 3D seismic acquisition has been conducted, more than 150 exploration and appraisal wells have been drilled during this period and several new fields discoveries have been found in both offshore Vietnam and overseas. The total incremental reserves is one of the good examples to demonstrate that Petrovietnam's intention in the oil and gas exploration, appraisal and production domain is correct.

An exploration and appraisal plan for 2015 and a strategy for further campaigns of exploration and appraisal have also been dealt with in this document with the main points and real events being emphasized. This paper also presents the importance of extending co-operation, sharing experiences and strengthening the ability to form in overseas petroleum contracts by applying a diplomatic petroleum policy.

Content

In the context of a background global economic crisis, the petroleum industry in Vietnam is facing an important challenge, how to continuously affirm Petrovietnam as a key industry with the receipt per year of around 25 - 30% of Vietnam's GDP. It is requested that Petrovietnam needs to have the right orientation in this new stage, in order to maintain stable national power security.

Although Petrovietnam's functions comprise all up to down-stream activities, with exploration, appraisal and production in upstream, in mid-stream storage, transportation, export and import, processing, distribution and sales of petroleum, and downstream is refinery and petrochemistry, finance, banking, insurance and other related services, Petrovietnam always defines its core business to main function as exploration and production activities.

The real results of 2006 - 2012 have confirmed Petrovietnam's orientation in exploration and production both in Vietnam and overseas, was correct. Besides keeping oil production

stable and conducting exploration and appraisal activities in order to drill potential prospects and upgrade new discoveries to development and production, ensuring the incremental reserves were stable, was also very important to Petrovietnam during this period.

Since Petrovietnam took the initiative of seismic acquisition, up to June 2012, much seismic information

Year	Petroleum Contract
2006	5
2007	7
2008	7
2009	13
2010	4
2011	5
2012	11 (4)
to 2015	1 per year

Year	2006	2007	2008	2009	2010	2011	6/2012	Total
Well	17	21	13	15	17	11	4	98
Exploration	17	12	13	13	9	10	7	81
Appraisal	25	33	28	28	26	21	11	172

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- 18 ♦ Pre-Cenozoic basement structure in the Truong Sa archipelago and sea deep basins
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- 65 ♦ Establishment of a methodology for determination of the strength condition of fixed offshore jacket structures in deepwater, based on probabilistic model and reliability theory, and its application in Vietnamese sea conditions
- 74 ♦ The 10th ASCOPE Conference & Exhibition will be hosted by Petrovietnam for the first time
- 75 ♦ First gas from offshore Lan Do field
- 76 ♦ VPI has licensed doctoral level training in Petroleum Engineering
- 77 ♦ PVE organized the 1st Science and Technologies Conference

NEWS

Modeling of petroleum generation in Phu Khanh Basin by Sigma-2D software

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Abstract

The Phu Khanh Basin is a narrow, elongated basin extending from 11.5 to 14°N off the coast of central Vietnam. It is bounded to the west by the narrow Da Nang shelf and separated from the Quang Ngai Graben to the North by the Da Nang shear zone, and from the Cuu Long Basin to the South by the Tuy Hoa shear zone.

The purpose of this paper is to understand, by 2D modeling, the generation, migration and accumulation histories for oil and gas from source rocks in the Phu Khanh Basin. Several regional sections covering shallow to deep-water areas were modeled by SIGMA-2D software. In the sedimentary basin, Oligocene lacustrine source rock has generated oil since the Middle Miocene time and is in gas window in almost the entire area of the basin, with the main part in the deep water area at the present time. The Lower Miocene fluvio-deltaic source rock has generated oil since the Late Miocene time and is in gas window in the central part of the basin at the present time.

Oil and gas generated both in the Oligocene and Lower Miocene source rocks in deep water areas migrated along a regional carrier system in Lower Miocene (both sandstone and porous carbonate) after vertical migration of the Oligocene oil and gas by cap rock leakage and through faults. The oil and gas accumulated in structural highs in both deep water and in shallow water areas. Some were already found as oil seeps from onshore outcrops [1] and were encountered in exploration wells such as 124-CMT-1X.

1. Introduction

The Phu Khanh Basin is one of Vietnam's large offshore Cenozoic Basins located along the Western and Southern margins of the East Vietnam Sea. It is located at latitudes from 11 - 15°N offshore central Vietnam, as a narrow North - South trending basin approximately 250km long and 50 - 75km wide (Lee and Watkins, 1998). These basins have attracted increasing interest from the national and international oil and gas industry as significant hydrocarbon resources have been identified. While the Vietnamese sedimentary basins have generally been explored to some extent, with an open seismic coverage acquired over a period of 20 years from 1974 - 1993 [2]. In 2009, crude oil was

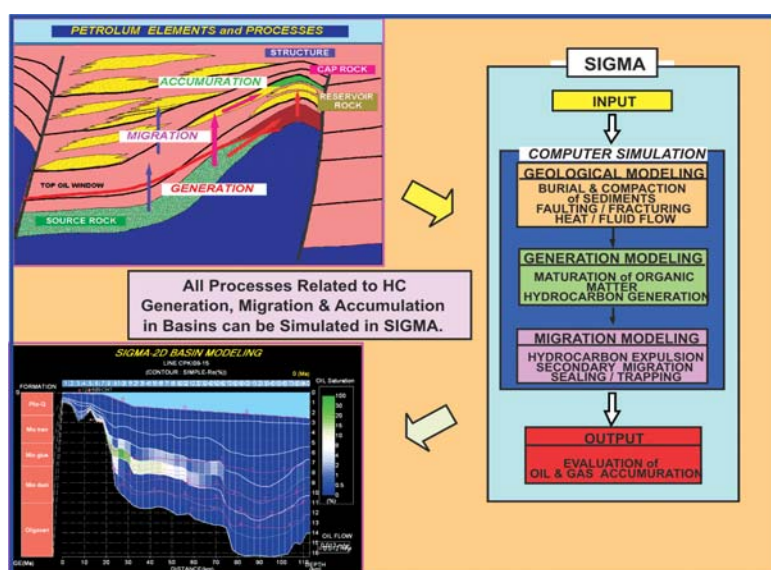


Fig.1. Concept of SIGMA modeling

discovered only at well 124 CMT in carbonate reservoirs, while the other well was dry in block 127.

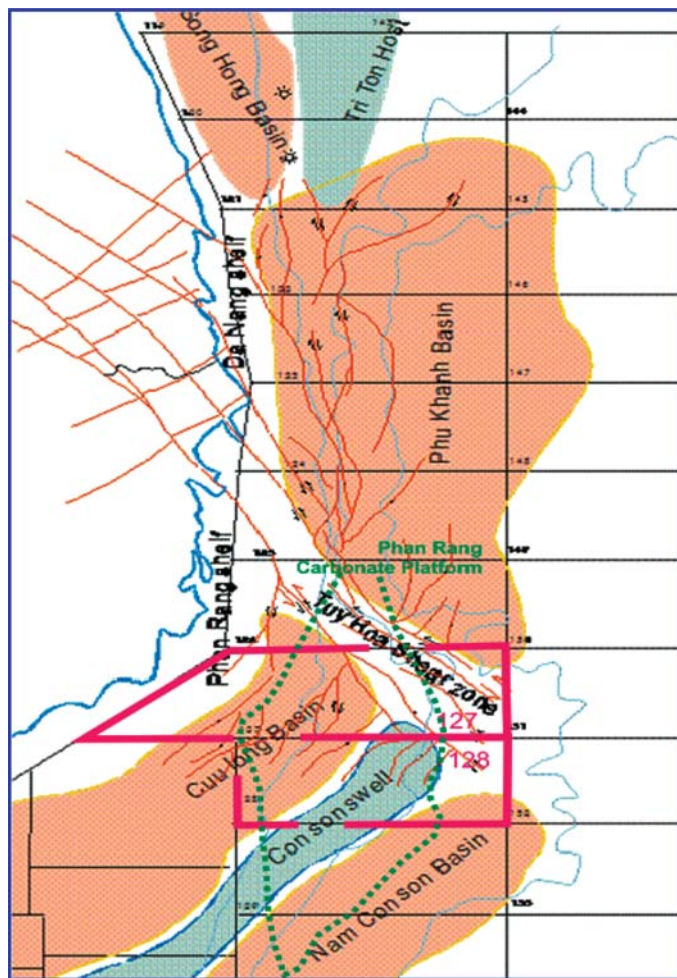


Fig.2. Structural elements of the Phu Khanh Basin
(after Nguyen Hiep, etc. 2007)

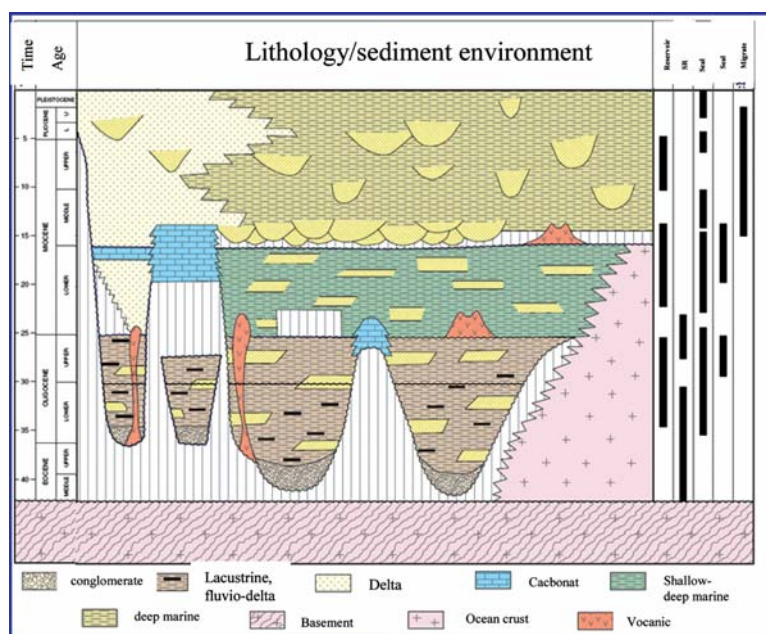


Fig.3. General stratigraphy of the Phu Khanh Basin

Multi-dimensional Basin modeling is a computer simulation technique, which is currently widely used for oil and gas exploration. Basin modeling can reproduce the processes relating to a petroleum system in computer simulation from past to present times thus enabling assessment of the timing and location of the generation, migration and accumulation of oil and gas (Fig.1) [7].

The basin modeling work started from the construction of input data. Depth sections for 2D modeling were created by seismic interpretation and depth conversion. Then, lithology distribution, thermal history and source-rock distribution were determined for each cross section and each map.

Two wells (120CS-1X, 121 CM-1X), were selected for the study area, these being useful to determine the above input data. Lithology at each well can be determined by electrical-logging interpretation. Routine geochemical analyses such as TOC, rock-eval and maceral analysis enables specification of source rock interval and properties at the wells. The temperature profile (geothermal gradient) and vitrinite reflectance can be used for the calibration of thermal history. New information was used only from well 124 CMT-1X (must not use original data because of sensitivity). After the construction of all input data, multi-dimensional basin modeling was conducted to reveal the history of generation, migration and

accumulation of oil and gas in the Phu Khanh Basin. This enables one to pick up any prospective exploration play and its fairway in the Phu Khanh Basin. SIGMA-2D Basin modeling was conducted for regional sections from shallow to deep-water area (blocks 121 - 127 and blocks 141 - 147). At first, calibrations of thermal and pressure histories at wells were done by the comparison of the calculated results with the observed data at wells.

2. Geological setting

The Phu Khanh Basin is an elongated, narrow basin extending from 11.5 - 14°N off the coast of central Vietnam (Fig.2) [2]. The basin is about 250km long from North to South and 50km wide from East to West. It is bounded to the West by the narrow Da Nang shelf, separated from the Quang Ngai graben

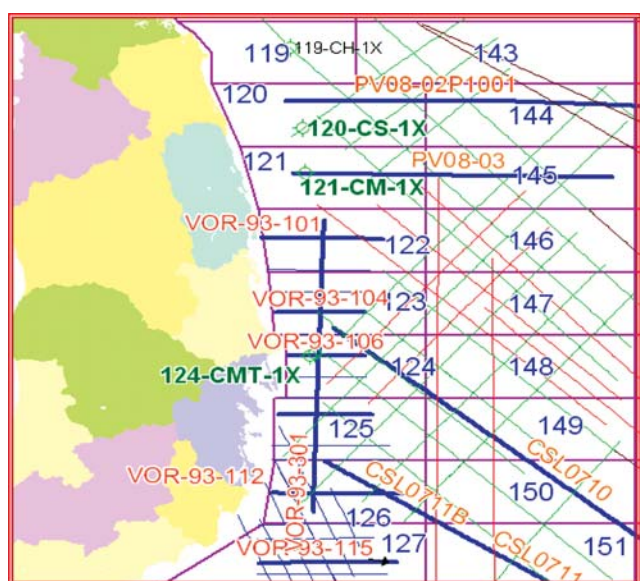


Fig.4. Seismic lines used for SIGMA-2D modeling

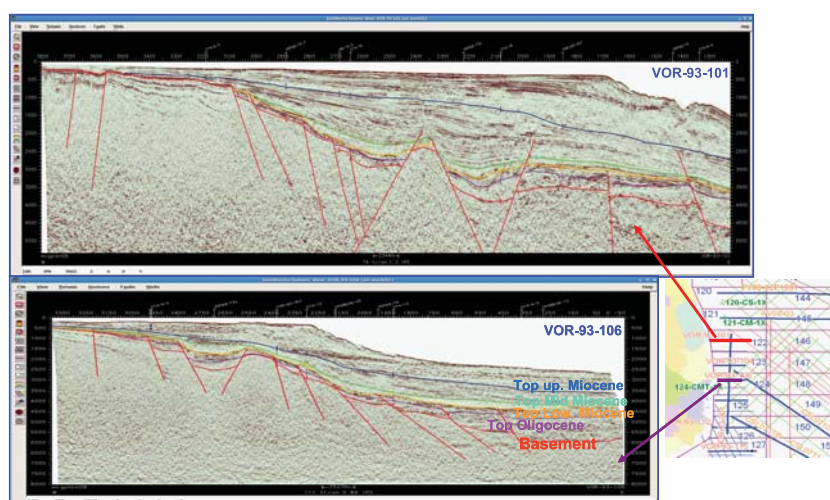


Fig.5a. Interpreted seismic lines (VOR 93-101 and 106) in shallow water areas of the Phu Khanh Basin

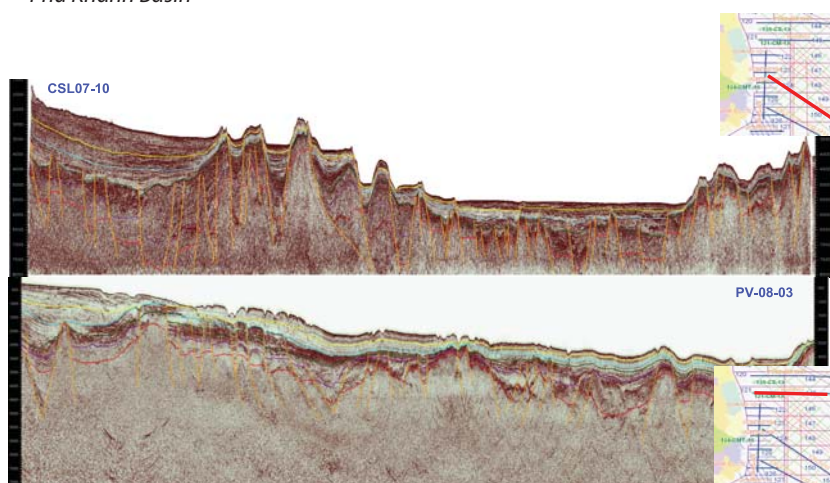


Fig.5b. Interpreted seismic lines (PV08-03 and CSL07-10) in deep water area of the Phu Khanh Basin

to the North by the Da Nang shear zone, and from the Cuu Long Basin to the South by the Tuy Hoa shear zone.

The water depth is less than 100m in the Western near shore areas increasing to more than 3.000m towards the deep-water basin to the East. The area comprises several major structural elements, which mainly trend from the North to the South.

The basin is a rift basin, formed during Eocene? - Oligocene times by crustal extension and stretching. Rifting and uplift appear to have resumed or to have continued locally during the Late Oligocene and Early Miocene epochs. The Oligocene and Lower Miocene sediments are covered by 100 - 3,000m of post-rift Middle Miocene - Quaternary sediments at the present time (Fig.3) [2].

3. Basin modeling

3.1. Depth Section

Seven seismic lines mainly covering shallow water areas and another 4 lines extending to deep water areas were selected for use in this study (Fig.4). These lines were merged to make regional 11 sections, which were used for 2D modeling.

Each seismic section was interrelated at 5 horizons (top of basement, Oligocene, Lower, Middle and Upper Miocene). Well tie was done at 120-CS-1X and 121-CM-1X wells. Fig.5a and 5b are the examples for such interpretations.

Depth conversion from time to depth relationship for sediments was derived from 120-CS-1X and 121-CM-1X wells.

3.2. Lithology, rock properties and fault properties

Lithology (Rock percentage) at each well was evaluated by electrical logging data (Fig.6). However, as no well drilled in the Phu Khanh Basin was permitted to use for this study, lithology was decided mainly by seismic character, basin history and settings.

Properties for each rock type such as porosity, permeability, irreducible water saturation, capillary pressure and thermal conductivity were taken from 2D modeling database (Fig.7). In addition, measured data at wells such as porosity (Fig.8) and formation pressure were used for the calibration for lithology and rock properties.

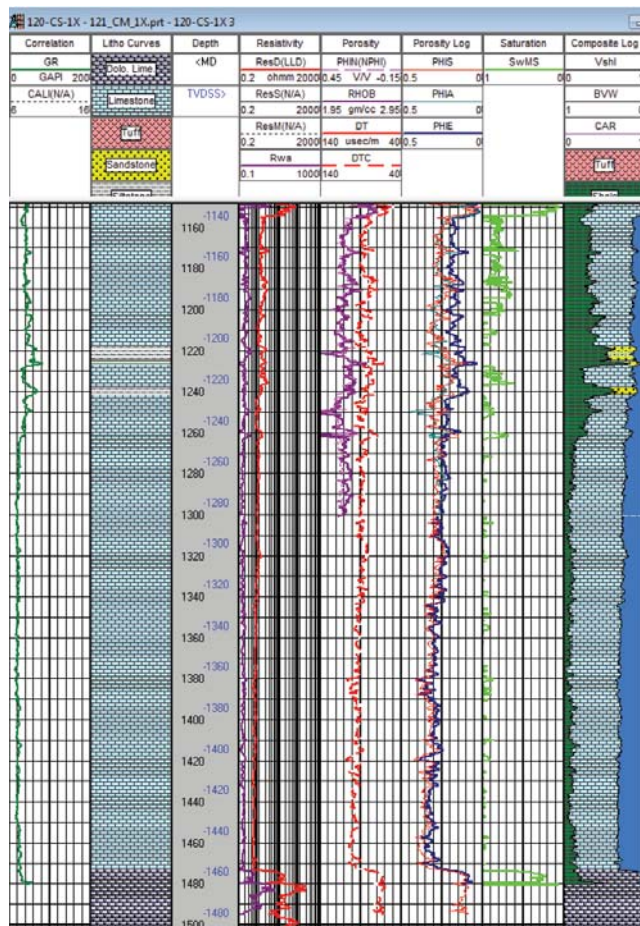


Fig.6. Interpretation of electrical logging data at the well 120-CS-1X

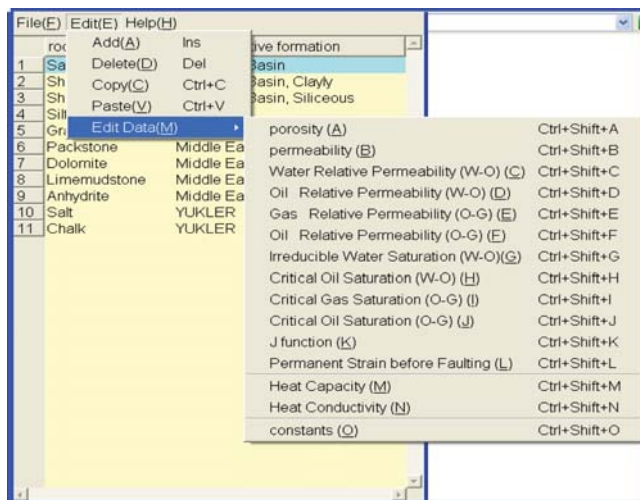


Fig.7. Properties for each rock type used for SIGMA modeling

Faults play important roles for vertical migration of oil and gas. Fault properties in SIGMA are defined by the duration of faulting, its width and permeability. For SIGMA Basin modeling in the Phu Khanh Basin, the duration of faulting was specified based on seismic sections and it was assumed that 10m of a fault zone has 10md permeability at maximum deformation.

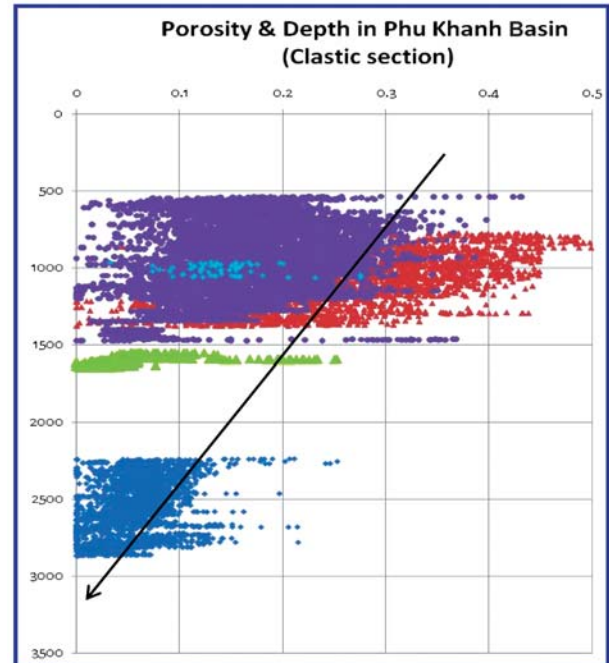


Fig. 8a. Porosity vs. Depth relationship in the Phu Khanh Basin (Clastic section)

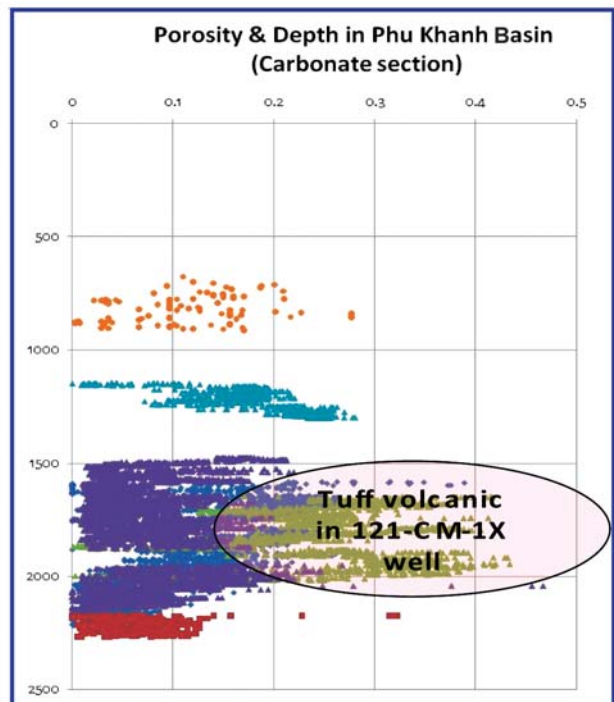


Fig.8b. Porosity vs. Depth relationship in the Phu Khanh (Carbonate section)

3.3. Source rock

As discussed above, no well data in the Phu Khanh Basin were allowed to be used for this study. Therefore, at first, oil seep samples collected from onshore outcrops were investigated by advanced geochemical analyses, which revealed that all the samples analyzed, originated from fluvio-deltaic source rocks [17]. Geochemical analyses result on oil seep samples). In addition, working of dual non- marine petroleum systems in the Phu Khanh Basin is consistent with adjacent basins such as the Nam Con Son [4] and the Song Hong, which have similar basin history at least until the Early Miocene before the opening of the East Sea.

Seismic data in the Phu Khanh Basin was also investigated in detail, which revealed that continuous

high amplitude and low frequency events are recognized in syn-rift sequences in some parts of the Phu Khanh Basin (Fig.5a, 5b). This character is specific for good lacustrine source rock in the Upper Oligocene of the Cuu Long Basin as well as widely in Southeast Asia, and therefore there is enough reason to suppose that such kind of good lacustrine source rock develops in the Oligocene sediments of the Phu Khanh Basin.

Based on these evaluations, source rock parameters for the SIGMA modeling were constructed as Fig. 9. Lacustrine source rock was assumed in the Oligocene, which has a total thickness of 1,000m of which the upper part has better source rock potential. Fluvial source rock (coal) was assumed to develop in the Lower Miocene, which has 60% TOC and 200mgHC/gTOC hydrogen index in 20m.

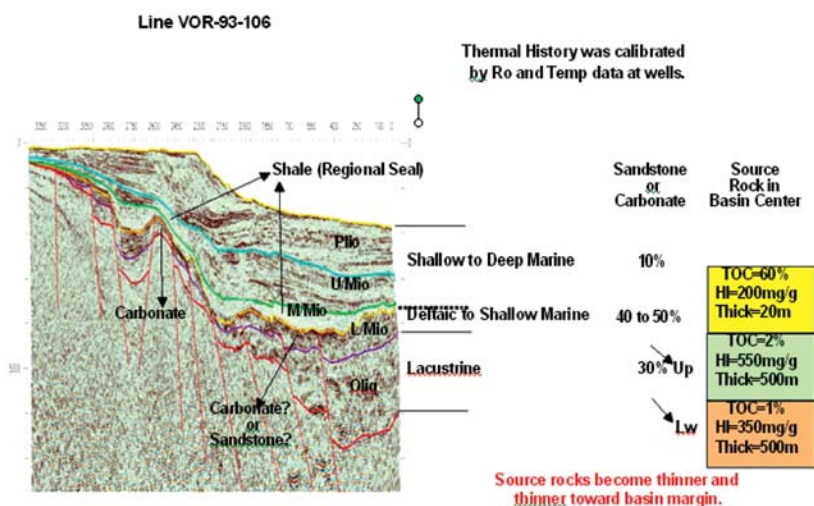


Fig.9. Input parameter for source rocks in the Phu Khanh Basin

3.4. Thermal history

Thermal history, especially heat flow, is difficult measure at wells. Therefore, these parameters are generally optimized by easily measurable data at wells. Since the present temperature gradient depends on surface temperature and basement heat flow at the present time, measured temperature data at wells were used to optimize present heat flow calculation. In addition, since vitrinite reflectance profile depends on surface temperature and basement heat flow in the past (accumulation of heat energy received until present time), analyzed vitrinite reflectance at wells is used to optimize the heat flow history.

In this study, the optimization of thermal history was conducted at 3 wells. Surface temperature was assumed as 20°C in shallow water area and was decreased to 5°C as water depth becomes larger toward the deep water area. Details of a complex heat flow history are difficult to assume and therefore a constant heat flow was assumed for this study. As the result of optimization, constant heat flow of 1.3 - 1.5 HFU (54 - 65mW/m²) was derived (Fig.10).

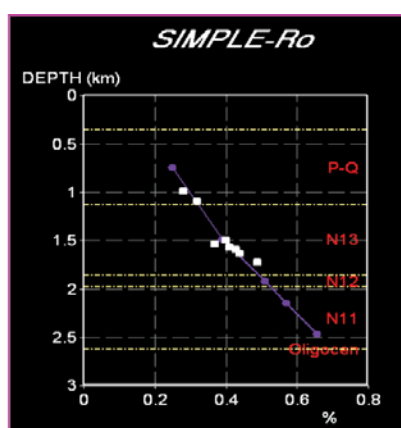


Fig.10a. Result of Optimization of Thermal History at well 121CM-1X. White Squares: Measured pressure reflectance at this well, Purple Line: Calculated Vitrinite Reflectance at this well

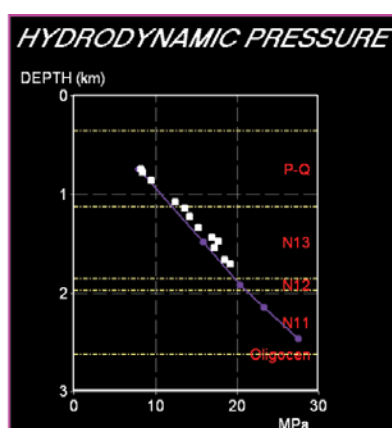


Fig.10b. Result of optimization of pressure profile at well 121CM-1X. White squares: Measured pressure at this well, Purple line: Calculated pressure at this well

4. Modeling of petroleum generation

Eleven cross sections were simulated by SIGMA-2D in the Phu Khanh Basin covering areas from shallow to deep water. The simulated generation history is different from line to line depending on the location of the section. However, the main part of the basin has the width of 150km [2], where more than 10km thickness of sediments can be seen from the seismic data. In addition, there can be seen other mini-basins on the more offshore side in the deep water area. However, sediments in these basins are thin, mostly less than 3,000m, since they are far from onshore source areas of sediment supply.

Oil and gas generations in the Oligocene source rock mainly occurred in Early Miocene time in the deepest

part of the main basin, which was followed by oil and gas generations in the Lower Miocene source rock since Middle Miocene time. These generations from dual source rocks have succeeded toward the basin margin until the present time.

Generated oil and gas migrated horizontally along the sandstones in the Oligocene and Lower Miocene formations, migrated vertically through faults and by making local columns and reached traps in these horizons. Additional leakage to Middle Miocene from Lower Miocene structures was also simulated, which may result in oil and gas accumulations in turbidite fans developed in the deep marine environment [5].

In offshore mini-Basins, only the deepest part, buried by more than 3,000m, generated some oil. However, effective migration has not commenced since the generation occurred recently and the amount generated is not enough to increase oil saturation in the source rock.

Line VOR 93-106 is extending from West to east in Block 124 covering shallow to deep water of the Phu Khanh Basin crossing the well 124-CMT-1X, where light oil was discovered from the Miocene carbonate. Input data for this section is shown on Fig.11a. The thickness of Tertiary sediments in shallow water is about 3,500m, which increases toward deep water and reaches 5,000m in this section. However, maximum thickness remains relatively thinner than in other sections since this line appears located on a ridge dividing the Phu Khanh Basin into Northern and Southern sub-basins.

Because of the location of this section, even the deepest part of the section (Column 39) reaches the temperature of 160°C and Vitrinite reflectance of 1.0%, which corresponds to peak oil generation [9]. The Oligocene and the Lower Miocene source rocks are matured enough to generate certain amount of oils from Pliocene times, but its migration has just started (Fig.11b). Due to this level of maturity of source rocks, gas generation

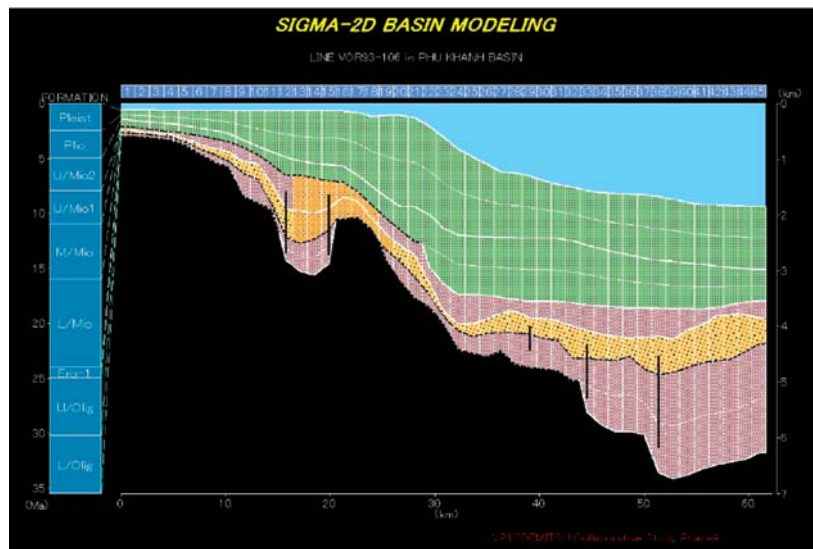


Fig.11a. Simulated section for line VOR 93-106

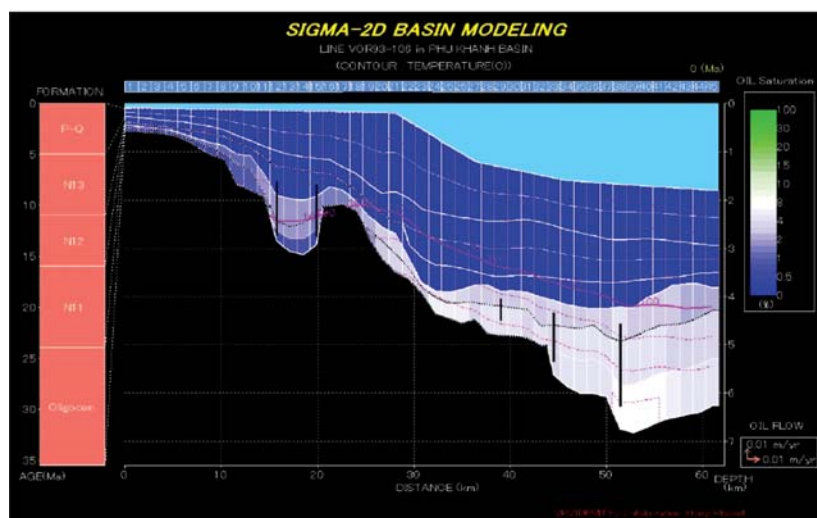


Fig.11b. Simulated result for line VOR 93-106 Color: Oil saturation, Contour: Temperature, Arrow: Oil flow

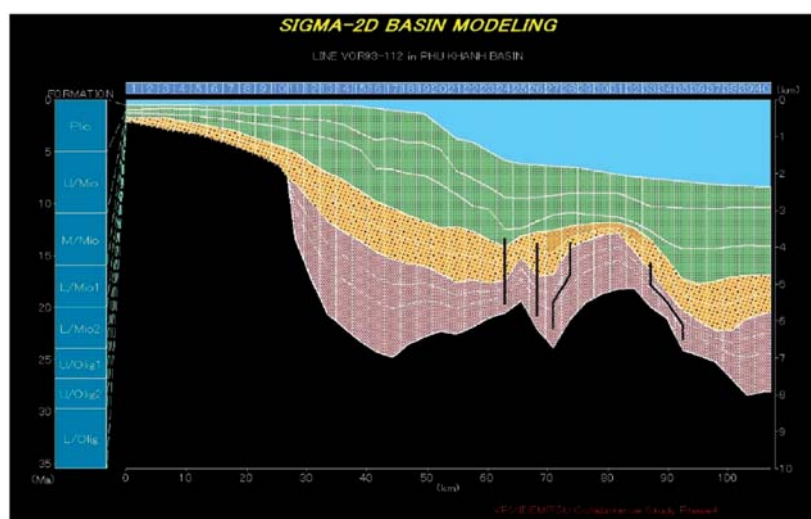


Fig.12a. Simulated section for line VOR 93-112

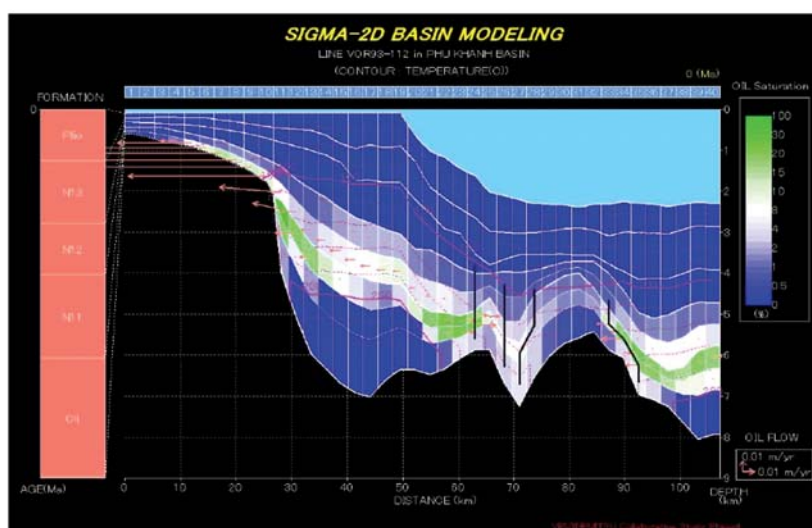


Fig.12b. Simulated result for line VOR 93-112 Color: Oil saturation, Contour: Temperature, Arrow: Oil flow

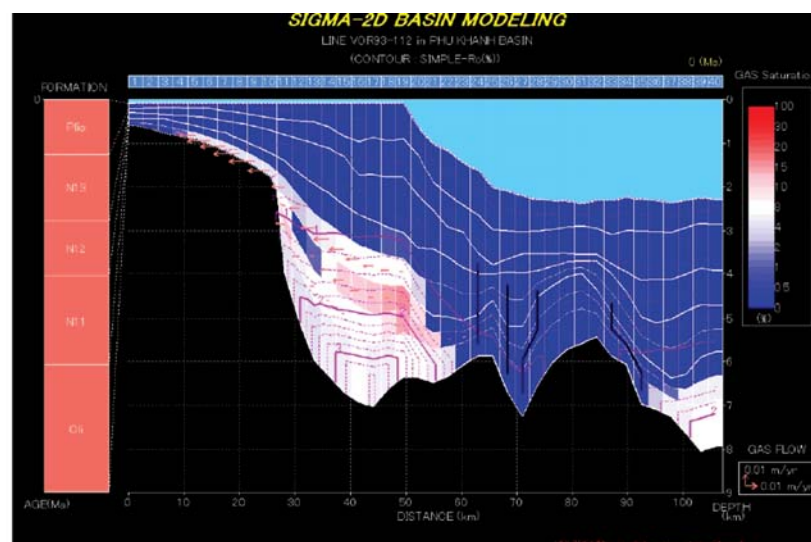


Fig.12c. Simulated result for line VOR 93-112 Color: Gas saturation, Contour: Vitrinite reflectance, Arrow: Gas flow

has not yet started. Oil and gas charge to the well 124-CMT-1X was not simulated on this section due to the late generation in source rocks on this section (Fig.11b). This suggested that the oil and gas charge to this structure did not occur from the East, but from the Northeast or the Southeast, which will be evaluated by the simulation on other sections.

A different oil and gas generation and migration history was simulated further to the south on the Line VOR 93-112. On this section, a thick and deep basin, whose thickness reaches about 7,000m, developed in shallow water, (Fig.12a). This basin extends to deep water with a local high in the middle. The thickness of the sediments in deep water is still 6,000m. This suggests that the main basin extends from Northeast to Southwest, and develops in shallow water on this section. Simulated results for this section demonstrate that the Oligocene lacustrine source rock is in the gas window and the Lower Miocene fluvio-deltaic source rock is in the oil window [4] in the main basin at the present time (Fig.12b, 12c). The Oligocene source rock had generated oil since Middle Miocene times (Fig.12d).

Generated oil migrated horizontally along the interbedded sandstone, and then leaked vertically to Lower Miocene by making its column in a local high where more sandstone and carbonate rocks develop as a regional carrier system below the Middle Miocene shaly section. This oil, together with the oil generated in the Lower Miocene source rock since the Late Miocene time, migrated horizontally along this regional carrier system to reach close to the coast at the present time (Fig.12b) [9].

The Oligocene source rock has been in the gas window since the Late Miocene and, therefore, any oil in source and carrier rocks were cracked to gas (Fig.12c,

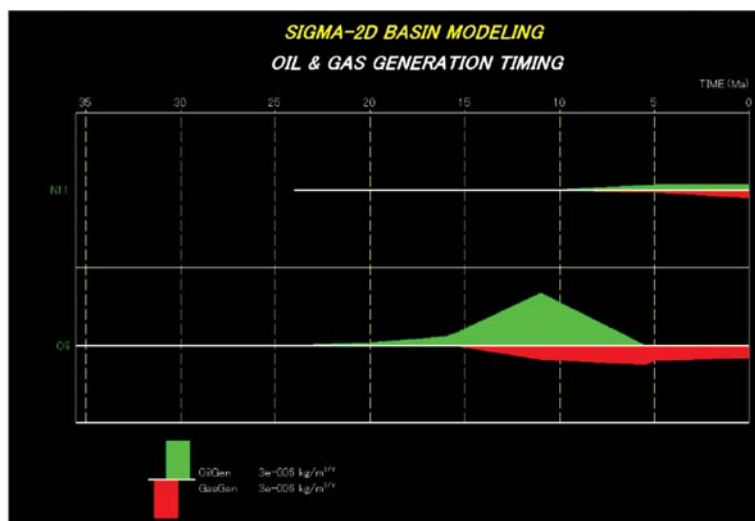


Fig.12d. Timing of oil and gas generation in deepest part of line VOR 93-112 (Column 17). Upper: Lower Miocene source rock, Lower: Oligocene source rock

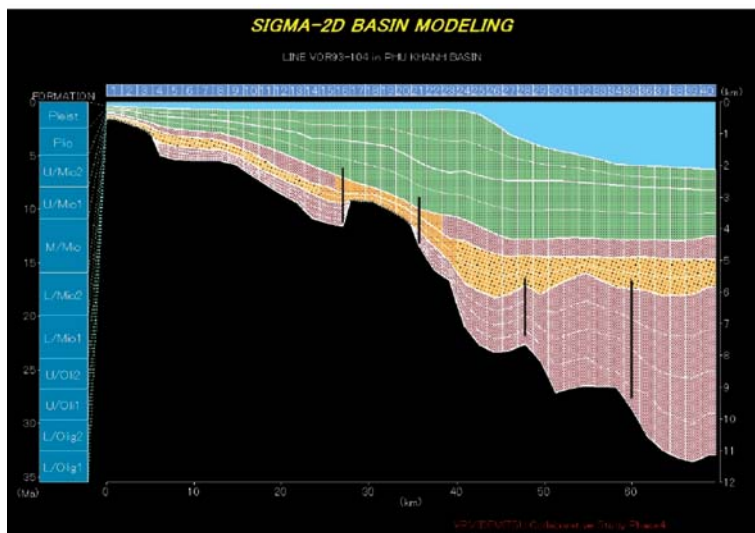


Fig.13a. Simulated section for line VOR 93-104

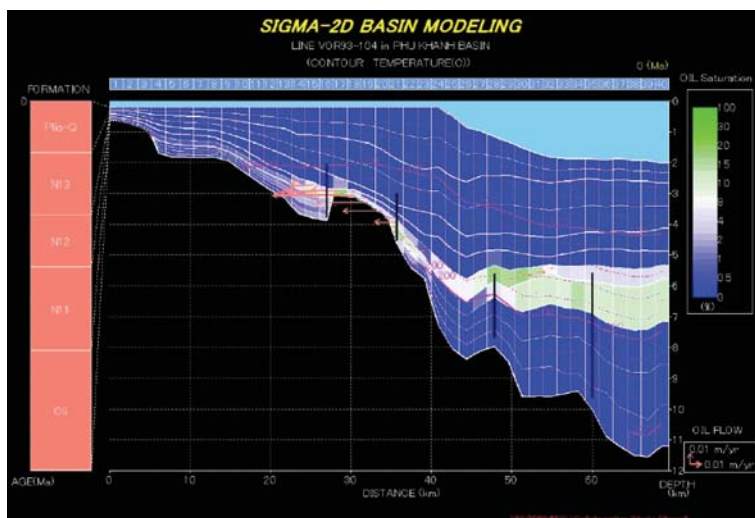


Fig.13b. Simulated result for line VOR 93-104 Color: Oil saturation, Contour: Temperature, Arrow: Oil flow

12d). This gas has migrated in the same way as oil and is also about to reach the coast at the present time.

4.1. Line VOR 93-104

Further to the North from Line VOR 93-106, oil and gas generation and migration history is a little different from that of Lines VOR 93-106 and 112. On this northern section the thickest part of the basin reaches 9,000m of sediments in the deep water area (Fig.13a). Around the shelf break of the section, a carbonate build-up trend developed in the Miocene section extending to Line VOR 93-106, where light oil was discovered in the well 124-CMT-1X.

The Oligocene lacustrine source rock is in the gas window and the Lower Miocene fluvio-deltaic source rock is in the oil window in the deepest part of the section at the present time (Fig.13b, 13c), which is a similar setting to the deepest part of the Line VOR 93-112. However the timing of generation is delayed on this section (Fig.14).

The main oil generation in the Oligocene source rock has occurred since Late Miocene times in the deepest part of this section (Fig.13d). In addition, oil generation in the Lower Miocene source rock and gas generation in the Oligocene source rock one has started since the Pliocene time. These timings are later than the deepest part of Line VOR 93-112 (Fig.12d).

The oil and gas migration style however is similar to that of Line VOR 93-112. At first, generated oil and gas in the Oligocene migrated horizontally along interbedded sandstone and reached local highs. Then, they leaked vertically to a Lower Miocene carrier system by forming their columns. Finally, this oil and gas, together with the oil generated in Lower Miocene source rock, migrated horizontally along sandstone to reach the carbonate build-up trend in the middle of the section (Fig.13b, 13c) [9]. In multi-dimensional direction, this oil and gas should also migrate towards the South to charge Block 124.

4.2. Line PV 08-03

This line is located at the boundary between the Song Hong and the Phu Khanh Basins so that sediment is still thin, especially for the deep water area (Fig.14). The Oligocene source rock is buried by more than 3,000m only in the shallow water area, where a narrow trough develops and some amount of oils were generated (Fig.14). The generated oil migrated along the Oligocene formation toward a high trend, where the well 121-CM-1X was drilled. Oil accumulation should be discovered if porous rock develops in this deep formation.

4.3. Line CSL 07-10

This regional line extends from the Northwest to the Southeast of the entire Phu Khanh Basin covering Blocks, 124, 149 and 150 from shallow to deep water. Since this line is distributed perpendicular to the structural trend, the geometry of the basin is clearly demonstrated (Fig.15a). The main part of the basin has a width of 150km, where more than 10km thickness of sediments can be seen from the seismic data. In addition, other mini-basins can be seen further offshore in the deep water area. However, the sediment thickness in these basins is mostly less than 3,000m since they are far from the onshore area and the sediment supply is insufficient for a thicker accumulation.

Simulated result predicted that the Oligocene lacustrine source rock in main basin is in gas window at the present time. Deepest part reaches the temperature more than 300°C and the vitrinite reflectance more than 4%. The Lower Miocene fluvio-deltaic source rock is also in gas window except marginal part of the basin (Fig.15b, 15c) [4].

Oil and gas generations in the Oligocene source rock mainly occurred in Early Miocene time in deepest part of main basin, which had followed by oil and gas generations in the Lower Miocene one since Middle Miocene time (Fig.15d). The generations in dual source rocks have succeeded toward Basin margin until the present time. These timings are earlier than the Lines VOR 93-104 and 112, since this line is crossing deepest part of main basin.

Generated oil and gas migrated horizontally along the sandstones in the Oligocene and Lower

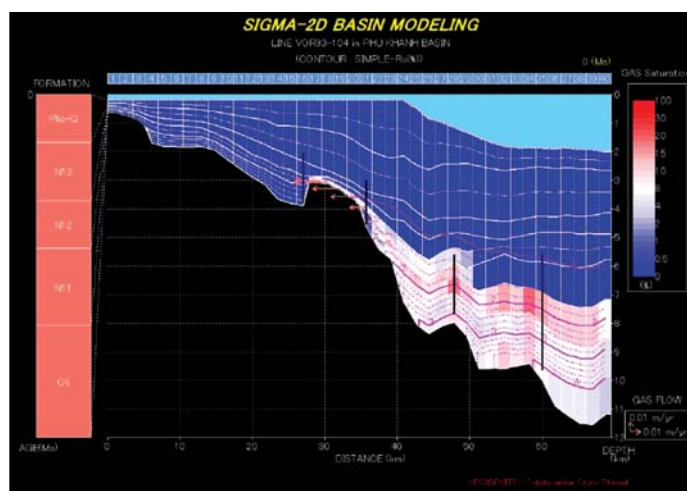


Fig.13c. Simulated Result for Line VOR 93-104 Color: Oil Saturation, Contour: Vitrinite Reflectance, Arrow: Oil Flow

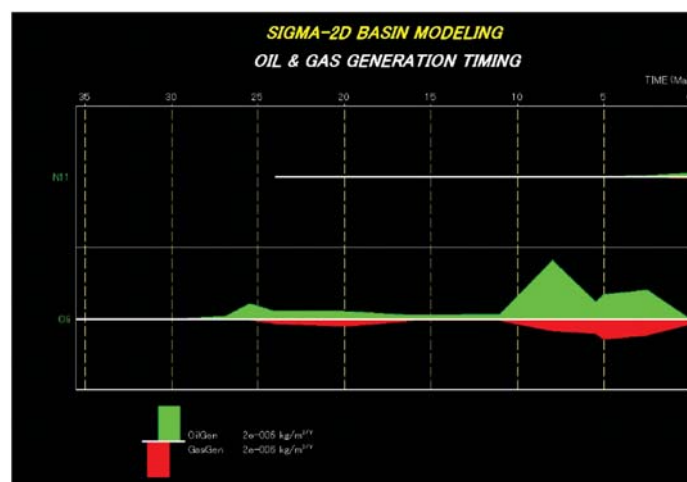


Fig.13d. Timing of Oil and Gas Generation in Deepest Part of Line VOR 93-104 (Column 38). Upper: Lower Miocene Source Rock, Lower: Oligocene Source Rock

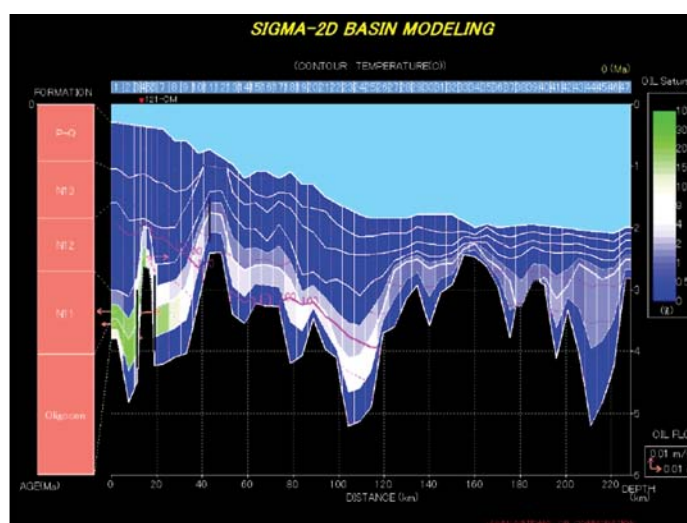


Fig.14. Simulated result for line PV 08-03 Color: Oil saturation, Contour: Temperature, Arrow: Oil flow

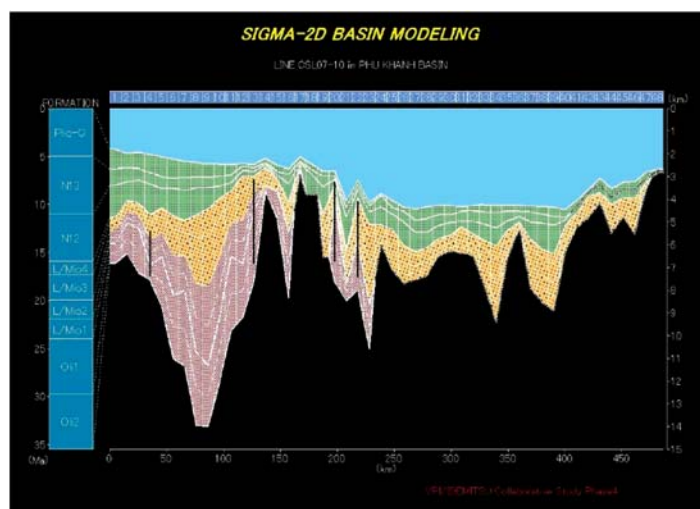


Fig.15a. Simulated Section for Line CSL 07-10

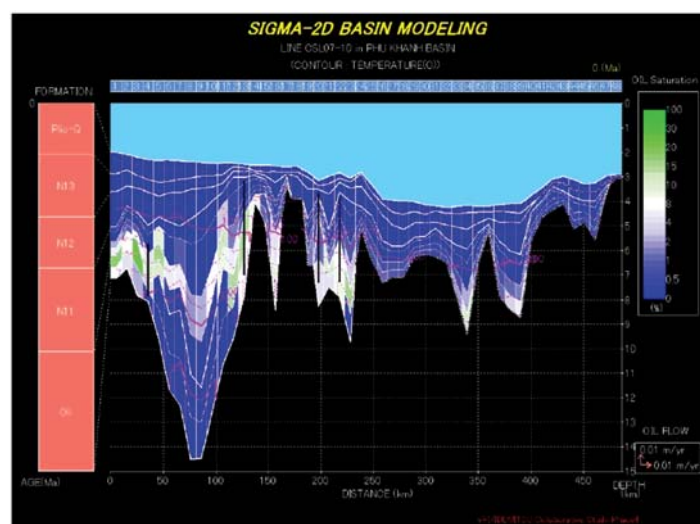


Fig.15b. Simulated result for line CSL 07-10 Color: Oil saturation, Contour: Temperature, Arrow: Oil flow

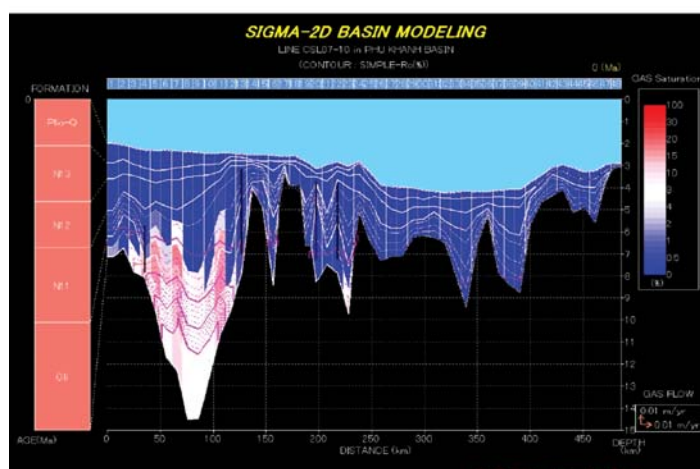


Fig.15c. Simulated result for line CSL 07-10 Color: Gas saturation, Contour: Vitrinite reflectance, Arrow: Gas flow



Fig.15d. Timing of oil and gas generation in deepest part of line CSL 07-10 (Column 9). Upper: Lower Miocene source rock, Lower: Oligocene source rock

Miocene formations, vertically migrated through faults and by making local columns and reached the traps in these horizons, as similar way to the Lines VOR 93-104 and 112, which was discussed in detail as above (Fig. 15b, 15c). Additional leakage to Middle Miocene from Lower Miocene structures was also simulated, which may result in oil and gas accumulations in turbidite fans developed in deep marine environment.

In offshore mini-basins, only deepest part which buried more than 3,000m generated some oils (Fig. 15b, 15c). However, effective migration has not been started, since the generation occurred recent and the amount generated is not enough to increase oil saturation in source rock.

5. Conclusions

The Oligocene lacustrine source rock had generated oil since the Middle Miocene time and is in gas window almost in entire area of the Basin (main part is in deep water area) at the present time. The Lower Miocene fluvio-deltaic source rock had generated oil since the Late Miocene time and is in gas window in central part of the Basin at the present time. Oil and gas generated both in the Oligocene and Lower Miocene source rocks in deep water area migrated along regional carrier system in Lower Miocene (both sandstone and porous carbonate) after vertical migration of the Oligocene oil and gas by cap rock leakage and through faults. These oil and gas made their accumulations in structural highs in deep water and in shallow water areas. Some of them were already found as oil seeps from onshore outcrops and encountered in exploration wells drilled such as 124-CMT-1X. Faults do not play main role for vertical

migration, since they started healing before main oil and gas generations since the Middle Miocene time.

More oil and gas accumulations were simulated in Southern sub-basins (Blocks 125 - 127) in most of cases. This is because the Southern sub-basins is larger, deeper and closer to shallow water area, where exploration wells can be more easily drilled. This kind of settings enables to generate more oil and gas in earlier timing of basin history, which results in more migration period for oil and gas. Oil and gas can migrate further, if more migration period is allowed. However, these results solely depends on the assumptions for the multi-dimensional basin modeling such as source rock properties, heat flow history, lithology distribution, etc. Therefore, future tuning of these input data after the drilling of new well is necessary to acquire more accurate view for petroleum system in the Phu Khanh Basin.

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Exploration and appraisal activities in 2006 - 2012, plan for 2015 and strategy for future upstream activities

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Abstract

One of the most important activities to the technical staff in general and petroleum geologists in particular is to orient the exploration activities, to evaluate the potential hydrocarbon reserves then to conduct its production logically. The first issue of this paper is to introduce to the readers and to colleagues (in and out of the petroleum domain), a summary of the exploration and appraisal activities of Petrovietnam in Vietnam as well as overseas during the period of 2006 - 2012 with the sudden changes reflecting, especially in background of the world's economic crisis that has occurred. Several petroleum contracts have been signed, the 2D and 3D seismic acquisition has been conducted, more than 150 exploration and appraisal wells have been drilled during this period and several new fields/ discoveries have been found in both offshore Vietnam and overseas. The total incremental reserves is one of the good examples to demonstrate that Petrovietnam's orientation in the oil and gas exploration, appraisal and production domain is correct.

An exploration and appraisal plan for 2015 and a strategy for further campaigns of exploration and appraisal have also been dealt with in this document with the main points and real events being emphasised. This paper also presents the importance of extending co-operation, sharing experiences and strengthening the abilities to farm-in overseas petroleum contracts by applying a diplomatic petroleum policy.

Content

In the context of a background global economic crisis, the petroleum industry in Vietnam is facing an important challenge, how to continuously affirm Petrovietnam as a key industry with the receipts per year of around 25 - 30% of Vietnam's GDP. It is requested that Petrovietnam needs to have the right orientation in this new stage, in order to maintain stable national power security.

Although Petrovietnam's functions comprise all up to down-stream activities, with exploration, appraisal and production in upstream; in mid-stream storage, transportation, export and import, processing, distribution and sales of petroleum; and downstream is refinery and petrochemistry, finance, banking, insurance and other related services, Petrovietnam always defines its core business (a main function) as exploration and production activities.

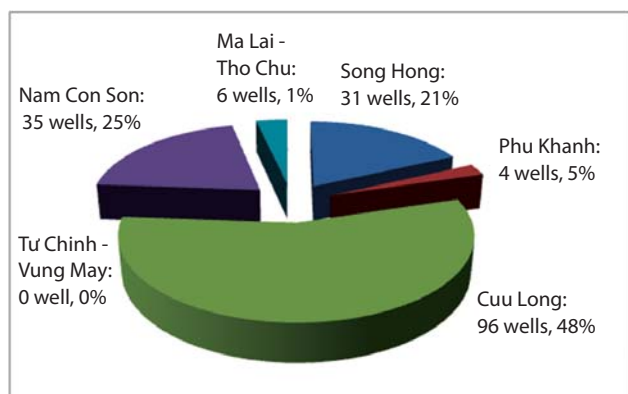
The real results of 2006 - 2012 have confirmed Petrovietnam's orientation in exploration and production both in Vietnam and

overseas, was correct. Besides keeping oil production stable and conducting exploration and appraisal activities in order to drill potential prospects and upgrade new discoveries to development and production, ensuring the incremental reserves were stable, was also very important to Petrovietnam during this period.

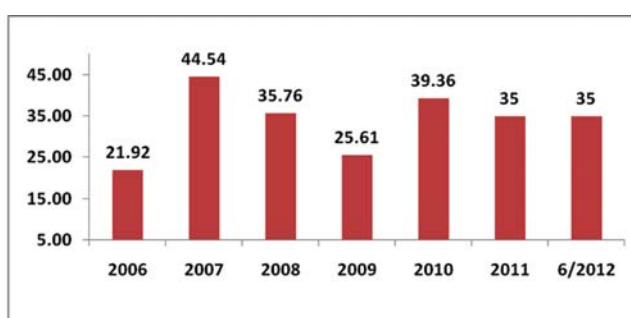
Since Petrovietnam took the initiative of seismic acquisition, up to June 2012, much seismic information

Year	Petroleum Contract
2006	5
2007	7
2008	7
2009	13
2010	4
2011	5
2012	1 (+4)
To 2015	5 per year

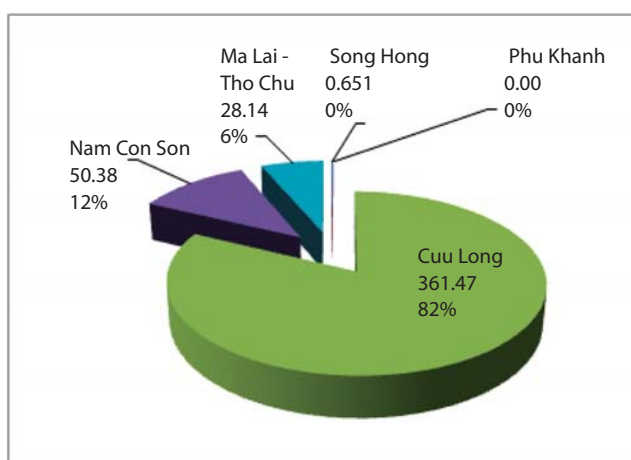
Well	2006	2007	2008	2009	2010	2011	6/2012	Total
Exploration	8	21	15	15	17	11	4	91
Appraisal	17	12	13	13	9	10	7	81
Total	25	33	28	28	26	21	11	172



Number of exploration and appraisal wells in 7 years (2006 - 2012)



Incremental Reserves in the last 7 years (2006 - 2012) (MM tons)



Cumulative production distribution in Vietnam (dated to June 30, 2012)

has been acquired with 85,000km² of 3D and 130,000km of 2D, covering all blocks and basins in Vietnam's continental shelf, both onshore and offshore.

In the period 2006 - 2012, there were 62 petroleum contracts in effect, with 3 - 5 petroleum contract per year in new areas and relinquished areas. This indicates the success of Petrovietnam in attracting foreign investment to Vietnam as well as Petrovietnam's own investment.

The exploration and appraisal activities therefore have been conducted vigorously, with more than 550

exploration and appraisal wells being drilled by operators and Petrovietnam/PVEP. During 2006 - 2012, 172 exploration and appraisal wells have been drilled focusing on the Cuu Long basin (96 wells), the Nam Con Son basin (35 wells) and the Song Hong basin (31 wells)... More than 375 million tons of oil equivalent have been produced (440 million cubic meter of oil equivalent) with most in the Cuu Long and Nam Con Son basins (in 2006 - 2012, 94.50 million tons of oil equivalent). The production was stable with 15 - 17 million tons of oil equivalent per year in Vietnam. The incremental reserves were still around 35 million tons in the recent years as the 5 year's plan 2006 - 2010, though Petrovietnam still faces with more challenges: The huge fields are now in a declining stage, the new fields/discoveries are mostly small (marginal fields) with high production expenditure...

The overall exploration overview shows that the Cuu Long basin is still important with the facilities and the infrastructure available, the exploration and production activities hence have been focused to upgrade the new discoveries/fields to develop (the number of exploration and production wells in the Cuu Long basin is 96/172 wells, with 48% of exploration and production wells in 2006 - 2012), the production reserves in the Cuu Long basin hence amount to 82% of the total reserves in Vietnam.

There are some kind of plays which have been found in the period of 2006 - 2012 called new play concept: Karstified carbonate basement (Ham Rong), stratigraphy trap in the Miocene (Cat Ba), new gas discovery in carbonate reef in the Lower Miocene with CO₂ not so high (Ca Voi Xanh) in the Song Hong basin; the petroleum system in the Phu Khanh basin has been confirmed with the reservoirs in carbonate reefs of Miocene age (Ca Map Trang, Tuy Hoa); the oil discovery in Pre-Tertiary weathered granite basement in Nam Con Son basin (Gau Chua - Gau Ngua - Ca Cho) has been evaluated as a new play with high potential resources in this basin which has high pressure, deep water, petroleum system. Based on new technology, it will be ready for development and production in the near future.

However, Petrovietnam has always thought that the potential resources in Vietnam are not great, hence the policy of speeding up the investment overseas has been the orientation of Petrovietnam since 2006 with remarkable success. Up to now (June 2012) 24 petroleum contracts have been signed by Petrovietnam/PVEP,

in which 18 projects have been conducted: fields in production such as Cendor (PM-304), D30 (SK-305) (Malaysia); North Khosedaiu, Visovoi (Russia); fields under development such as 433a & 416b (Algeria), Junin-2 (Venezuela), 39 (Peru), West Khosedaiu (Russia) and Nagumanov (Russia). Eleven projects are in the exploration phase, such as:

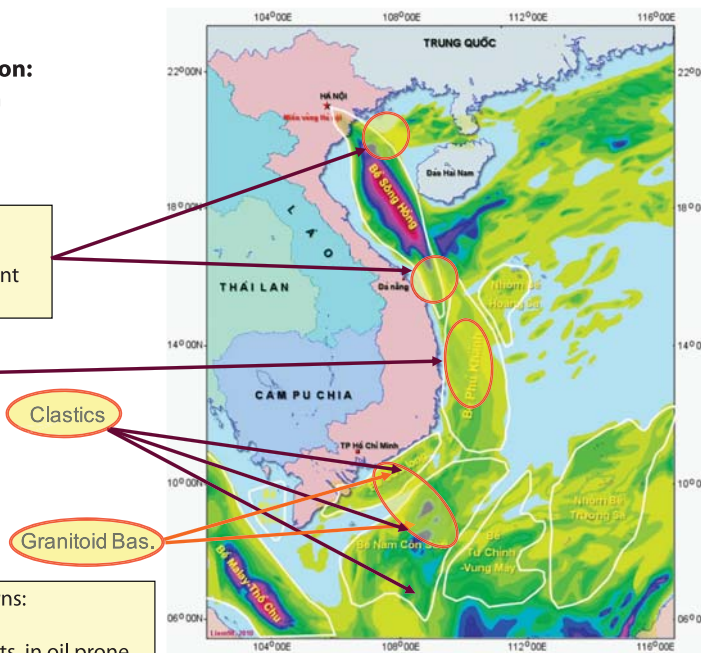
1. Block Champasak & Saravan (Laos);
2. Block Savanakheth (Laos);
3. Block XV (Cambodia);
4. Block Randugunting (Indonesia);
5. Block M2 (Myanmar);

6. Block Danan (Iran);
7. Blocks N31, N32, N42, N43 (offshore Cuba);
8. Block 162 - Ucayali basin (Peru);
9. Block Marine XI (Congo);
10. Block Majunga (Madagascar);
11. Block Kossor (Uzbekistan).

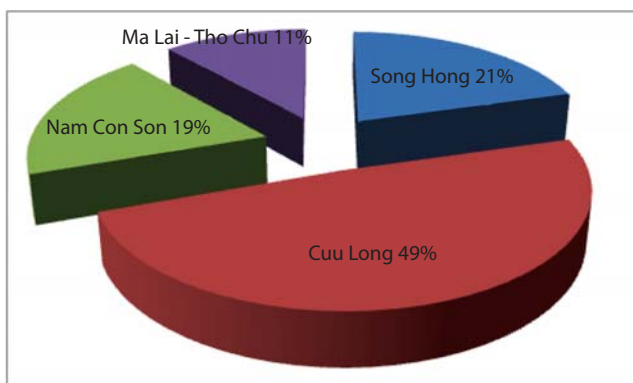
Up to June 2012, Petrovietnam acquired more than 18,500km of 2D seismic and 7,500km² of 3D seismic information and drilled 58 exploration/appraisal wells. The incremental reserves (shared for Petrovietnam/PVEP's percentage) is around 175 million tons of oil equivalent (1.3 billion barrels of oil equivalent), getting 24 million tons of oil equivalent per year with probability of success (POS) as 36%, higher than that of the 5 year's plan 2006 - 2010 (25%).

**Vietnam briefly evaluation:
Important discoveries in
2006 - 6/2012**

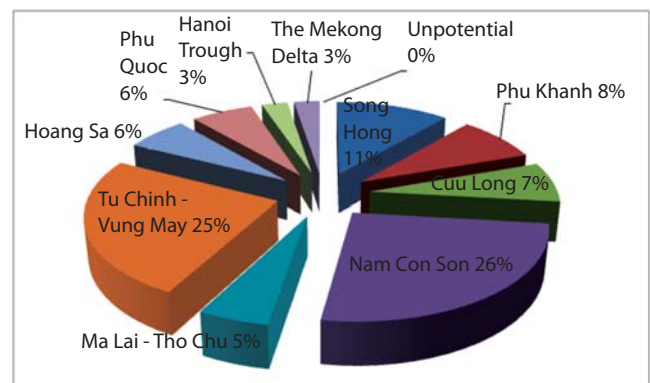
Song Hong: New plays: - Stratigraphy - Buried carbonate basement - Carbonate reef	
Phu Khanh - Petroleum existed - Carbonate reef	
Cuu Long: New plays: - Middle Miocene - Oligocene (E, F)	
Nam Con Son: Lesson Learns: - Granitoid basement - Oil disc. in closures w/faults, in oil prone	



As the annual hydrocarbon reserves and potential resources report (dated to 31 December, 2011) approved by Petrovietnam's President and CEO shows, the recoverable resources are around 1.85 - 4.80 billion cubic meter of oil equivalent, in which reserves are 1.40 billion cubic meter (Song Hong



Recoverable Resources (un-mapped) around 1.45 - 3.40 billion cubic meter of oil equivalent



Recoverable reserves (includes the discovery) around 1.40 billion cubic meter of oil equivalent



Acquisition Vessel: Binh Minh 02



Jack up - PVD 1

21%, Cuu Long 49%, Nam Con Son 19% and Ma Lai - Tho Chu 11%). With 450 million cubic meter of oil equivalent produced, the remaining reserves are around 950 million cubic meter of oil equivalent. The remaining recoverable resources in Vietnam are around 1.45 - 3.40 billion cubic meter of oil equivalent, of which: Nam Con Son comprises - 26%, Tu Chinh - Vung May - 25%, Song Hong - 11%, Phu



DST #2: Kinh Ngu Trang - 1X (Oligocene: 1,200 - 1,500pbd)

Khanh - 8%, Cuu Long - 7%, Phu Quoc - 6%, Hoang Sa - 6%, Ma Lai - Tho Chu - 5%, Hanoi trough - 3% and Cuu Long trough - 3%.

With the policy of speeding up the exploration and production activities in deep water, Petrovietnam's plan to 2015 and the strategy beyond is to continuously conduct seismic acquisition in these areas including: Phu Quoc, South - East Nam Con Son basin and Phu Khanh deep water areas. Petrovietnam will negotiate in order to sign more new petroleum contracts, joint studies, bilateral/trilateral contracts, non-exclusive seismic acquisition contracts and self-investment contracts based on co-operation and co-development between all regional countries. The main target of Petrovietnam's exploration and production in Vietnam is keeping in balance the production of 30 - 35 million tons of oil equivalent per year.

For its overseas exploration and production strategy, Petrovietnam will continuously conduct effective exploration and production activities in the areas where petroleum contracts have been signed, speed up new discoveries/fields to development/production stages with the incremental reserves 50 - 75 million tons of oil equivalent to 2015; trying to get the overseas production as 10 million tons of oil equivalent by 2015 (3.3 million tons of oil equivalent per year). Petrovietnam would also like to farm-in the overseas petroleum contracts by the petroleum diplomatic policy in order to get more discoveries/fields in development/production phases to supplement to the internal reserves, and to expand the exploration and production activities in regional areas as well as worldwide.

Pre-Cenozoic basement structure in the Truong Sa archipelago and sea deep basins

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Abstract

The structure of marine Cenozoic basement is a problem that has greatly concerned marine geologists and geophysicists engaged in geological study and oil-gas exploration. In this paper, the author has applied a methodology involving gravity data interpretation including frequency filtering, horizontal gradient and maximum horizontal gradient, to define clearly the structure and form of faults and uplift zones in basement as well as the seafloor spreading axis and crustal boundary in the Truong Sa archipelago and the East Sea deep basins.

These results allow some initial remarks concerning the structure of the Cenozoic basement in the Truong Sa archipelago and the East Sea deep basins to be made.

Introduction

The Cenozoic basement structure in the Truong Sa archipelago and the East Sea deep basin area have been studied for a long time, but such studies developed most strongly in recent decades when the process of oil-gas exploration became active. Especially, in recent years, when earthquake events have occurred, fault tectonics are increasingly considered by scientists. The structure of fault systems, uplift and depression zones of basement as well as crustal boundaries, which are possible features of the East Vietnam Sea, have been the subjects of previous studies by scientists both inside and outside Vietnam. Interpretation of gravity data, in combination with other recently acquired geological-geophysical datasets, is now possible in order to determine the nature of the structure of the Cenozoic basement.

In the study area, data derived from shipboard and satellite surveys are abundant. Using such gravity field and seismic data along with new methodologies and modern interpretation techniques allows us to determine the fault geometric parameters, fault zone characteristics and uplift and depression zones of basement with greater accuracy.

Overview of previous studies

In the period 1991 - 1995, in National Project KT-03-02, Bui Cong Que, Nguyen Giao et al. constructed geophysical

maps, crustal deep cross-sections and geodynamic systems in the Vietnam continental shelf and the East Sea.

In the period of 1996 - 2000, in National Project KHCN-06-04, KHCN-06-12, Bui Cong Que, Pham Nang Vu, Nguyen Giao et al. (collaboration between Hanoi Institute of Oceanography and Vietnam Petroleum Institute) constructed geological-geophysical maps of the East Vietnam Sea and adjacent areas. Based on these data, deep crustal cross-sections, fault systems, geodynamic and geotectonic sketches were established in the Vietnam continental shelf, at a scale of 1:500,000 [2, 6].

The fault systems, tectonic and geodynamic activities in the Vietnam continental shelf and the East Sea have also been studied by Le Duy Bach (1987, 1990), Bui Cong Que (1985, 1990, 1999, 2000), Nguyen Dinh Xuyen (1996, 2004), Cao Dinh Trieu (1999, 2005), Phan Trong Trinh (2000), Nguyen Trong Tin (1997, 2005), Tran Huu Than (2003) and Tran Tuan Dung (2003, 2006) [2, 5, 7, 8].

In the recent years, in National Project KC-09-02, Bui Cong Que et al. (2001 - 2005) have collected and supplemented new datasets, which are satellite and shipboard data, from oil-gas companies in order to construct a series of geological-geophysical maps (including gravity map). These data sources are very valuable and important for new studies of the geological structure and tectonics in the East Vietnam Sea.

Besides, studies of the geological structure of the East Vietnam Sea have also been carried out by scientists from outside Vietnam. In the 1970's, US geologists presented a study of tectonic structure in the tectonic context of the East Sea (Parke, 1971 - Emery, 1972). Hayes and Taylor (1978 - 1980) have published geophysical maps and structure of the Southeast Asian Sea. In 1989, Kulinic et al (Far-East geological Center, Soviet Union Academy of Science) resented a monograph, "Earth crustal evolution and tectonics in Southeast Asia". The monograph integrated results of studies of geology-geophysics such as tectonics, crustal structure and geodynamics. The structural characteristics of the main deep crustal boundaries, fault system and the tectonic and geodynamic activities involved have been illuminated by the studies of Hayes (1975, 1980), Parke (1985), Wujimin (1994), Lieng Dehua (1993), Rangin (1986,1990), Watkins (1994) and Hinz et al., (1985, 1996). In the years from 1980 - 1990, French scientists such as P. Tapponnier, A. Briaud et al. introduced some tectonic-geodynamic models that involved the movement of the Indian subcontinent and Asian plate [2, 6].

Gravity data

The gravity data in the East Vietnam Sea is mainly collected from joint shipboard surveys between Vietnam and foreign countries such as Russia, America, France,

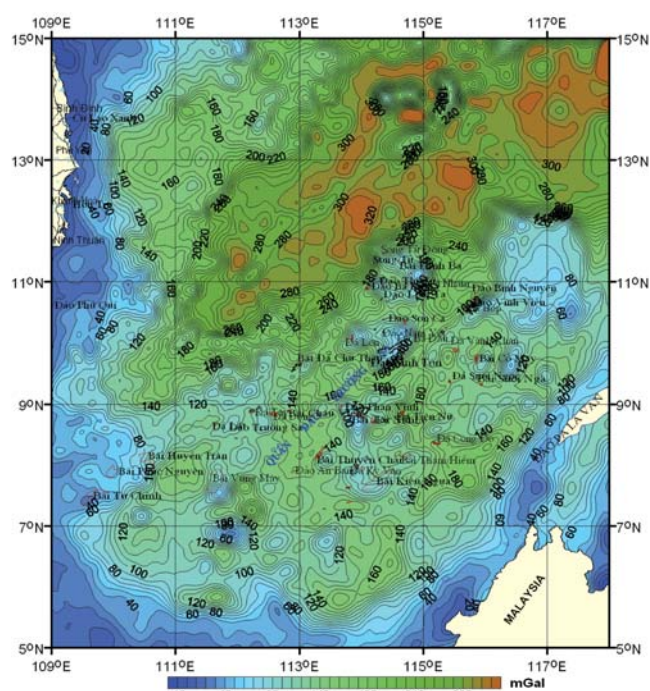


Fig.1. Bouguer gravity anomalies in the Truong Sa archipelago and the East Sea deep basins

Germany and Japan... Also the author has used the gravity data from National Research Projects which are carried out by the Hanoi Institute of Oceanography and the Vietnam Petroleum Institute and others; such as project 48B-III-2 (1986 - 1990), KT-03-02 (1991 - 1995), KHCN-06-04 (1996 - 1998), KHCN-06-12 (1999 - 2000), and KC-09-02 (2001 - 2005). These projects have revealed new and useful results. A gravity anomaly map at a scale of 1:500.000 has been constructed for the whole study area [2, 6] (Fig.1).

On this gravity map (Fig. 1) it can be seen that the gravity anomalies are quite high. The range of the various gravity anomalies is within -10 to +300mGals. These can be simply depicted as follows:

In the Western part of the study area, the gravity anomalies are quite small and with varied range from -10 to + 50 mGals. There are also some small gravity anomalies that appear scattered in the central and South-Eastern part. Here, the gravity anomalies are characteristic of gravity anomalies of continental crust alternating with sedimentary basins. The main trends of the gravity anomalies are meridional and sub-meridional.

In the central and Southern part of the area, it can be seen very clearly that gravity anomalies vary stably from +100 to +200mGals. These anomalies have a blocky shape and developed on transitional crust between continental and oceanic crust. They clearly manifest the blocky geological structures in the archipelago area.

In the Northern part, the gravity anomalies are high, up to +300mGals. These are gravity anomalies of the oceanic crust. Here, gravity anomalies have a banded form and developed in a Southwest - Northeast direction (Fig.1). Also, the major faults and sea-floor spreading axis are clearly indicated on the gravity map by gravity gradient bands in a Southwest - Northeast direction, some of hundreds of kilometer length.

Determination of Cenozoic basement structure

In this study, the faults and uplift zone on the seafloor surface are not discussed. It is concentrates on determination of the Cenozoic basement structure and faults at different, greater depths.

Frequency filtering of gravity field

In general, the high frequency component of the gravity field with short wavelength relates to geological

bodies at small depth. On the contrary, the low frequency component of the gravity field, with long wavelength, reflects geological structures at greater depth. In this study, the frequency filtering method is applied to separate the gravity effect of Cenozoic sedimentary layers from the total gravity field. After that, residual gravity fields can be used to determine the density boundaries, uplift zones and fault characteristics in basement or at greater depth.

To select a suitable wavelength λ for the process of frequency filtering of the gravity field, the following steps were used:

- *Step 1:* Constructing the model of Cenozoic basins based on seismic data (for area for which seismic data is available)
- *Step 2:* Calculating gravity effect to determine the residual gravity field caused by the Cenozoic sedimentary layers.
- *Step 3:* Carrying out the filtering of the gravity field at different wavelength λ (from 20 - 150km). Comparing residual gravity fields at these wavelengths λ with residual gravity field at *step 2*, one by one. The comparative result with the smallest error will be used to select wavelength λ .

From the results of the three steps above, a filter with wavelength $\lambda =$ was selected to separate the gravity effect that is likely caused by the Cenozoic sedimentary layer. With the wavelength selected, the low frequency gravity anomaly is calculated for the whole area by the following formula [6]:

$$\Delta g_{LPF}(x, y) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Delta g(\lambda_x, \lambda_y) p(\lambda_{cutoff}) \exp[i(\lambda_x x + \lambda_y y)] d\lambda_x d\lambda_y$$

With Gauss filter:

$$p(\lambda_{cutoff}) = 1, |\lambda| \leq \lambda_{cutoff} \quad p(\lambda_{cutoff}) = 0, |\lambda| > \lambda_{cutoff}$$

After separating the gravity effect of the Cenozoic sedimentary layer from the total gravity field, the remaining gravity anomalies are used to define the horizontal gradient and maximum horizontal gradient (magnitude and vector) for the Cenozoic basement and greater depths in the Truong Sa archipelago and the East Sea deep basins [3], [6], [7].

Horizontal gradient and maximum horizontal gradient of gravity anomalies

In this paper, the Bouguer gravity anomalies and residual gravity anomalies filtered at wavelength $\lambda = 50, 100\text{km}$ are used to calculate the horizontal gradient and the maximum horizontal gravity gradient, respectively.

Calculating steps are as follows:

- *Step 1:* Calculating magnitudes of the horizontal gradient at the above-mentioned filtering levels by selected formula along x and y direction of data grid [6]:

$$H[\Delta g]_{i,j} = \sqrt{\left(\frac{d\Delta g(x,y)}{dx}\right)^2 + \left(\frac{d\Delta g(x,y)}{dy}\right)^2}$$

$\Delta g(x,y)$ is gravity anomaly at each grid intersection. $H[\Delta g]_{i,j}$ is the horizontal gradient at each grid intersection. In fact, the horizontal gradient often reflects faults, edges of vertical bodies or igneous intrusive blocks.

- *Step 2:* Calculating magnitudes of maximum gravity horizontal gradient [1].

The maximum horizontal gradient is calculated by using magnitudes of the horizontal gradient at *step 1* above. The locations of the maximum horizontal gradient on the data grid are defined by comparing $H[\Delta g]_{i,j}$ at each grid intersection with its eight nearest neighbors in four directions. The comparison follows the below-mentioned inequalities [1], [6]:

$$\begin{aligned} H[\Delta g]_{i-1,j} &< H[\Delta g]_{i,j} > H[\Delta g]_{i+1,j} \\ H[\Delta g]_{i,j-1} &< H[\Delta g]_{i,j} > H[\Delta g]_{i,j+1} \\ H[\Delta g]_{i+1,j-1} &< H[\Delta g]_{i,j} > H[\Delta g]_{i-1,j+1} \\ H[\Delta g]_{i-1,j+1} &< H[\Delta g]_{i,j} > H[\Delta g]_{i+1,j+1} \end{aligned}$$

Here, a counter N is increased by one for each satisfied inequality. At any intersection of data grid, the maximum number of satisfied inequalities is $N=4$ and minimum is $N=0$. Some previous studies have shown that locations and magnitudes of the maximum horizontal gradient are fully defined when $N \geq 2$ [1, 4, 6].

In this study, when $N \geq 2$ then locations and magnitudes of the maximum horizontal gradient $H[\Delta g]_{i,j}$ are defined by a second-order polynomial as follows:

$$X_{Max} = \frac{bd}{2a}; \quad G_{Max} = aX_{Max}^2 + bX_{Max} + H[\Delta g]_{i,j}$$

Here, d is the distance between grid intersections, a, b are developed coefficient of the polynomial, which are calculated from the grid of gravity anomalies [1].

- *Step 3:* Determining directions of the maximum horizontal gradient vector

Direction of the maximum horizontal gradient vector is determined by a formula as follows:

$$\alpha = \arctg \left[\frac{\frac{d\Delta g(x,y)}{dy}}{\frac{d\Delta g(x,y)}{dx}} \right]$$

The maximum horizontal gradient manifests clearly the rock density boundaries, of course, from a certain point of view, it can be said that they are faults. The maximum horizontal gradient vector has a very special significance in defining spatial structure of the faults. The faults are often displayed by bands of the maximum horizontal gradient vectors in the same direction. The rock blocks, which have the higher density compared with that of the surroundings, are shown by the maximum horizontal gradient vectors that trend outward from the center of the blocks [1, 4, 6]. Analyzing and linking the locations and magnitudes of the maximum horizontal gradient by suitable methods will give a general picture of fault distribution, uplift zones in the Cenozoic basement and at greater depth concerning their spatial locations and developed directions.

Results

The horizontal gradient magnitudes as well as locations and directions of the maximum horizontal gradient vectors of the Bouguer gravity anomalies and of the gravity field

filtered at wavelength $\lambda = 50$ and 100km are calculated and are represented on the Figs. 2, 3, 4, respectively.

On the Fig.2, the distributions of the horizontal gradient magnitudes, locations and directions of the maximum horizontal gradient vector of the Bouguer gravity anomalies are shown. These distributions, caused by near-seafloor geological structures, are very complicated and multiform. The Fig.2 gives us a general view about local geological structure, uplift and depression blocks, also possible basalt blocks and fault systems. However, it is very difficult to link these structures together.

Fig.3 also shows the distributions of the horizontal gradient magnitudes, locations and directions of the maximum horizontal gradient vector of the gravity field filtered at wavelength $\lambda = 50$ km (it is reckoned as the distribution in Cenozoic basement). With respect to the study of faults based on gravity data, then the above-mentioned distributions are the distributions of the faults system and rock density boundaries as well. The fault systems are displayed by bands of maximum horizontal gradient vectors. Although the distribution of the maximum horizontal gradient vectors are still quite complicated, Fig.3 clearly indicates the main faults as well as density boundaries, uplift and depression blocks and geological structures in the area (Fig.3).

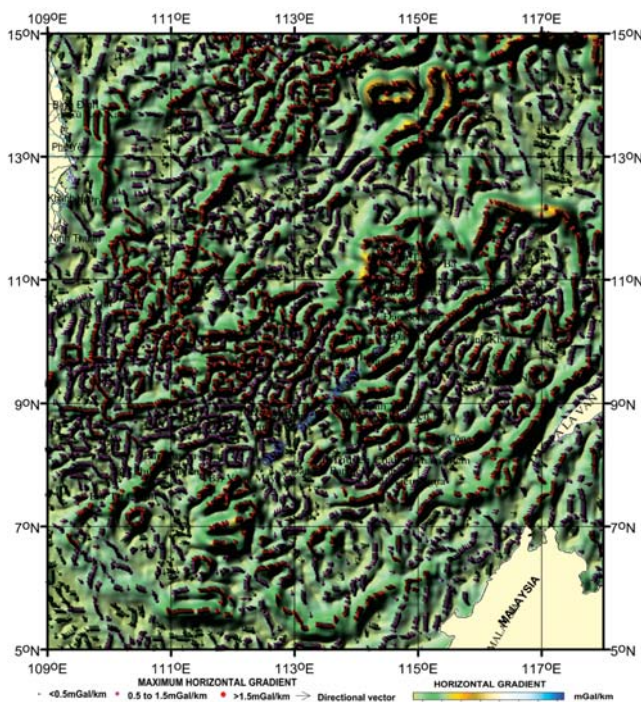


Fig.2. Horizontal gradient magnitudes and maximum horizontal gradient vector of Bouguer gravity anomalies

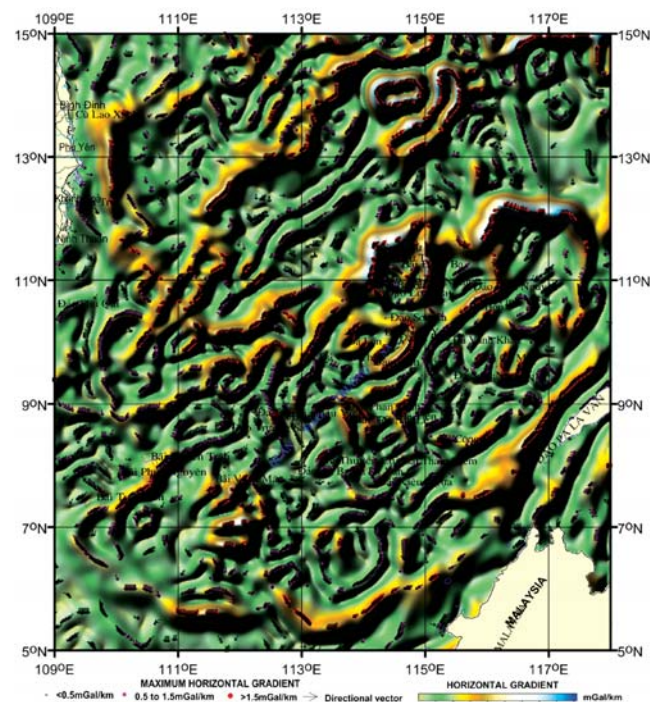


Fig.3. Horizontal gradient magnitudes and maximum horizontal gradient vector of gravity anomalies (filtered at wavelength $\lambda = 50$ km)

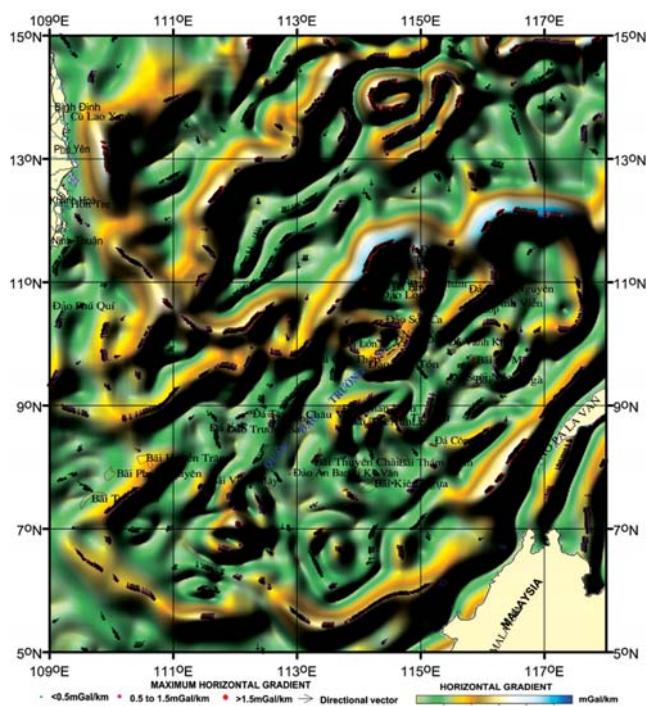


Fig.4. Horizontal gradient magnitudes and maximum horizontal gradient vector of gravity anomalies (filtered at wavelength $\lambda = 100\text{km}$)

On the Fig.4 are shown the horizontal gradient magnitudes, locations and directions of the maximum horizontal gradient vector of the gravity field filtered at wavelength $\lambda = 100\text{km}$. With this wavelength, we only the deep faults, regional structural blocks, crustal boundaries and sea-floor spreading axis are seen. The faults and structures at smaller depths have almost vanished. In Cu Lao Xanh a deep fault appears that runs along the Southern part of the Hoang Sa archipelago and meets the South Hai Nam fault in its Eastern part. In Fig. 4 also can be seen very clearly the change in direction of the 109° meridional fault after going through the Tuy Hoa shear zone. The main fault systems, which separate individually the sedimentary basins, are also represented very clearly in the Fig.4.

This study has analyzed and linked the results obtained, along with the bathymetry, seismic data and other geology-geographical data, to construct the fault systems, uplift and depression structures in the Cenozoic basement, the sea-floor spreading axis and crustal boundaries in the Truong Sa archipelago and the East Sea deep basins (Fig.5). The structural characteristics of the Cenozoic basement are depicted as in Fig.5.

The East Sea Western faults system (109° meridional fault) is clearly manifested by the maximum horizontal

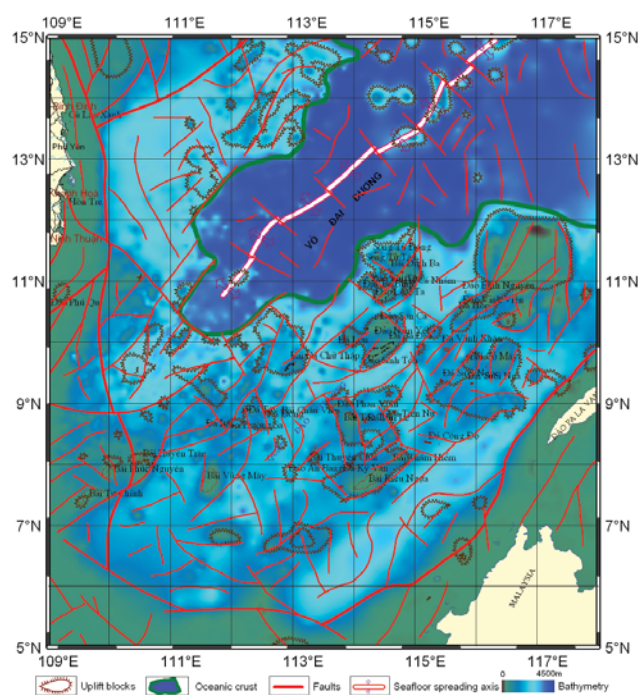


Fig.5. Structure of Pre-Cenozoic basement in the Truong Sa archipelago and in the East Sea deep basin area

gradient bands that have magnitudes $>1.5\text{mGal/km}$ with meridian-directional extension in the Western part of the study area. At Cu Lao Xanh area (Binh Dinh) appear a series of faults with branched shape, which run to South Hai Nam Island. At Khanh Hoa, it can be seen that the 109° meridional fault is shifted eastward by the Tuy Hoa shear zone. The greater the depth, the more clearly the Tuy Hoa shear zone is manifested by the maximum horizontal gradient bands (Fig.4). The shear zone extends toward the East Sea deep basin in a Southeast - Northwest direction and bends at the place that is possible the boundary between the continental and oceanic crusts. From the results obtained, it is possible to speculate that the Tuy Hoa shear zone is the likely Southwestern boundary of the continental and oceanic crusts (Fig.5). The above results prove the cohesive relationship of geological structure between the Truong Sa archipelago area and the Cuu Long, Nam Con Son, Tu Chinh - Vung May Basins.

After passing through the Tuy Hoa shear zone, the 109° meridional fault seems to be divided into two branches: The first branch runs southwards along the boundaries of the Cuu Long and Nam Con Son Basins then goes to the Ma Lai - Tho Chu Basin. The second branch runs southwards along the 110° meridional and its direction changes to sub-parallel direction at 6° and

extends continuously to 114° meridian to connect with a reversed fault in the Borneo basin.

On the Fig.5, it can be seen very clearly that the sedimentary basins such as the Cuu Long, Nam Con Son, Tu Chinh - Vung May are bounded by large faults. Especially, the Tu Chinh - Vung May Basins are separated by regional faults that extend from the North to South of the area. Therefore, it may be concluded that the Tu Chinh - Vung May are two distinct basins, and they are not a united structure.

At the central part of the East Sea appear the maximum gradient bands with high magnitudes. It could be affirmed that these are signs of a seafloor spreading axis, a crustal boundary (continental and oceanic crusts) and uplift zones. In the Truong Sa archipelago area, there are lots of closed maximum horizontal gradient bands. These are possible uplift blocks or intrusive blocks in the Cenozoic basement, which are often of higher density than that of the surroundings.

The fault systems in the Truong Sa archipelago can be divided into two main groups. The larger fault group is developed in a Southwest - Northeasterly direction and the smaller fault group is developed in a southeast-northwesterly direction.

In the East Sea basin area are transverse faults perpendicular to the seafloor spreading axis. Besides, there are several small fault systems that are developed in a sub-meridional direction.

Remarks and conclusions

The methodology of horizontal gradient and maximum horizontal gradient of gravity anomaly is efficient and reliable in determining structure and form of faults as well as crustal density boundaries. The frequency filtering method can be used to separate the gravity effects which are caused by geological bodies at different depths, with higher accuracy and reality than those of other methods.

The results achieved have revealed that the main structures in the area are generally controlled by deep faults. Also, the sedimentary basins such as Phu Khanh, Cuu Long, Nam Con Son, Tu Chinh - Vung May and Truong Sa are controlled by deep regional faulting.

Especially, the results of this study have shown that the Tu Chinh - Vung May basins seem to be two individual sedimentary basins. Moreover, it is possible to conclude

that the Tuy Hoa shear zone is the probable Southwest boundary of the continental and oceanic crusts. These results have proved the cohesive relationship of the geological structure between the Truong Sa archipelago area and the Cuu Long, Nam Con Son, Tu Chinh - Vung May Basins.

Based on the newest datasets, along with modern methodology, this study has produced a new and objective picture of the structure and form of the faults, uplift zone in basement as well as the seafloor spreading axis and crustal boundaries in the Truong Sa archipelago and in the East Sea deep basins.

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Multi-phase flow in single fracture

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Abstract

For the successful development of a fractured reservoir, it is important to estimate the multi-phase fluid flow behavior in a single fracture. However, how the wettability of the fracture surfaces, the interfacial tension between water and oil, and the geometries of the fracture surfaces affect the multi-phase flow behavior is not understood sufficiently well.

In this study, in order to understand these problems, we try to conduct a visualization experiment of water flooding in a single fracture, and then we try to simulate the multi-phase flow behavior observed in the experiment by using the lattice Boltzmann method (LBM). Consequently, we have gained a good understanding of the multi-phase flow behavior in a single fracture, and we can estimate the effect of the wettability and the interfacial tension on the multi-phase flow behavior.

1. Introduction

To estimate the multi-phase fluid flow through a fracture is important for the successful development of fractured oil and gas reservoirs and for environmental problems, especially for the geological sequestration of CO₂. This is because the reservoir fluids or the injected CO₂ mainly flow through fractures since the fractures have higher permeability than the matrix of rock masses.

Generally, the fracture permeability has been estimated by the cubic law, that is, the volumetric flow rate in a fracture is directly proportional to the cubic of its aperture. This law is valid for the laminar flow between two perfectly smooth parallel plates. However, the fractures have complicated rough surfaces. This makes the fluid flow through them anisotropic and their permeability deviate from the cubic law. In addition, the two straight lines satisfying the relation of $k_{r,nw} + k_{r,w} = 1$ have been used for the fracture relative permeability curves based on the experimental works by Romm (1966), where $k_{r,nw}$ and $k_{r,w}$ are the relative permeability of the non-wetting phase and wetting phase respectively. This type of the relative permeability curves physically means that the each phase flows in its own flow path without interference. But, some theoretical or experimental work and some numerical

simulations to the two-phase flow in a single fracture has shown that the each phase flows with strong phase interference¹⁻⁴. However, these works are not sufficient to understand the phase interference flow behavior for the correct estimation of the fracture relative permeability. Therefore, additional detail research on the multi-phase flow in a single fracture must be performed.

In this study, we try to conduct a visualization experiment of water flooding in a single fracture, and then we try to simulate and to estimate the relative permeability to the single fracture models having complex surface geometry by performing two-phase flow simulations using the lattice Boltzmann method (LBM). Moreover, we investigate the effect of the wettability and the interfacial tension on the multi-phase flow behavior and the relative permeability by the LBM two-phase flow simulations.

2. Visualization experiment of water flooding

2.1. Specimen for the visualization experiment

It has been shown that the topography of a fracture surface is a self-affine fractal and the power spectral density function of fracture surface profiles, $G(f)$, shows a decaying power law that can be described as

$$G(f) = Cf^{-(5-2D)} \quad (1)$$

where D is the fractal dimension; C is a constant; f is the spatial frequency [5, 6]. The two meeting surfaces of a single fracture correlate each other in lower spatial frequency band and do not correlate in higher spatial frequency band. By this frequency dependent correlation, the meeting fracture surfaces interlock with each other and the aperture distribution is formed.

In order to numerically generate the two meeting fracture surfaces, we used the Glover's method [7]. The fractal dimension and roughness of generated fracture surface can be set by changing the slope and intersection of the decaying power law respectively on the double logarithmic plot. Here, we set the fractal dimension 2.2 and the roughness 0.254mm in root mean square height. The numerically generated single fracture whose size is 50mm x 50mm is shown in Fig. 1. The black areas in this figure are contact areas.

For the visualization experiment of water flooding, we prepared a transparent specimen containing a single fracture by the following procedures. Firstly, we carved the two meeting fracture surfaces separately on a modeling wax using a numerical controlled (NC) modeling machine, PNC-300G produced by Roland DG. The numerical height data comes from the above mentioned numerically generated fracture. Secondly, we individually copied the two carved surfaces with white silicon gum and transparent acrylic resin. Finally, we mated them together. By using silicon gum, we can easily seal the fracture at both sides and both ends and easily change the contact condition of the fracture. The prepared specimen is shown in Fig.2.

2.2. Procedure of the visualization experiment

The water flooding visualization experiment was carried out on the prepared specimen. In the experiment, the fracture was first saturated with motor oil, and then dyed water was injected into the fracture using a syringe pump under the constant flow rate of $0.2\text{cm}^3/\text{min}$. The small back pressure was applied by adjusting the metering valve set at the outlet. During the flooding experiment, the flow behavior was recorded by a CCD camera. The schematic diagram of the flooding experiment system is shown in Fig.3.

2.3. Results of the visualization experiment

The characteristic four images obtained in the experiment are shown in Fig.4. In these images, the fluid

flows from the left to the right. From this figure, it can be observed that injected water does not flow in the whole non-contact areas but it selectively flows in the relatively large apertures and forms clear conduits. This is because the surface of the silicon gum is oil wet, and the water cannot flow in the small apertures without the additional flowing pressure that is greater than the capillary

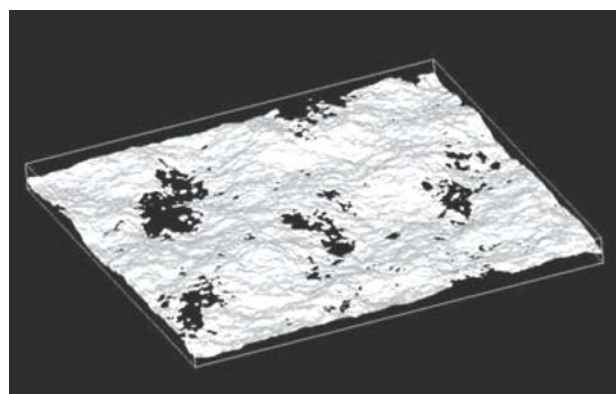


Fig.1. The numerically generated fracture model using Glover's method

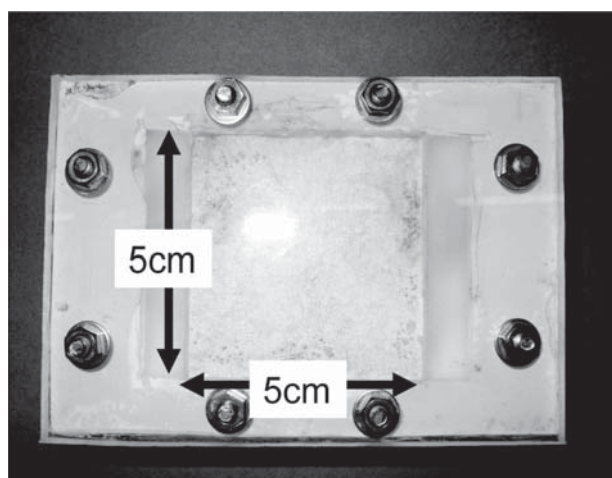


Fig.2. The specimen for the visualization experiment of water flooding

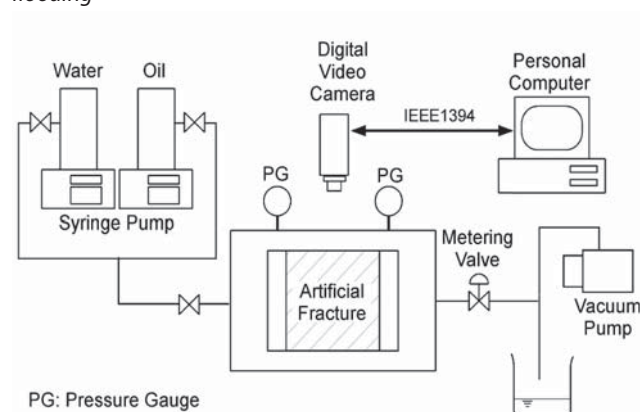


Fig.3. The schematic diagram of the flooding experiment system

pressure. The capillary pressure increases with the decrease in the aperture. Furthermore, it can be observed that the conduits cannot develop and the flow reaches a steady state condition after the water break through. This is because the capillary pressure drop occurs in the water phase when the continuous water phase is formed at the water break through, and the flowing pressure in the continuous water phase becomes low after the water break through. The sweep efficiency of this water flooding experiment was 35%.

3. Water flooding simulation in a single fracture by LBM

3.1. Multi-phase LBM

The LBM has succeeded in the flow simulation of complex boundary problem that conventional program codes by Navier-Stokes equation are hard to calculate. It solves a lattice Boltzmann equation for an ensemble-averaged distribution of moving and interacting particles on a discrete lattice. Motion of the particles is limited on the paths connecting the lattice nodes, and all particles on a given path have the same velocity. Interaction of the particles occurs at the lattice nodes by a Boltzmann collision operator. The macroscopic fluid mass and momentum for a given node are obtained by summing the mass and momentum of all particles on the paths emanating from the node. In the LBM, a local equilibrium particle distribution, which determines the Boltzmann collision

operator, is assigned so that the macroscopic fluid mass and momentum may satisfy the Navier-Stokes equations.

In order to simulate the immiscible two-phase flow of oil and water, the Boltzmann equation for the colored particles, red (oil) and blue (water) was used in this study. It is given by the following equation.

$$f_i^k(x + c_i \Delta t, t + \Delta t) = f_i^k(x, t) + \Omega_i^k(x, t) \quad (2)$$

where $f_i^k(x, t)$ and $\Omega_i^k(x, t)$ are the particle distribution function and the collision function respectively. They are defined to every kind of particle k , red and blue, and to every direction of particle motion i at the position x and time t . In Equation (2), c_i is the particle velocity in i direction on the lattice, and Δt is the time step during which the particles travel one lattice spacing. The particle velocity vectors on the D3Q15 (3D-LBM with 15 velocities) lattice used in this study is given by

$$c = \begin{bmatrix} 0 & 1 & 0 & 0 & -1 & 0 & 0 & 1 & -1 & 1 & 1 & -1 & 1 & -1 & -1 \\ 0 & 0 & 1 & 0 & 0 & -1 & 0 & 1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 \\ 0 & 0 & 0 & 1 & 0 & 0 & -1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & 1 \end{bmatrix} \quad (3)$$

The collision function is decomposed into two terms as Equation (4).

$$\Omega_i^k(x, t) = (\Omega_i^k(x, t))^A + (\Omega_i^k(x, t))^B \quad (4)$$

The first term of the right side of Equation (4) represents the relaxation from the collision perturbing condition to the local equilibrium condition. This term determines the effect of fluid viscosity in the LBM simulation. The second term represents the surface tension between the two kinds of immiscible fluid.

The first term of the collision function is defined as Equation (5) applying BGK (Bhatnagar-Gross-Krook) collision operator.

$$(\Omega_i^k(x, t))^A = -\frac{1}{\tau^k} (f_i^k(x, t) - f_i^{k(eq)}(x, t)) \quad (5)$$

where τ^k is the relaxation time to the local equilibrium condition after collision, and $f_i^{k(eq)}$ is the local equilibrium particle distribution function. In this study, in order to get numerical stability, the value of τ^k is set to 1. On the other hand, the second term of the collision function is defined by Equation (6) applying the interfacial tension model proposed by Grunau *et al*⁸.

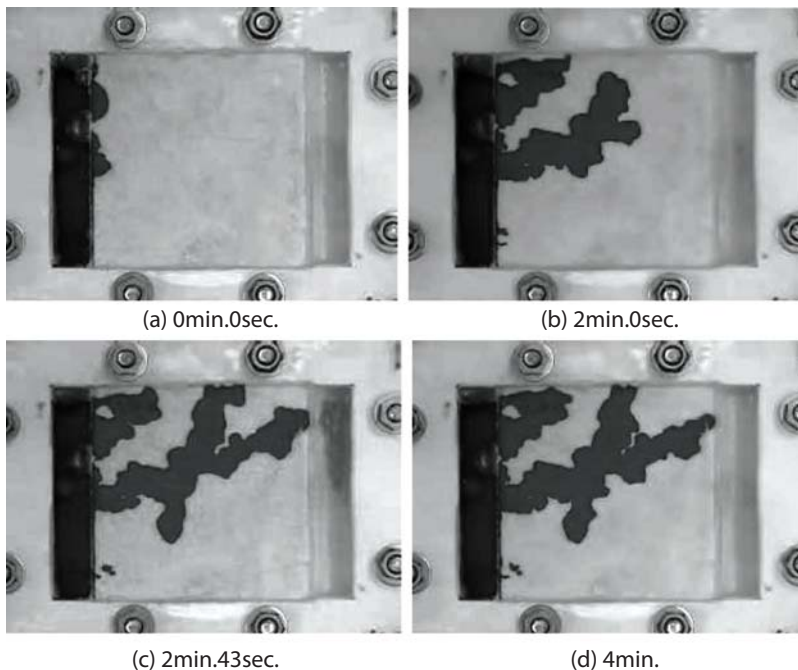


Fig.4. The characteristic images obtained in the water flooding experiment. Water breaks through at 2min. 43 sec., (c)

$$(\mathcal{Q}_i^k(\mathbf{x}, t))^B = A \left| \mathbf{F} \left(\frac{(\mathbf{c}_i \cdot \mathbf{F})^2}{|\mathbf{c}_i|^2 |\mathbf{F}|^2} - K \right) \right| \quad (6)$$

where A is the coefficient which controls the magnitude of interfacial tension, and K is the coefficient determined from the mass conservation depending on the lattice model. In this study, A is set to 1.0×10^{-3} for the base case of interfacial tension. K is $1/3$ for the 3D15Q lattice model. $\mathbf{F}$ is a function called the local color gradient. It is defined by Equation (7).

$$\mathbf{F}(\mathbf{x}, t) = \sum_i \mathbf{c}_i (\rho_r(\mathbf{x} + \mathbf{c}_i \Delta t, t) - \rho_b(\mathbf{x} + \mathbf{c}_i \Delta t, t)) \quad (7)$$

where ρ_r and ρ_b are the density of red fluid and blue fluid respectively. This function has a contribution at the interface of immiscible fluids.

4. Single fracture model used for the simulation

Water flooding simulations were performed to a square single fracture cut out from the single fracture model shown in Fig.1. The size of the single fracture model is 100 lattices in side length and 64 lattices in thickness. As shown in Fig.5(a), 10 lattices in length and 64 lattices in

thickness of fluid buffer were added to the both sides of the inlet and outlet. The actual lattices interval is 0.05mm. The aperture distribution is also shown in Fig.5(b). In Fig.5(b), the aperture is shown by the unit length scale of lattice interval. The average aperture of the fracture model is 4.2 lattices and the maximum aperture is 12 lattices. In the both Fig.5(a) and Fig.5(b), one black area is the surface contact area.

5. Water flooding simulation in a single fracture

In the water flooding simulation, the fracture was perfectly saturated with water at first, and then oil was injected under a constant pressure gradient until irreducible water saturation was accomplished. After that, the water flooding was carried out. In this simulation, the wettability of the fracture surface is perfectly water wet, and the viscosity ratio between oil and water is 4.5. The interfacial tension was set to the base case; $A = 1.0 \times 10^{-3}$.

6. Results of the water flooding simulation

The change of the oil saturation is shown in Fig. 6 in the progress of time step. In this figure, the surface contact area and the water saturated areas are indicated by black and blue respectively, and the oil is indicated by the gradation of green color according to its saturation. The deeper green indicates higher oil saturation, and the lighter green indicates lower oil saturation. From this Figure and Fig.5(b), the following are observed. First, oil does not saturate the whole fracture especially the small apertures.

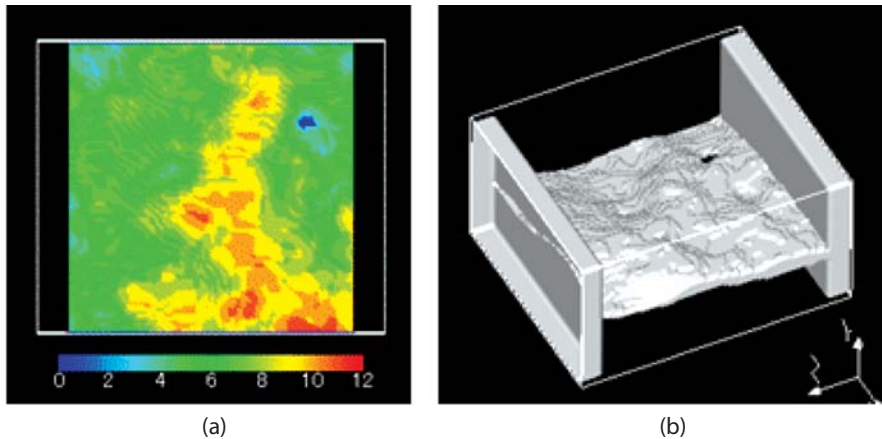


Fig.5. The bird view, (a), and the aperture distribution, (b), of the single fracture model used for the water flooding simulation

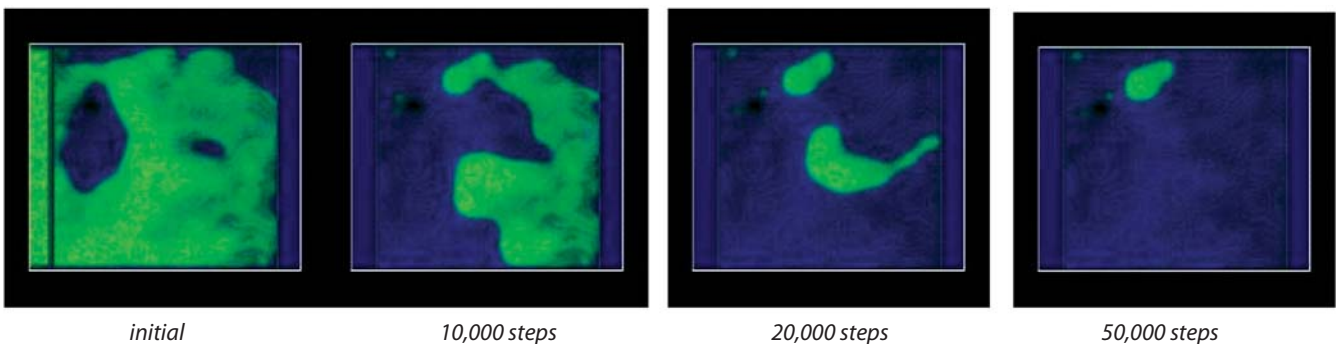


Fig.6. The change of the oil saturation observed in the water flooding simulation under the perfectly water wet, the base case of the interfacial tension, and the viscosity ratio of 4.5. The oil is indicated by the gradation of green color according to its saturation

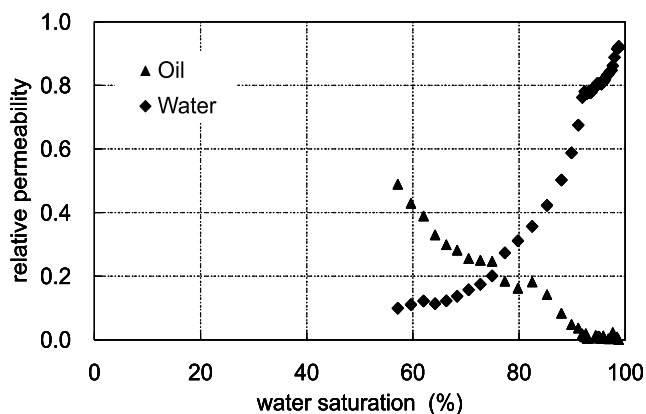


Fig.7. The fracture relative permeability curves of oil and water obtained from the water flooding simulation

The initial water saturation is 49.5% as the result. Second, water flows even into the small apertures avoiding the oil saturated large apertures. Some independent oil islands are formed as the result and they are flooded out discontinuously. The residual oil saturation is finally 1.7%. These fluid flow behavior would be caused by the perfectly water wet state of the fracture surface.

7. Relative permeability of single fracture

7.1. Relative permeability estimation

The relative permeability of the single fracture model was estimated from the average flux of each phase and the water saturation obtained from the water flooding

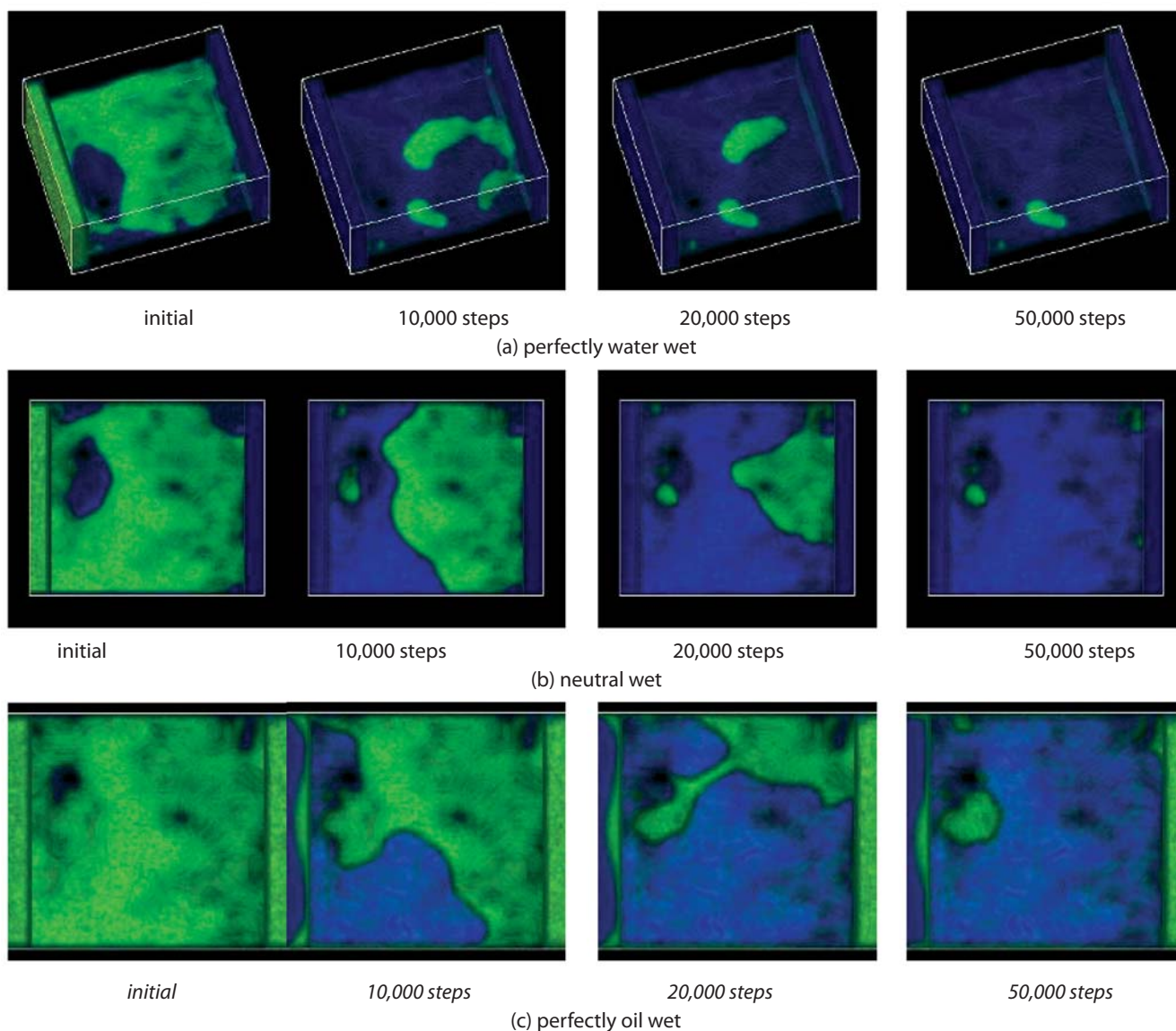


Fig.8. The change of the oil saturation observed in the water flooding simulation with changing the wettability to the perfectly water wet (a), the neutral wet (b) and the perfectly oil wet, (c). The oil is indicated by the gradation of green color according to its saturation

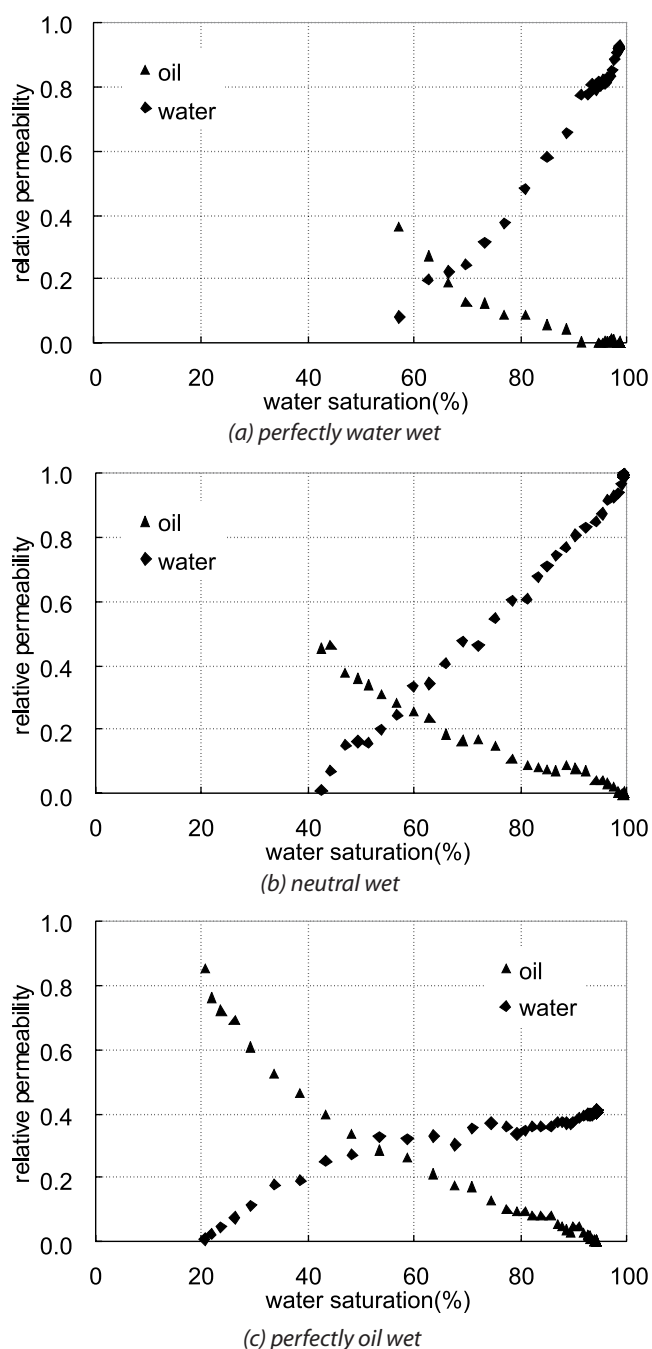


Fig.9. The relative permeability to the three cases of the wettability, (a) perfectly water wet, (b) neutral wet, and (c) perfectly oil wet

simulation mentioned above. To oil and water, the relative permeability curves concaving downward are obtained as shown in Fig.7. It can be recognized that the relative permeability curves of a single fracture are not straight lines satisfying the relation of $k_{r,nw} + k_{r,w} = 1$. This is probably because each phase of fluid flows are avoiding or pushing each other in the complex aperture distribution of the fracture, and the flow pass consequently becomes as tortuous as the porous reservoir rocks.

7.2. Effect of wettability on relative permeability

The relative permeability would be affected by the wettability and the topography of the fracture surface, the property of aperture distribution, the interfacial tension between oil and water, and the viscosity ratio of the oil viscosity to the water viscosity. Among these affecting factors, the effect of the wettability was first investigated.

Water flooding simulations were performed to the perfectly water wet, the neutral wet, and the perfectly oil wet for the same single fracture model as mentioned above. However, the viscosity ratio is set to one in order to diminish the effect of viscosity. The initial water saturation is 57.2% to the water wet, 42.6% to the neutral wet, and 20.7% to the oil wet. From this initial water saturation condition, water was injected into the fracture under the constant pressure gradient.

The change of the oil saturation is shown in Fig.8 to each case of the wettability in the progress of time steps. In the case of the perfectly water wet, Fig.8(a), the aspect of the flooding is the same as above mentioned although the viscosity ratio is different. The residual oil saturation is 1.5%. In the case of the neutral wet, Fig.8(b), the oil is flooded out continuously without forming the independent oil islands. The residual oil saturation is 0.74%. In the case of the perfectly oil wet, Fig.8(c), the water flows selectively to the large apertures. Two flow paths are formed as the result of avoiding the surface contact area, and the two flow paths surround the small apertures around the surface contact area. The oil in those small apertures is finally left. The residual oil saturation is 5.7% that is the highest among the three cases of wettability.

The relative permeability curves are shown in Fig.9 for each case of wettability. In the case of the perfectly water wet, the water relative permeability is difficult to increase during the small water saturation, because the water flows by avoiding the oil occupying large apertures. But it increasingly increases with the increase in the water saturation, as the water flows through almost the whole fracture. Consequently, the water relative permeability curve concaves downward. In the case of the neutral wet, both relative permeability curves of oil and water become almost straight lines. This is because each phase of the fluid can flow without capillary force. In the case of the perfectly oil wet,

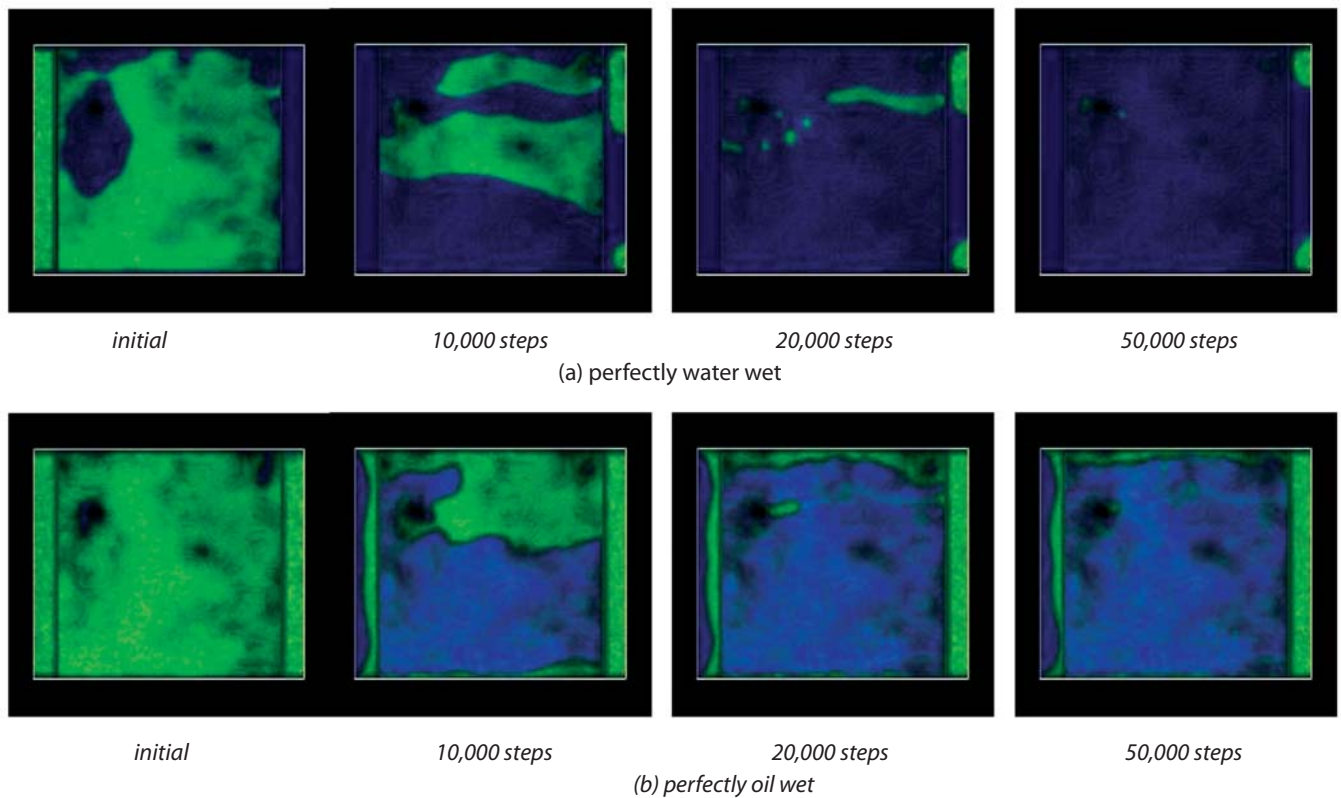


Fig.10. The change of the oil saturation observed in the water flooding simulation with changing the interfacial tension to 1/10 of the base case for the case of perfectly water wet (a) and the perfectly oil wet (b)

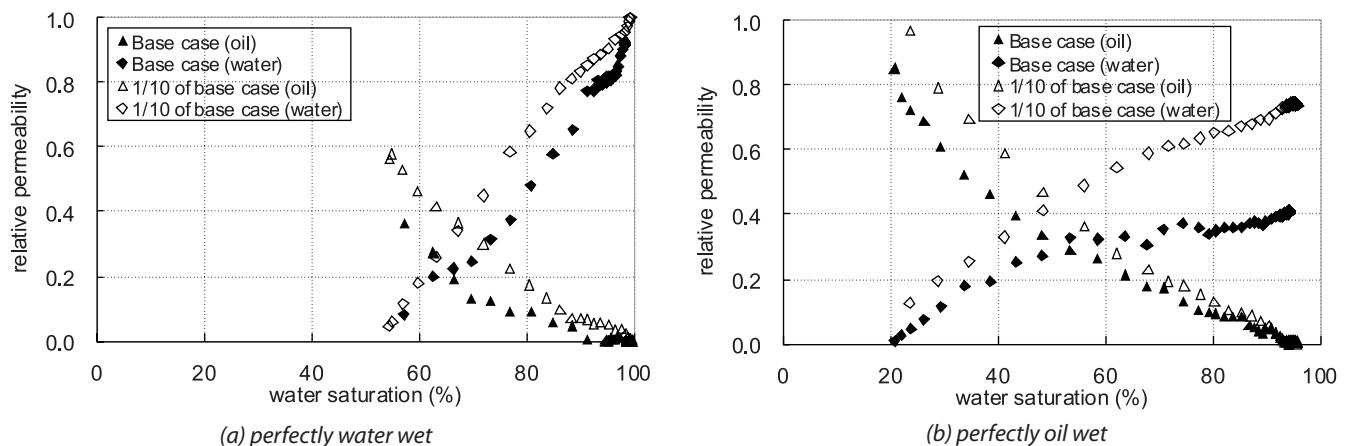


Fig.11. The change of the relative permeability with the change of the interfacial tension for the case of the perfectly water wet (a) and the perfectly oil wet (b)

the relative permeability curve concaving upward is obtained. This is because the water flows selectively to the large apertures at first and then it spreads into the small apertures. The flow rate of the water decreases as the result.

7.3. Effect of interfacial tension on relative permeability

The effect of the interfacial tension on the relative permeability was then investigated. We set the value of

interfacial tension controlling coefficient, A , 1/10 of the base case, and performed the water flooding simulation to the cases of perfectly water wet and perfectly oil wet. The pressure gradient and viscosity ratio are the same as the previous simulations.

The change of the oil saturation is shown in Fig.10 for each case of the wettability in the progress of time steps. Although the flow pattern of both cases of the wettability is almost the same with the base case of the interfacial

tension, the residual oil islands become smaller in the case of the perfectly water wet and the water flows into the smaller apertures in the case of the perfectly oil wet by reducing the interfacial tension. The residual oil saturation decreases in the both cases of the wettability. The residual oil saturation is 0.04% for the perfectly water wet and 4.2% for the perfectly oil wet.

The relative permeability curves are shown in Fig.11 for each case of the wettability. In the both cases of wettability, the relative permeability curves approach a straight line. This is probably because the capillary effect becomes small and the flow behavior of the both fluids becomes independent of the aperture distribution.

Conclusions

The water flooding behavior in a single fracture having a complex surface topography are well understood by the visualization experiment and the multi-phase LBM simulation. Moreover, the relative permeability of oil and water for a single fracture is estimated well by the water flooding simulation using the LBM.

From this study, it has been confirmed that the fracture relative permeability curves of oil and water are not straight lines but are curves whose shapes depend on the wettability of the fracture surface and the interfacial tension between oil and water. The water relative permeability curve is concave downward when the wettability is perfectly water wet, the relative permeability curves are almost straight lines when the wettability is neutral wet, and the water relative permeability curve is concave upward when the wettability is perfectly oil wet. Furthermore, the relative permeability curves approach a straight line regardless of the wettability when the interfacial tension between oil and water is reduced.

Some causes of these aspects of the fracture relative permeability have been discussed in this study, but some additional simulation studies for the other conditions of the fracture are necessary to enable more detailed discussions about the affecting factors of the relative permeability.

Acknowledgement

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Heat flow study results and geothermal energy distribution in the Vietnam offshore sedimentary basins

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Abstract

The study of the heat flow in Vietnam's offshore oil basins has been carried out at the Vietnam Petroleum Institute by using data from 80 exploratory wells, distributed from the Song Hong basin in the North to the Nam Con Son basin in Southern part of the Vietnam East sea. The thermal conductivities of 427 cores were measured using equipment from CCOP, brought to Vietnam by Dr. O.Matsubayashi and simultaneously using the Thercon 2 - 1992, high quality new Vietnamese-made equipment designed and manufactured by Prof. Dam Trung Don of Hanoi University. The temperature gradients of wells were calculated from well log data and from well tests data. The average heat flow values of sedimentary basins in offshore Vietnam are as follows: Song Hong basin (119mW/m²), Da Nang basin (89mW/m²), Cuu Long basin (64mW/m²), Nam Con Son basin (80mW/m²).

The distribution pattern of heat flow in a sedimentary basin is believed to be related to its tectonic history. The heat flow and temperature history are the consequence of the geological history of a basin, therefore the main phases of rifting and phase of recent volcanic activity will be the primary sources of thermal energy in Vietnam's sedimentary basins (Fig.2).

The Red River Fault (RRF) in the Song Hong basin, the North - South trending fault in the Bac Bo gulf, and others faults are important thermal channels in offshore Vietnam. The coal beds in the Song Hong basin, the Rotalit shale in the Cuu Long basin and the local shale layers in all basins are good thermal sealing layers. Due to the differences in geological characteristics and heat flow regime, Vietnam's sedimentary basins have different geothermal energy distributions. Their thermal regimes are generally conducive for providing the conditions necessary for the maturation of hydrocarbon source rocks and facilitating the migration of oil to the traps. Also, with high heat potential, the geothermal energy of some regions is favourable for power generation and for other industrial and human needs.

1. Introduction

Geothermal energy is thermal energy generated and stored in the earth. At the core of the earth, temperatures may reach over 5,000°C. Heat is conducted from the core to surrounding cooler rocks. High temperatures and pressures cause some rock to melt, creating magma which migrates upwards since it is lighter than the solid rock. The magma heats rock and water in the crust, sometimes up to 370°C. The earth's internal energy flows to the surface by conduction at the rate of 44.2 terawatts (TW) and is replenished by radioactive decay of minerals at a rate of 30TW. These power rates are more than double humanity's current energy consumption from all primary sources, but most of this energy flow is not recoverable. In addition to the internal heat flows, the top layer of the earth's, surface to a depth of 10m, is heated by solar energy during the summer and releases that energy and cools during the

winter. In most of the world, excepting these seasonal variations, the geothermal gradient of temperatures through the crust is 25 - 30°C per kilometer of depth. The conductivity heat flux averages 0.1MW/km². These values are much higher near tectonic plate boundaries where the crust is thinner. They may be further augmented by fluid circulation, either through magma conduits, hot springs and hydrothermal circulation or a combination of these. Geothermometry is a branch of geophysics which has the objective to study and elucidate these problems.

Discovering the origin and distribution of regional heat flows is of great practical importance because they can help us to understanding the geological development history, especially the geodynamic regime of the studied areas. In the petroleum domain, geothermal research contributes to determination of the source rock maturation (e.g. the cooking process

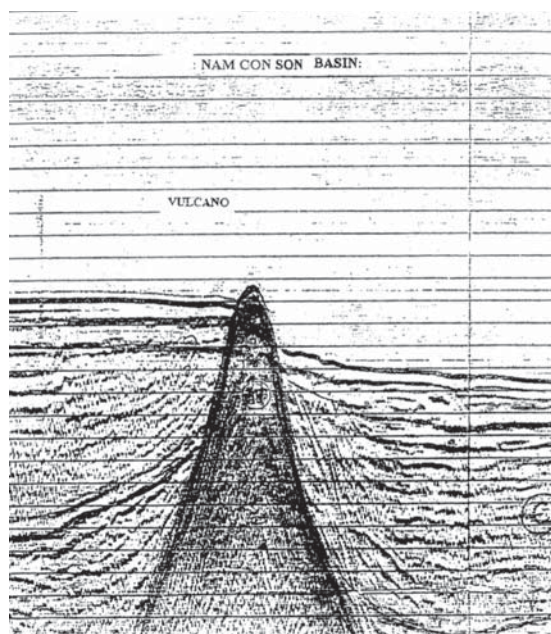


Fig.1. The recent volcanic activity of Nam Con Son basin is from seismic data. In offshore Vietnam, the main phases of rifting and the phase of recent volcanic activity are the primary sources of thermal energy in its sedimentary

whereby organic matter in a rock is converted into gaseous and liquid hydrocarbon), the migration of oil from source rock into a more permeable medium and movement through the permeable conduit into the reservoir as well as the remobilization of reservoir petroleum. Defining thermally anomalous zones in a prospect is a very important task in the selecting the drilling technology in order to avoid technical risks in the drilling process [1 - 4].

2. Study results

2.1. Thermal conductivity

Thermal conductivity is dependent on the composition and geometry of the rock matrix, on porosity and on pore medium. Additional influences in the situation of a deeply buried rock are pressure and temperature. Measurements of thermal conductivity cover a wide spectrum of techniques that can be subdivided into direct (laboratory) and indirect (well-logging) approaches. The indirect approach can potentially circumnavigate the problem of based single-point rock sampling for laboratory measurements and also provide thermal conductivity values along the entire borehole profile, but its use depends on the quality and the number of logs available.

In our study, thermal conductivity was measured in more than 427 conventional core samples covering

representative stratigraphic intervals of 80 exploratory wells in four oil basin areas of Vietnam. Core samples having a flat surface with an approximate area of 12 x 8 cm and a thickness of 6 cm were smoothed and soaked in water for 48 hours before being measured at a constant room temperature of about 26°C. The thermal conductivity values obtained by the two instruments mentioned above were corrected by calibrating them with a fused quartz standard sample, which has a thermal conductivity of 1.16 kcal/mhK° (Fig. 3).

By knowing the thermal conductivity and thickness of each rock type the unit-averaged thermal conductivity K_f and the average for a well K_w can be calculated using the following equations:

$$K_f = (t_1/k_1 + t_2/k_2 + \dots + t_n/k_n) / (t_1 + t_2 + \dots + t_n)$$

$$K_w = (t_a/k_{fa} + t_b/k_{fb} + \dots + t_n/k_{fn}) / (t_a + t_b + \dots + t_n)$$

Where $k_1, k_2, \dots, k_n$ are the averaged thermal conductivity of each rock type after correction for the effect of in-situ temperature; K_f and K_w are respectively the thermal conductivities of the stratigraphic unit and the whole section of a well, and t_1, t_a are respectively the thickness of individual rock types and stratigraphic units. The thermal conductivities in some other wells were also calculated based on the well-log data. The following formula was used in the calculation:

$$K = R_s / [K_s^{(1-\phi)} \times K_{w_a}^{(\phi)}] + R_m / [K_m^{(1-\phi)} \times K_{w_a}^{(\phi)}]$$

Where K, K_s, K_m, K_{w_a} are the thermal conductivity of bulk formation, of sandstone, of mudstone and of formation water; " ϕ " is average porosity, R_s and R_m stand for fractions of sand and mudstone (shale) content, where $R_s + R_m = 1.0$.

The average thermal conductivity of 80 wells was calculated, and Table 1 shows the average conductivity of each of the sedimentary basins studied in this work. The following generalizations can be noted:

- In the Cuu Long basin the average conductivity value is the lowest of the basins studied;
- In the Song Hong basin the thermal conductivity value onshore (3.37 W/mK°) is higher than offshore (2.98 W/mK°) due to coarse grained sediments onshore and more fine-grained sediments offshore. The highest thermal conductivity is observed in the North-Western part. Conductivity decreases gradually towards the South-East (where K° - Kelvin degree);

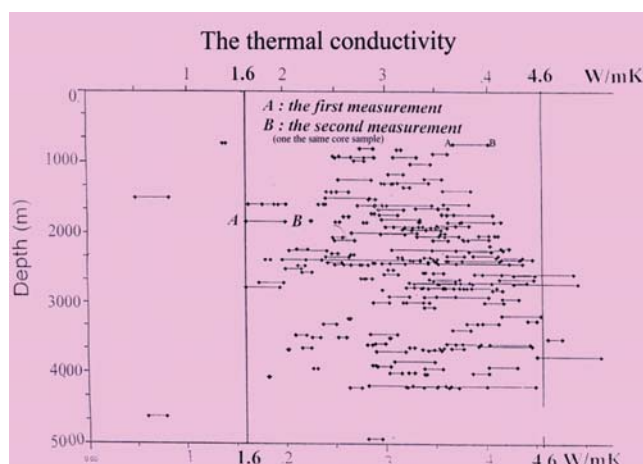


Fig.2. The thermal conductivity results from core samples in the Vietnam offshore sedimentary basin in Vietnam offshore oil basin by QTM Thercon 2-1992 - Made in Vietnam and QTM N0911 - Made in Japan

- For the Nam Con Son basin, thermal conductivity is higher in the Western part (4.14W/mK°), where coarser-grained deposits predominate. However, in the Southeastern, Northeastern and central parts it tends to be lower (2.47W/mK°) because of finer grained deposits in these areas;
- In the Da Nang area, thermal conductivity is higher in the Northeastern part (3.00W/mK°) than in the Southeastern part (2.16W/mK°). This rapid decrease towards the South may be due to carbonate deposition in the South.

2.2. Geothermal gradient

Geothermal gradient is the rate of change of temperature with depth in the earth. Here, the temperature gradient was computed by extrapolation of the successive bottom hole temperatures (BHT) of wells and assuming a surface temperature of 80°F (26.67°C). The temperature derived from well-logs is corrected to obtain the true formation temperature by using Dowdle and Cobb's (1975) method as expressed by the following formula:

$$TF = TL + C \log[(t_1 + t_2)/t_2]$$

Where:

TF: True formation temperature;

TL: Measured temperature (BHT) at time t2 during geophysical logging;

t1: Circulation times after drilling stopped and before the bit pulled;

t2: Times between cessation of circulation and measuring TL;

C: A constant.

In order to obtain true formation temperature values for all the wells studied (in the Nam Con Son, Da Nang, Cuu Long and offshore Song Hong basins) the authors used a nomogram based on the above formula. For all the wells in onshore Song Hong basin, true formation temperatures were obtained by temperature logging under taken from four days to two years after the circulation of drilling fluids stopped. The temperature gradient (G) was computed by using the following formula:

$$G = dT/dz = (BHT \text{ corr} - 26.67)/z$$

The average temperature gradient of each basin are summarized in Table 1. Individual basins have the following characteristics:

- In general, in the basinal areas of Vietnam, temperature gradients decrease with depth;
- The temperature gradient of the Cuu Long basin is the lowest of the offshore basins studied;
- In the Song Hong basin, the temperature gradient increases rapidly towards the central part and decreases to the Northeast;
- In the Nam Con Son basin, the temperature gradient decreases rapidly to the West, with a value of 26K°/km in the Northwest, and increases to the East to about 40K°/km;
- In the Da Nang area, the temperature gradient increases rapidly to the North and Northeast, and decreases gradually to the South;
- In the Cuu Long basin, the temperature gradient is highest in its central part.

2.3. Heat flow

Terrestrial heat flow (Q) is obtained as the product of thermal conductivity (K) and temperature gradient (G):

$$Q = K \times G = K \times dT/dz$$

The average heat flow of 80 exploration wells in Vietnam was calculated by using the above formula and the results for each basin are shown in Table 1. The average heat flow value of Vietnam's sedimentary basins is 82.95mW/m². This is higher than the world average (63mW/m²), but is similar to those in adjacent zones

Neogene sediments in Vietnam consist of a large thickness of alternating sandstone, siltstone and claystone distributed all over the continental shelf. They overlie the eroded Paleogene sediments and are overlain in turn by 30 - 500m thick quaternary sediments. Due to the difference in tectonic characteristics and sediment supply sources, the depth of occurrence and thickness of Neogene formations differ in different basins. The water-bearing formations consist of medium to fine grained sandstone, fractured and weathered shelf limestone and coral limestone. In almost all sedimentary basins, the clay/sand content of the Neogene sediments reaches about 40 - 50%. The thickness of sandstone and of shelf and coral carbonate layers varies from a few meters to some tens meters. The temperature of the water varies from 30 - 100°C, the total dissolved solids (TDS) is relative low and tends to increase with depth from 1 - 3g/l. The chemical composition of the thermal water is mainly HCO_3ClNa . According to the result of C^{14} radiometric dating, the age of the thermal water in Neogene strata is 5 - 25Ma.

The geothermal energy distribution in Neogene sediments is as follows: Prognostic geothermal energy in the reservoir of Song Hong Neogene is $Q_r = 3,923.31 \times 10^{18}\text{J}$; of Nam Con Son Neogene is $Q_r = 3,227.55 \times 10^{18}\text{J}$, and of Cuu Long Neogene is $Q_r = 1,353 \times 10^{18}\text{J}$.

Paleogene sediments in Vietnamese basins comprise alternations of claystone and sandstone sequences, of which the clay component is predominant, varying from 60 - 70%. The distribution of the sediments is very complicated due to the uplift and erosion causing them to completely or partially disappear in some places. In the depressions, a complete sequence is most likely to be present. However, so far in those locations, no wells have been drilled.

In the Song Hong basin, due to the very complicated geological conditions and low density of wells drilled, the Paleogene sediments have not been thoroughly investigated. Some wells have encountered these sediments in the continental shelf such as 103TH-1X, 103TG-1X, 107PA-1X, 112BT-1X, 114KT-1X, 119CH-1X and on the mainland such as GK204, 104, 110, 81, 203, 200, D14-STL. The thickness of these sediments varies considerably over large range.

On the contrary, in the South of the Vietnam continental shelf, the Paleogene sediments cover nearly all over the sedimentary basins and their thickness varies from 100 - 1,400m. In the Cuu Long basin, the Paleogene sediments occur at depths from 1,580 - 4,300m. In the

Nam Con Son basin they are encountered at depths from 1,850 - 4,300m and in the Ma Lai - Tho Chu basin from 1,850 - 4,300m.

The water-bearing formation of the Paleogene consists of sandstone, volcanic rocks, and pyroclastic sediments with thickness varying from a few tens to hundreds of meters. The temperature of the ground-water varies in the range 80 - 115°C and, in the main, its chemical composition is HCO_3ClNa . The DTS varies from area to area depending on the paleoclimatic and paleohydrochemical conditions of the area. The DTS of the groundwater in the Cuu Long basin varies from a few g/l to some tens of g/l; in the Nam Con Son basin from 1.5 - 3.5g/l and in the Malay - Thochu basin from 1.2 - 3.5g/l. The age of the Paleogene thermal groundwater varies from 27 - 35Ma, according to the C^{14} radiometric dating result.

Prognostic geothermal energy in the reservoir is as follows: $Q_{r \text{ Song Hong}} = 4,848.49 \times 10^{18}\text{J}$;

$$Q_{r \text{ Nam Con Son}} = 4,314.65 \times 10^{18}\text{J}; Q_{r \text{ Cuu Long}} = 190.66 \times 10^{18}\text{J}.$$

The weathered and fractured basement has good water bearing capacity. In the Song Hong basin the Pre-Cenozoic basement was encountered in some wells such as 112BT-1X, 112HO-1X, 112AV-1X, 115A-1X, 104QV-1X. The basement rocks consist mainly of dolomite, dolomite-carbonate, siliceous rocks, limestone and terrigenous sediments with moderate porosity. The total thickness of the weathered zone reaches as much as thousands of meters.

In the Cuu Long basin, the basement is met in numerous wells in the Bach Ho, Rong, Rang Dong, Hong Ngoc, Ba Vi... fields and is mainly composed of granite and granodiorite. The fractured zones are usually oriented in a vertical direction, therefore the liquids with high temperature, rising up from the great depths, are likely to form local thermal water reservoirs in the old uplifted basement. To the present day, geothermal energy in the basement is not yet studied as there are still insufficient data for determining the in-situ geothermal energy reserves of the weathered - fractured basement.

3. Geothermal classification by temperature

In the sedimentary basins of Vietnam, the temperature distribution is as follows:

Therefore, in the sedimentary basins of offshore Vietnam at the depth from 500 - 4,000m, minimum temperature varies from 44.1 - 115°C; maximum

temperature from 54.1 - 185.0°C and average temperature from 49 - 151°C (Table 2). The thermal water sources in terms of temperature can be divided as follows:

- Low temperature: < 90°C;
- Medium temperature: 90 - 150°C;
- High temperature: > 150°C.

Normally, high and medium temperature geothermal sources are used for electricity generation, whereas the medium and low temperature geothermal source may be used directly for heat pumps. With the above classification, the geothermal sources in the Tertiary sedimentary basins of Vietnam can be evaluated and classified as the low and medium temperature class (to the depth of 3,000m). In particular, the geothermal sources in the South of the Bac Bo plain (block 112, 113, 114, 115) down to the depth of 4,000m can be classified a high temperature resource.

The Song Hong basin has more favorable conditions for thermal energy exploitation due to the higher geothermal gradient and smaller depth. Here, at the depth of 2,000m, the mean temperature may reach 110°C, whereas in the Nam Con Son basin the temperature is lower.

Examining all conditions as a whole, the Hanoi depression and Southern Deo Ngang areas can be seen as the regions of greatest geothermal energy potential in Vietnam's sedimentary basins [6,7].

4. Conclusion

1. The sedimentary basins in the Vietnam continental shelf contain large and valuable energy resources - oil and gas, coal and geothermal energy but up to now the geothermal regime is poor studied. Therefore, it is very important to have a comprehensive policy for investment and for further investigation to evaluate the geothermal energy potential in more detail through application of advanced technologies for these activities.

2. Geothermal energy of offshore Vietnam can be exploited in Neogene and Paleogene formations at depths from 500 - 3,000m. The geothermal temperature of sedimentary basins is from moderate to high, favorable for the use of geothermal energy for power generation and directly for industrial and human needs.

According to the preliminary calculation, for

Table 2. Distribution of the temperature versus depth

Depth (m)	Min (°C)	Max (°C)	Average (°C)
500	44.1	54.1	49
1,000	56.2	77.8	67
1,500	67.3	107.8	87
2,000	78.0	118.0	98
2,500	87.3	136.0	112
3,000	98.1	155.0	127
3,500	106.0	170.0	138
4,000	115.0	185.0	151

the objective of power generation, the prognostic geothermal energy reserves of the whole shelf are 21,393.4 x 10¹⁸J, equivalent to 6,030MWh. The onshore reserves are also fairly large. Therefore, we propose that the Ministry of Sciences and Technology, Petrovietnam should develop an adequate research program for exploration and exploitation of geothermal potential in our country, especially in the Hanoi trough and South Deo Ngang areas, to serve for the state sustainable energy development program to the year of 2020 and beyond.

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CO₂-CH₄ exchange in the context of CO₂ injection and gas production from methane hydrates bearing sediments

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Abstract

In recent decades, scientists have made an amazing discovery: Methane hydrates in the ocean floor. These solid compounds could represent an important energy reserve. Today it is estimated that they contain equivalent carbon in the form of methane in a huge quantity, twice as much as all deposits of natural gas, oil and coal.

In the near future, we need evaluate the possibility to produce this new source of energy, particularly in replacement of oil and coal. The main question concerns the technology to be used because the methane hydrates are distributed in sediment, and they participate to their consolidation.

In this paper, we present a method which doesn't modify the structure of the sediment, by replacing the methane hydrate by CO₂ hydrate after injection of CO₂ gas.

1. Introduction

Gas hydrates are solid compounds. They are formed from the combination of gas (such as methane, ethane, propane...) and water under high pressure and low temperature. Clathrate hydrate has been first discovered in 1778 by Joseph Priestley as a laboratory curiosity. Nowadays, gas hydrates have the potential for numerous applications in the oil and gas industry and the energy sector, as for example through the use of clathrate hydrates as a means of gas storage, for the capture and sequestration of carbon dioxide, in air-conditioning systems in the form of hydrate slurries, in the water desalination and treatment, and the separation of different gases from flue gas streams to name but a few (Eslamimanesh et al, 2012). However, despite the potential applications of gas clathrate hydrates, like the ones mentioned above, there are also negative aspects to be mentioned in the discussion of these solid solutions. The uncontrolled decomposition of naturally occurring methane hydrates for example has been discussed as being capable of potentially contributing to the

greenhouse gas effect (Englezos, 1993; Leggett, 1990), in particular if it is realised that the global warming potential (GWP) of methane within a period of 100 years is greater by a factor of 25 than the GWP value of carbon dioxide (Solomon et al, 2007). Moreover, gas clathrate hydrates have been identified as a source of problems in the oil and gas industry, for example. when being formed in drilling applications (Barker and Gomez, 1989) or in gas pipelines due to their ability of causing pipeline blockages (Eslamimanesh et al, 2012).

2. Context of the work

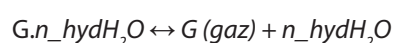
Methane is a natural component in sediments, originated from thermal degradation of fossil reservoirs or from bio-degradation of biological materials. Under pressure, in deep sea conditions, it forms methane hydrate reservoirs in many places of the world and in huge quantities. On the other hand, carbon dioxide is a molecule which presents a better affinity to clathrate structure. The concept consists in injecting CO₂ in methane hydrate reservoirs in order to shift the equilibrium and form a CO₂ hydrate in the place of methane hydrate, and to recover methane.

The objective of our work is to study thermodynamic of CO₂-CH₄ methane hydrate, in presence of salts, and to understand the crystallization mechanism during the replacing of CH₄ by CO₂. In this work, we present a set of experimental results in order to validate a thermodynamic model which predicts the equilibrium conditions; pressure, temperature and composition of phases in presence of a mixture of CO₂ and CH₄.

3. Structure of gas hydrates

Gas clathrate hydrates are solid crystalline compounds which are built up by a network of hydrogen bonded water molecules comprising cage-like structural units, each of which can encapsulate one appropriately sized guest molecule. The guest species, which are generally molecules of low molecular weight gases and organic compounds (Sloan and Koh, 2008), stabilize the solid solvent, the thermodynamically metastable host lattice, by interacting with the water molecules of the cage through van der Waals forces (Ribeiro and Lage, 2008). Gas clathrate hydrates are thermodynamically stable in regions of ambient or lower temperatures (above or below the normal freezing point of water) and elevated pressures (typically more than 0.6MPa) (Englezos, 1993; Sloan, 2003) and crystallise in three different structures, the cubic structures I (sI) and II (sII), and the hexagonal structure H (sH). Structure I, which predominates in the earth's natural environments and contains small (0.4 - 0.55nm) guest species (Sloan, 2003), possesses a network of water molecules based on two different polyhedra as building units, which according to the nomenclature of Jeffrey (Jeffrey, 1984), are written as 5¹² and 5¹²6². The cubic structure II hydrates, the lattice of which is composed of the polyhedra 5¹² and 5¹²6⁴, generally occur with larger (0.6 - 0.7nm) guests in mostly man-made environments (Jeffrey, 1984). Hydrates of hexagonal structure H, occurring in either environment, but only with mixtures containing both small and large (0.8-0.9 nm) guest species (Jeffrey, 1984), comprise three types of cavities, the polyhedra 5¹², 4³5⁶6³ and 5¹²6⁸.

The combination of the gas molecules with the water can be described by the equation:



Where n_{hyd} is the hydration number. In the structure I, hydrate crystallize as 5.77 ≤ n_{hyd} ≤ 7.4 (Sloan and Koh 2008).

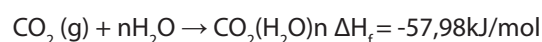
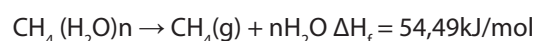
The concept of exchanging carbon dioxide with methane in deposits of natural gas hydrates is regarded as a possible way of producing methane and sequestering CO₂ (Ohgaki et al, 1996; Hirohama et al, 1996). This concept is considered as a rupture technology, to be added in the portfolio of technologies, alongside to concepts such as thermal stimulation, depressurization or chemical shifting.

4. Advantages of using CO₂ gas for replacement of CH₄ hydrate in sediment

Firstly, the method consisting to replace the methane in the methane hydrates reservoirs by CO₂ will contribute to drop the emissions of greenhouse gases.

Secondly, the hydrate structure still remains in place in the sediment, only the gas content being shifted. So, it can be assumed that the mechanical stability of the reservoir is not modified.

Lastly, the heat of CO₂ hydrates dissociation (57.98kJ/mol) is slightly higher than the heat of methane hydrates dissociation (54.49kJ/mol) (Naval Goel 2006). Therefore, the transformation of methane hydrate into carbon dioxide hydrate is practically athermic:



Where n is hydrate number (n about 6) for methane and carbon dioxide

On Fig.1, we can determine the (pressure - temperature) area where carbon dioxide can be injected for dissociation of methane hydrate. It is the region A or B in which the methane hydrate is not longer stable, but the carbon dioxide still remains stable.

Ohgaki et al. (1996) have demonstrated experimentally the possibility of producing methane gas from the hydrate by injecting carbon dioxide. They found that the mole fraction of carbon dioxide in the hydrate phase becomes higher than in the gas phase, at the equilibrium. Furthermore, Hirohama et al (1996) showed that the pressure in reservoir after methane hydrate dissociation remains approximately the same as before dissociation.

Seo et al. (2001) suggest that if the mole fraction of carbon dioxide is kept above 40% in the CO₂-CH₄ gas mixture, the concentration of carbon dioxide in the hydrate phase will be more than 90%.

5. Experimental approach

5.1. Experimental set-up

The experimental apparatus (Fig.2) is designed to measure the thermodynamic equilibrium points in the presence of gas mixture and to determine the composition of all phases (gas, liquid and hydrate). The reactor consists of a 2.5 liter autoclave reactor in which the pressure can reach up to 10MPa. The autoclave is provided with two sapphire windows (12 x 2cm) on both sides of the reactor to see inside the reactor. The reactor is equipped with a vertical stirrer with four blades. The stirring rate can vary between 0 and 600rpm. The reactor is temperature controlled by a double jacket in which is circulated a fluid at constant temperature from a cryostat HUBERT CC-250. A Pyrex cell is laid inside the reactor and filled with water containing Li⁺ as an anion tracer. The concentration of the anion is controlled in the range 0 - 10ppm by using a HPLC pump (JASCO). Temperature is monitored by 2 Pt100, at the bottom and the top of the reactor. Pressure is measured with an accuracy of 0.01MPa in the range 0 - 10MPa. A ROLSI sampler is mounted on the reactor. It allows sampling the gas online sending the sample into a gas chromatograph (GC Varian model 38002) equipped with a TCD detector and two columns PoraBOND Q and CP-Molsieve. This system allows two columns in parallel to separate a wide range of gases. The peak integration is possible with software provided by Varian Galaxie. A sampling system can retain the liquid phase through a valve. It is analyzed off-line by ion chromatography and refractometry. The data acquisition (pressure, temperature) is saved on the personal computer.

5.2. Procedure of our experiences

The experiments are realized following 4 steps:

Step 1: Injection of pure methane gas:

Initially, the reactor is evacuated by a vacuum pump. The methane or carbon dioxide gas is injected and purged three times to ensure that air is totally evacuated. Then, the reactor is loaded with the first gas (the same that has just been used for purges).

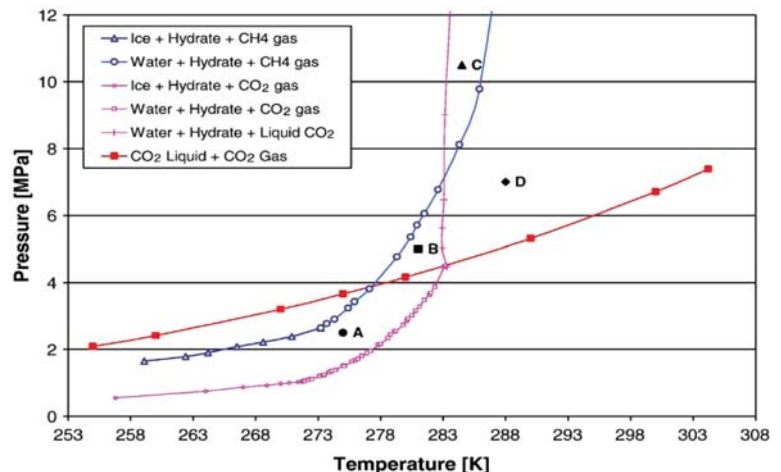


Fig.1. Equilibrium conditions of hydrate CO₂ and CH₄ (Naval Goel 2006)

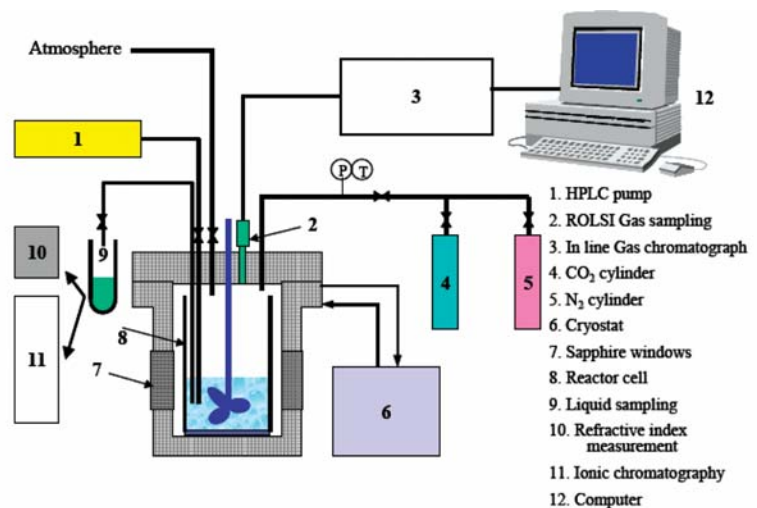


Fig.2. Experimental device

Step 2: Injection of CO₂ gas:

After the pressure is stable (to calculate the quantity of gas), another gas is added up to the required total pressure. The gas mixture is cooled and maintained at the operating temperature with the cryostat. It is stirred at a rate of approximately 400rpm.

Step 3: Injection of water for crystallization of mixed CO₂-CH₄ hydrates:

The stirrer is stopped. Water containing 10ppm of a lithium tracer is added by an HPLC pump (high pressure). The mass of the injected solution is controlled, about 800g. Pressure, temperature and gas composition are monitored. Then, the stirrer is run again. After a delay corresponding to the induction time, the crystallization starts, gas is consumed and the pressure is dropped down to the equilibrium. The crystallization is occurring during hours and days and the gas phase is sampled. The liquid

phase is also sampled and analyzed later by ion exchange chromatography.

Step 4: Dissociation of hydrates:

When the system is in equilibrium (temperature and pressure), the temperature is increased by steps of 1°C until full dissociation of hydrates (Fig.3). During each step, the pressure in the reactor increases due to the dissociation of hydrates. After complete dissociation of hydrate, the pressure in the reactor continues to increase but only in respect to the dilatation of gases and decrease of the solubility of gases. At each stage of dissociation, the gas and liquid phases are sampled and respectively analyzed by gas chromatography and ion exchange chromatography to determine the gas compositions in gas phase and the lithium concentration in the liquid phase.

5.3. Results

5.4. Calculations for gas composition in the different phases

According to mass balance of each component, the quantity of CH₄ and CO₂ in different phases can be calculated by the following equations:

$$n[\text{CH}_4]^H = n[\text{CH}_4]^{\text{initial}} - n[\text{CH}_4]^G - n[\text{CH}_4]^L \quad (1)$$

$$n[\text{CO}_2]^H = n[\text{CO}_2]^{\text{initial}} - n[\text{CO}_2]^G - n[\text{CO}_2]^L \quad (2)$$

$$n[\text{CH}_4]^G = nG.X\text{CH}_4 \text{ in reactor} \quad (3)$$

$$n[\text{CO}_2]^G = nG.X\text{CO}_2 \text{ in reactor} \quad (4)$$

$n[\text{CH}_4]^L$, $n[\text{CO}_2]^L$ are calculated by equation from Henry following the correlation of Holder (1980) where $n[\text{CH}_4]^H$; and $n[\text{CO}_2]^H$ are the moles fractions of CH₄ and CO₂ respectively in the hydrate phase; $n[\text{CH}_4]^G$; and $n[\text{CO}_2]^G$ are the moles fractions of CH₄ and CO₂ in gas phase in the reactor; $n\text{CH}_4$; released and $n\text{CO}_2$; nG is the number of moles of gas in the reactor, which is determined by equation of state; n released is the number of moles of the released gas from the reactor.

$$H_i = H_{i,Psat} \exp\left(\frac{v_i^\infty (P - P_i^{sat})}{RT}\right) \quad (5)$$

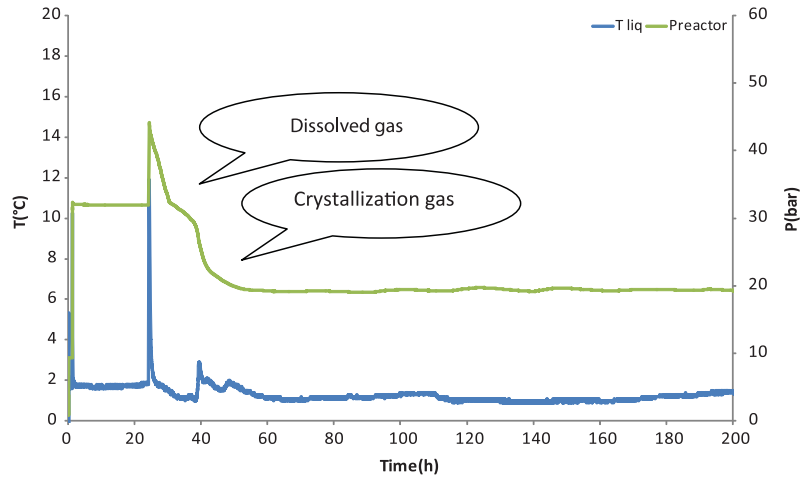


Fig.3. Evolution of pressure and temperature during the step of crystallization

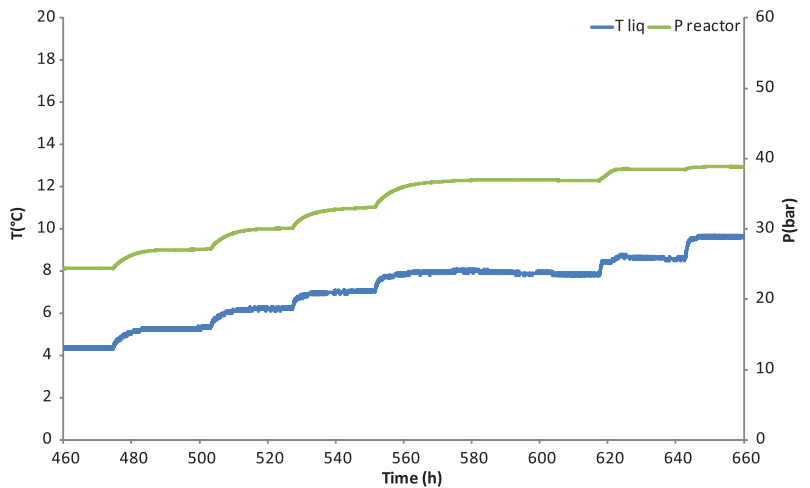


Fig.4. Evolution of pressure and temperature during the step of dissociation

Table 1. Constant for Henry constant calculation with Holder (1980)

Gas	A	B	v_i^∞ (cm ³ /mol)
CH ₄	15.826277	-1559.0631	32
CO ₂	14.283146	-2050.3269	32

$$H_{i,Psat} = \exp\left(A + \frac{B}{T}\right) \quad (6)$$

Where H_i is the Henry coefficient, A and B are constants in Table 1.

The volume of liquid in equilibrium is determined by following the concentration of a tracer (Li⁺) in the liquid phase

$$V_{eq}^L = \frac{[Li^+]_{ini} V_w^0}{[Li^+]_{eq}} \text{ and } V_w^H = V_w^0 - V_{eq}^L = V_w^0 - V_w^0 \frac{[Li^+]_{ini}}{[Li^+]_{eq}}$$

$$= V_w^0 \left(1 - \frac{[Li^+]_{ini}}{[Li^+]_{eq}}\right)$$

Where V_w^H , V_w^0 , V_{eq}^L are the volume of water in hydrate phase, initial and liquid phase at equilibrium.

A summary of steps of calculation is presented in the Fig.5.

The Fig.6 shows the phase diagram of hydrate of CO_2 - CH_4 mixture at temperature of 2.2°C . These results are compared with the model from the GasHyDyn software. The experimental results are close to the simulated values and new experiments are still under testing.

6. Conclusion

This work contributes to the long term issue to produce methane from methane hydrate bearing sediments. The method consists in injecting CO_2 in to sediments and shifting the chemical equilibrium of methane hydrate, to form carbon dioxide clathrate hydrates. So, this thematic

theme relates the topic of gas production, but also to CO_2 mitigation.

In the work, we presented experimental results about the equilibrium of CO_2 - CH_4 gas mixture. Our experiments indicate that we can form a solid in thermodynamic equilibrium with the gas mixture.

The next step is to study the kinetics of replacement of methane by carbon dioxide in the hydrate structure. The work is undergoing (Herri and Kwaterski, 2012). Currently, we start looking to model the formation of methane hydrate and replace it with the CO_2 in the reactor, depending on conditions such as temperature and pressure of the tank.

We produce a dispersion of crystals of methane hydrate in a wetting medium, with an excess of liquid water. It forms slurry. Then, these crystals are destabilized by CO_2

injection and we monitor the composition of the gas that is enriched in methane because of the dissociation of methane hydrate and formation of CO_2 - CH_4 hydrate following the equilibrium given in (Fig.6). It will allow us, after developing a suitable model to quantify the kinetics of conversion of a solid phase to another solid phase.

Subsequently, we want to build a new device which will crystallize methane hydrates in porous media, following the procedure that we have experimented (Tonnet and Herri, 2009). These hydrates are then subjected to a flow of CO_2 through the porous medium, and then we can observe the different limitations.

This technology is a new technology developed from the needs of gas industry. In our laboratory, it contributes to the development of new technologies taking advantage of the physical properties of gas hydrates.

Among the new technologies we are developing, we can also cite the CO_2 capture to recover the carbon dioxide from gas power station (Herri et al, 2011; Herri and Kwaterski, 2012; Kwaterski and Herri, 2012) or other industries such a steel making plants (Duc et al, 2005).

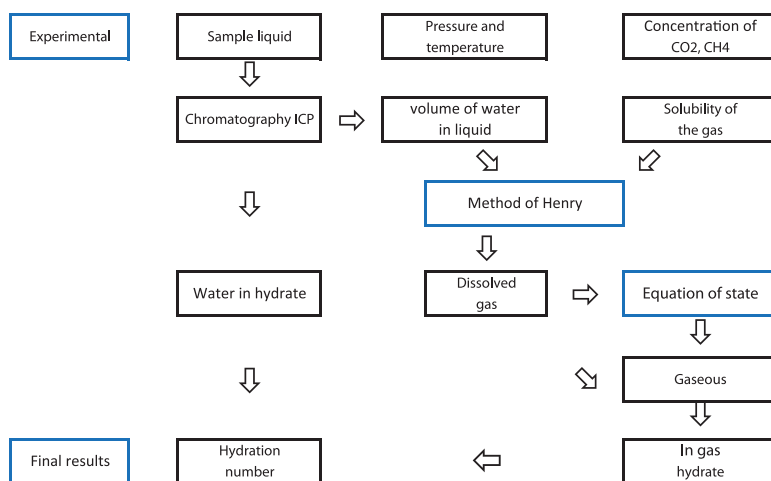


Fig.5. Treatment of data

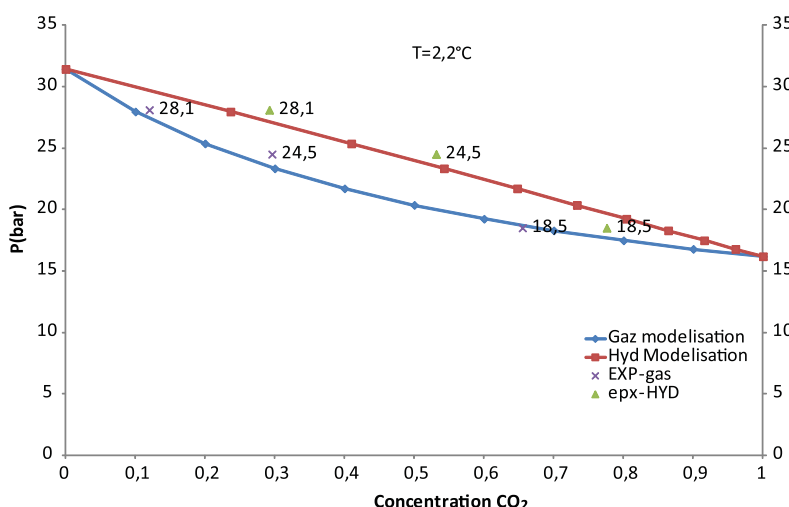


Fig.6. Phase diagram of hydrate CO_2 - CH_4 mixture at 2.2°C

We can cite also the technology consisting in storing energy under the form of a slurry of clathrate hydrate, for air condition applications (Darbouret et al, 2005; Douzet et al, 2012).

If clathrate hydrates can be used with a profitable objective, they still remain a problem in the oil industry because they can form crystals in the different facilities after extraction of the oil, especially in deep sea conditions. Our laboratory is also specialized in the flow assurance to prevent the nucleation, growth and agglomeration (Herri et al, 1999; Pic et al, 2000, 2001; Cournil and Herri, 2003, Fidel Dufour et al, 2005; Cameirao et al, 2012), and to propose solutions if a plug forms (Nguyen Hong Duc et al, 2005).

Our laboratory also specialises in the determination of physical properties of gas hydrates, such as Hamaker constant with application to the evaluation of agglomeration (Bonnefoy et al, 2005) or determination of refractive index (Herri and Gruy, 1996; Bonnefoy et al, 2005) with application to the conception of particle sizes (Herri et al, 1999).

Our competences can be applied to other domains, and we cite the extrapolation of our work concerning thermodynamics to the planet science, and the modelling of the atmospheric behavior on Mars, at very low pressure and temperature, both in the recent period (Herri and Chassefière, 2012) or in the ancient time (Chassefière et al, 2012).

So, the applications of gas hydrates concerns a great number of industries (Gas production, CO₂ mitigation, Refrigeration, flow assurance) and a great number of scientific domains (Geosciences, Industrial crystallization, Chemical Engineering, Planetary sciences), and can be probably be fruitfully applied in Vietnam (Nguyen Hong and Herri, 2006).

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Predicting the temperature/pressure dependent density of biodieselfuels

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Abstract

The purpose of this work was to develop a method for predicting temperature/pressure dependent density of biodiesel based on fatty acid ester composition. The PC-SAFT equation of state combined with a modified group contribution method was used to calculate density of mixtures of fatty acid esters. Prediction errors at atmospheric pressure were less than 0.5% for 10 multi-component mixtures of fatty acid ethylesters. Compared with experimentally measured density at 0.1 - 45MPa, the predicted densities of soybean, rapeseed, palm, mixture of soybean and rapeseed, mixture of palm and rapeseed, mixture of soybean and palm, mixture of soybean and rapeseed and palm, sunflower biodiesel were all within 1%.

Introduction

Biodiesel is a promising alternative energy resource for diesel fuel. Typically, biofuel consists of alkyl monoesters of fatty acids, obtained from vegetable oils or animal fats combined with a short-chain alcohol [1, 2]. Those esters have properties similar to ordinary diesel fuel made from crude oil and can be used in conventional diesel engines without any motorization transformation. Of the various alternate fuels under consideration, at this moment, biodiesel is the most promising alternative fuel to conventional diesel fuel (derived from fossil fuels; hereafter just "diesel") due to the following reasons [3, 4]:

- Biodiesel can be used in existing engines up to certain percentages (normally 20%) without any modification.
- Biodiesel is made entirely from vegetable sources. Therefore, biodiesel does not contain any sulfur, aromatic hydrocarbons, metals or crude oil residues.
- Biodiesel is an oxygenated fuel; emissions of carbon monoxide and soot tend to be reduced compared to conventional diesel fuel.
- Unlike fossil fuels, the use of biodiesel does not contribute to global warming as CO₂ emitted is once again absorbed by the plants grown for vegetable oil/biodiesel production. Thus CO₂ balance is maintained;

- The Occupational Safety and Health Administration classifies biodiesel as a non-flammable liquid (flash point of 160°C).

- The use of biodiesel can extend the life of diesel engines because it is more lubricating than petroleum diesel fuel.

- Biodiesel is produced from renewable vegetable oils/ animal fats and hence improves fuel or energy security and economic independence.

To optimize biodiesel manufacturing, many reported studies have built simulation models to quantify the relationship between operating conditions and process performance. For mass and energy balance simulations, it is essential to know the four fundamental thermophysical properties of the feed oil: liquid density (ρ^L), vapor pressure (P^{vap}), liquid heat capacity (C^{PL}), and heat of vaporization (ΔH^{vap}) [5 - 8].

Biodiesel fuel has to fulfil a number of quality standards. In Europe, the biodiesel fuel standards are compiled in the Norm CEN EN 14214 [9], in USA, in the ASTM D6751 [10] and in Vietnam in the TCVN 7717-07 [11]. Norms specify minimum requirements and test methods for biodiesel fuel to be used in diesel engines and for heating purposes, to increase the biodiesel fuel quality and its acceptance among consumers. Density is

an important fuel property because injection systems, pumps, and injectors must deliver an amount of fuel precisely adjusted to provide proper combustion [12]. As Tziourtzioumis and Stamatelos [13], Boudy and Seers [14] explained, from the evaluation of the effect of different fuel properties on the injection process of common rail direct-injection systems, density is the main property controlling the pressure wave in common rail systems and, subsequently, the total mass injected. Density data are required to be known to properly design reactors, distillation units and separation process, storage tanks, and process piping [15]. Knowledge and description of biodiesel densities as a function of the pressure and temperature are therefore required for a correct biodiesel formulation and a proper design and optimization of common rail engine injection systems for a precisely adjusted amount of fuel to be delivered to provide a proper combustion while minimizing NO_x emissions [16]. Knowledge of the density at varied temperature and pressure conditions is necessary in calculations of design equipment and to simulate the physico-chemical processes (they are involved in the equations of heat, mass, and momentum transfer). The density of liquids can be determined experimentally, but may be correlated and estimated by different analytical relations. These analytical expressions and models are usually based on adjustable parameters for each fluid and on the group contribution methods [17].

Rapeseed, soybean, and palm oils are the most commonly used oils to produce biodiesel although non-edible oils, such as *Jatropha*, are becoming more important [15]. The capacity to correctly predict biodiesel densities is of major relevance for a correct formulation of an adequate blend of raw materials aiming at producing biodiesel according to the required quality standards with the lowest production costs. Three main types of methods exist for estimating liquid densities of pure compounds. The first types are the methods based on the corresponding states theory, such as the Rackett equation and the Spencer and Danner method [15, 18 - 20]. These methods have, however, some disadvantages, such as the requirement of critical properties, and because they often use experimental-data-adjusted parameters, they have a limited predictive ability. The second type of method is based on mixing rules, such as Kay's [21] that allow for the estimation of a mixture density provided that the composition of the fuel and the densities of the pure compounds are known. They are only applicable to

simple mixtures with a near ideal behavior. Finally, group contribution models are another approach that only requires the chemical structure of the desired molecule to be known to estimate the thermophysical properties, such as liquid densities. The group contribution method GCVOL [22] is a predictive model that was able to provide pure fatty acid methyl ester (FAME) density descriptions within 1% deviation [23].

This article presents the results from a comprehensive evaluation of the methods for predicting liquid density of various biodiesel in function of temperature and/or pressure. The predictive capability of the modified GC-PC-SAFT model was tested against experimental data from 278 - 363K and 0.1 - 45MPa for 10 biodiesels.

PC-SAFT Equation of state (PC-SAFT EoS)

The PC-SAFT EoS has a clear physical molecular model, which assumes that the molecule is composed of chains of freely jointed spherical segments. Several intermolecular forces are considered. They are divided into different contributions, correspondingly [24]. For non-associating compounds, it consists of an ideal gas contribution, a hard-chain contribution, and a perturbation contribution which accounts for the attractive interactions. The residual Helmholtz free energy is given in terms of a perturbation expansion:

$$a = a^{\text{id}} + a^{\text{hc}} + a^{\text{disp}} + a^{\text{dipole}} \quad (1)$$

More details of PC-SAFT EoS are described clearly in the original literature [24]. PC-SAFT is applied to mixtures using the van der Waals one-fluid model [24, 25] and modified Lorentz-Berthelot mixing rules that relate the potential parameters ϵ_{ij} and σ_{ij} for cross-interactions i-j to those of self-interactions i-i and j-j:

$$\epsilon_{ij} = (1 - k_{ij}) \sqrt{\epsilon_{ii} \epsilon_{jj}} \quad (2)$$

$$\sigma_{ij} = (1 - l_{ij}) \left(\frac{\sigma_{ii} + \sigma_{jj}}{2} \right) \quad (3)$$

In many cases, pure prediction may be obtained by setting $k_{ij} = l_{ij} = 0$ [26 -28]. In this study, we will therefore retain this hypothesis here as well.

The dipole term

The a^{dipole} term refers to any contributions of the relevant contributions developed to account for polar interactions. Dipole-dipole is the most prominent electrostatic force in oxygenated compounds, such as

alkyl-esters. We consider only the dipole-dipole expressions from Gross and Vrabec (GV) [29] and from Jog and Chapman (JC) [30].

Jog and Chapman [30] developed a dipolar contribution by visualizing non-spherical polar molecules as hard-sphere chains containing both polar and non-polar segments. In this approach, the reference fluid is an equimolar mixture of non-polar and polar hard spheres, where the latter possesses a dipole vector at the center of the sphere. The thermodynamic properties of the polar hard spheres were calculated using the u-expansion [31]. Jog and Chapman showed, using computer simulation, that g^R can be approximated by the hard-sphere rdf, g^{hs} , up to a moderate dipole strength provided that the segment dipole vector is aligned perpendicularly to the line joining the center of the dipole segment to that of the adjacent segment. The dipolar term was presented as a perturbation expansion in Padé approximant (JC approach) [32]:

$$a = a_0 + a_2 \left[\frac{1}{1 - \frac{a_3}{a_2}} \right] \quad (4)$$

$$a_2^{dipole} = -\frac{2\pi N\rho}{3kT} \sum_{\alpha\beta} x_\alpha x_\beta x_{p\alpha}^\mu x_{p\beta}^\mu m_\alpha m_\beta \frac{\mu_\alpha^2 \mu_\beta^2}{d_{\alpha\beta}^3} J_{\alpha\beta}^{(6)} \quad (5)$$

$$a_3^{dipole} = \frac{32}{135} \left(\frac{14\pi}{5} \right)^{1/2} \frac{N\rho^2}{(kT)^2} \sum_{\alpha\beta\gamma} x_\alpha x_\beta x_\gamma x_{p\alpha}^\mu x_{p\beta}^\mu x_{p\gamma}^\mu m_\alpha m_\beta m_\gamma \frac{\mu_\alpha^2 \mu_\beta^2 \mu_\gamma^2}{(d_{\alpha\beta} d_{\alpha\gamma} d_{\beta\gamma})} K_{\alpha\beta\gamma} (222;333) \quad (6)$$

Where m stands for chain parameter; ρ is the number density of molecules; k is the Boltzmann constant; T is the temperature; $d_{\alpha\beta}$ is the average diameter of segment α and β , μ_α are the dipole moment of component α . $x_{p\alpha}$ refer to the fraction of polar segment in α chain of component α , whereas x_α is the mole fraction of component α . J and K are the angular pair and triplet correlation. These integrals are a function of reduced density and temperature and have the empirical form as described in [33].

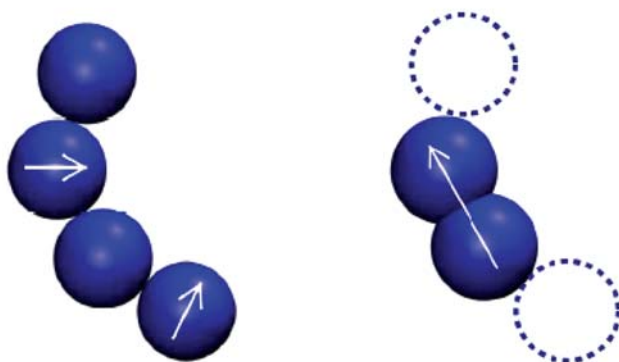


Fig.1. Orientation of the dipole moment within a chain molecule, following the JC (left) or the GV (right) approach. In the JC approach, the dipole vectors, shown as white arrows, are placed on specific segments within a chain, perpendicular to the vector connecting the centers of adjacent segments. In the GV approach, the dipole moment is stretched across a maximum of two segments, and placed along the central axis. Its position, with respect to the other non-polar segments, is irrelevant

The notion of x_p as an adjustable parameter is, however, not entirely correct. Various authors [34, 35] chose to correlate x_p by assigning a constant value to the product $m \cdot x_p$ for a particular homologous group. To determine this constant, the smallest member of the series is fitted to vapour pressure and liquid density data, with no constraints on x_p . The product $m \cdot x_p$ stemming from the final set of parameters is then held constant for the rest of the homologous group. Different authors [32, 36] observed the problem of multiple solutions when fitting a set of ϵ/k , σ , m parameters, and suggested the incorporation of a single set of binary data in the regression. Any mixture with a second component free of functionality (e.g. n-alkanes) could be used.

Such segment approach of the JC term differs from that of the GV term in that the dipolar moment is not placed along the molecular axis of the molecule. In the GV approach, the location of the stretchable dipole in the chain is not considered. This is depicted graphically in Fig. 1. The dipole segments exist site-like in a JC chain; thus the distance of closest approach of the dipole is represented. Furthermore, the segment approach also accounts for multiple dipolar functional groups. Al-Saifi et al. [37] compared the Helmholtz free energy contribution to the reduced chemical potential from the two dipolar terms, and found the JC approach to have a higher contribution among the two.

Modeling esters using a modified group contribution method

Such a thermodynamic treatment of esters requires first a definition of the chemical groups found in an ester molecule. Let us recall that the general chemical formulas of esters $RCOOR'$

where R and R' are hydrocarbon chains. In this work, we have considered only the case when R and R' were linear alkyl chains. This means that R and R' may be explicitly written as $\text{CH}_3-(\text{CH}_2)_n$ and $\text{CH}_3-(\text{CH}_2)_{n'}$ with $n, n' \geq 0$. Therefore, three different chemical groups are used in this work: CH_3 , CH_2 , and COO .

In the spirit of the GC method mentioned above, the EoS parameters of a given ester RCOOR' are computed by the following relations [38]:

$$\varepsilon = \sqrt[n^T]{(\varepsilon_{\text{CH}_2})^{n_{\text{CH}_2}} (\varepsilon_{\text{CH}_3})^{n_{\text{CH}_3}} (\varepsilon_{\text{COO}})^{n_{\text{COO}}}} \quad (7)$$

$$\sigma = \frac{\sigma_{\text{CH}_2} \cdot n_{\text{CH}_2} + \sigma_{\text{CH}_3} \cdot n_{\text{CH}_3} + \sigma_{\text{COO}} \cdot n_{\text{COO}}}{n^T} \quad (8)$$

Where n_{CH_2} , n_{CH_3} and n_{COO} are respectively the numbers of groups CH_2 , CH_3 , and COO in the ester molecule and $n^T = n_{\text{CH}_2} + n_{\text{CH}_3} + n_{\text{COO}}$ is the total number of groups in the molecule. The chain parameter m may be correlated through a simple linear correlation to the different group numbers, involving a chain contribution parameter denoted R_i for each group i .

$$m = S_{\text{CH}_2} R_{\text{CH}_2} \cdot n_{\text{CH}_2} + S_{\text{CH}_3} R_{\text{CH}_3} \cdot n_{\text{CH}_3} + S_{\text{COO}} R_{\text{COO}} \cdot n_{\text{COO}} \quad (9)$$

S_{CH_2} , S_{CH_3} , S_{COO} are "shape factor" which corresponds to the proportion of the spherical united-atom group that contributes to the properties of the molecule, in this work, S_{CH_2} , S_{COO} are unity and S_{CH_3} were reused from a previous paper [39].

As suggested by a similar approach [40] proposed to model and to make a distinction between two oxygenated isomers using the chain lengths m of the two molecules, R_{COO} is regarded as a function of the COO group position p in the ester chain, defined by $p = \min(n_R, n_{R'}) + 1$ [40]. The dipole moment was supposed to follow an empirical linear relation with $n_R - n_{R'}$ that is written for RCOOR' as:

Where μ_0 , μ_1 , and μ_2 are adjustable parameters [40].

$$\mu = \mu_0 - \mu_1 \left(1 - \frac{1}{n_R}\right) - \mu_2 \left(1 - \frac{1}{n_{R'}}\right) \quad (10)$$

Parameterization of the PC-SAFT

Depending on the form of the PC-SAFT employed, different numbers of pure component parameters must be determined for the model. To reflect real substance behaviour, the parameters are regressed to experimental data of thermodynamic properties. For non-associating substances, the chain segment m ; the segment diameter σ ; and the depth of energy well ε/k are always included

in the regression. The parameters m and σ are geometric parameters and reflect the packing extent of the molecule. Data on liquid density (ρ^L) supply information on the magnitude of these two parameters. ε/k is an attractive energetic parameter that holds molecules together. Its magnitude affects the molecules' tendency to disperse and form a vapour phase. Values of the vapour pressure (P^{sat}) are required to tune the parameter.

As with multi-parameter EoS, the parameterization of PC-SAFT is subjected to the modeler's preferences. The central theme of this work is the application of PC-SAFT to the calculation of thermodynamic properties. Therefore we devise herein a systematic procedure for tuning the model for phase equilibria purposes. The procedure outlined below can be easily modified to yield different sets of parameters adapted for alternative purposes:

- Visualize the compound. This helps identify whether the compound is associating/non-associating, polar/non-polar, and define chemical group structure;
- Compile data. As explained, experimental data on liquid densities and vapour pressures are essential, and as many data as possible should be collected from the triple point to the critical point. This ensures the parameters are applicable for the entire range of vapour-liquid coexistence.
- Eliminate unwanted data. It is useful to obtain empirical correlations for the liquid volumes and vapour pressures. A plot of the collected data and an empirical correlation on the same axes may reveal significant outliers that would otherwise mislead the regression if retained. These outliers should be removed.
- Parameter regression. Using logical initial guesses to regress the relevant parameters so as to minimize the objective function F :

$$F = 100 \sum_{Tp} \frac{1}{N_{\text{exp}, Tp}} \sum_i^{N_{\text{exp}, Tp}} \left(\frac{\theta_{Tp,i}^{\text{exp}} - \theta_{Tp,i}^{\text{cal}}}{\theta_{Tp,i}^{\text{exp}}} \right)^2 \quad (11)$$

Where Tp is the thermodynamic property to be fitted; NTp is the total number of different types of thermodynamic properties to be considered in the overall regression; $N_{\text{exp}, Tp}$ is the total number of experimental datapoints considered for thermodynamic property Tp ; and $\theta_{Tp,i}^{\text{exp/cal}}$ is the i^{th} experimental/calculated value of the thermodynamic property Tp . Only discrete experimental data are used in the regression.

- Evaluate the results. The absolute average deviation, AAD (in % unit), is calculated as following:

$$AAD_{Tp} = \frac{100}{N_{exp,Tp}} \sum_i^{N_{exp,Tp}} \left(\frac{\theta_{Tp,i}^{exp} - \theta_{Tp,i}^{cal}}{\theta_{Tp,i}^{exp}} \right) \quad (12)$$

PC-SAFT is not sufficiently high for such purpose, and over-expansion of objective function only serves to complicate the optimization routine. However, the predictions of the heat capacity (Cp) and the speed of sound (w) for some non-associating and associating compounds, whose parameters were regressed to liquid densities and vapour pressures. Even though Cp and w were not included in the regression of pure-component parameters, qualitative agreements with experimental data could still be achieved. This emphasizes the appropriateness of the choice of ρ^L and P^{sat} as target properties, as well as the physical basis of the model.

Parameters for Fatty acid methyl esters

Fatty acid methyl esters (FAME) of high molecular weights are the main products of the transesterification of triglycerides to form biodiesel components [41]. Accurate determination of thermodynamic properties such as vapour pressure (normal boiling point), density, viscosity and latent heat of vaporization are important to ensure

good fuel quality control. Nguyen Thi et al. [42] used a group-contribution SAFT (GC-SAFT) approach to model heavy esters from methyl propanoate to eicosanoate using three different versions of SAFT and the Kraska and Gubbins dipolar term. Nguyen Huynh et al. [40] later extended this work to mixtures of heavy esters, using the Jog and Chapman dipolar term. Tihic et al. [43] applied the group-contribution simplified PC-SAFT (sGCPC-SAFT) to the prediction of vapour pressures of heavy esters, and presented calculations on phase equilibria and infinite dilution activity coefficients. Pratas et al. [44] used CPA EoS to predict the high-pressure density data of pure FAMES and biodiesels. As far as the Perturbed-Chain form of the SAFT EoS is concerned, the various sources proceeded to present similar errors in predicting vapour pressures, ranging from 1% to as high as 40% deviations. While the different approaches adopted by the above sources make them not strictly comparable, most highlighted the importance of experimental data to improve the predictability of their models.

The objective in this work is to present parameters (predict) for FAME from methyl caprate ($C_{11}H_{22}O_2$) to methyl lignocerate ($C_{25}H_{50}O_2$), which could be used with the PC-SAFT EoS. There is a striking lack of thermodynamic data

Table 1. Relative deviations on vapor pressures and saturated liquid volumes of the regression database compounds (accepted data in DIPPR[50])

Compounds	Formular	Npt.	T _{rang} (K)	AAD P ^{sat} (%)	Npt.	T _{rang} (K)	AAD ρ^{liq} (%)
Alkyl acetate (CCOOR')							
Ethyl acetate	CCOOC ₂	16	233 - 522	2.79	13	273 - 503	5.89
Propyl acetate	CCOOC ₃	14	273 - 543	3.38	14	273 - 533	2.91
Butyl acetate	CCOOC ₄	8	326 - 410	2.96	12	273 - 393	0.25
Pentyl acetate	CCOOC ₅	12	281 - 599	4.40	12	273 - 417	0.71
Hexyl acetate	CCOOC ₆	7	304 - 441	2.33	10	273 - 363	1.01
Heptyl acetate	CCOOC ₇	10	349-462	3.41	5	273 - 303	1.06
Octyl acetate	CCOOC ₈	8	334 - 484	6.39	7	293 - 368	1.22
Nonyl acetate	CCOOC ₉	11	293 - 661	16.95	2	288 - 298	1.02
Decyl acetate	CCOOC ₁₀	9	348 - 518	11.18	6	293 - 368	1.04
Methyl ester (RCOOC)							
Methyl propanoate	C ₂ COOC	29	253 - 530	1.13			
Methyl butanoate	C ₃ COOC	10	293 - 313	2.72			-
Methyl pentanoate	C ₄ COOC	7	293 - 328	3.17			-
Methyl hexanoate	C ₅ COOC	8	297 - 333	5.05			-
Methyl heptanoate	C ₆ COOC	8	310 - 340	1.29			-
Methyl octanoate	C ₇ COOC	7	312 - 348	5.85			-
Methyl nonanoate	C ₈ COOC	10	308 - 353	3.45			-
Methyl decanoate	C ₉ COOC	11	310 - 351	4.89			-
Methyl Undecanoate	C ₁₀ COOC	7	331 - 351	1.13			-

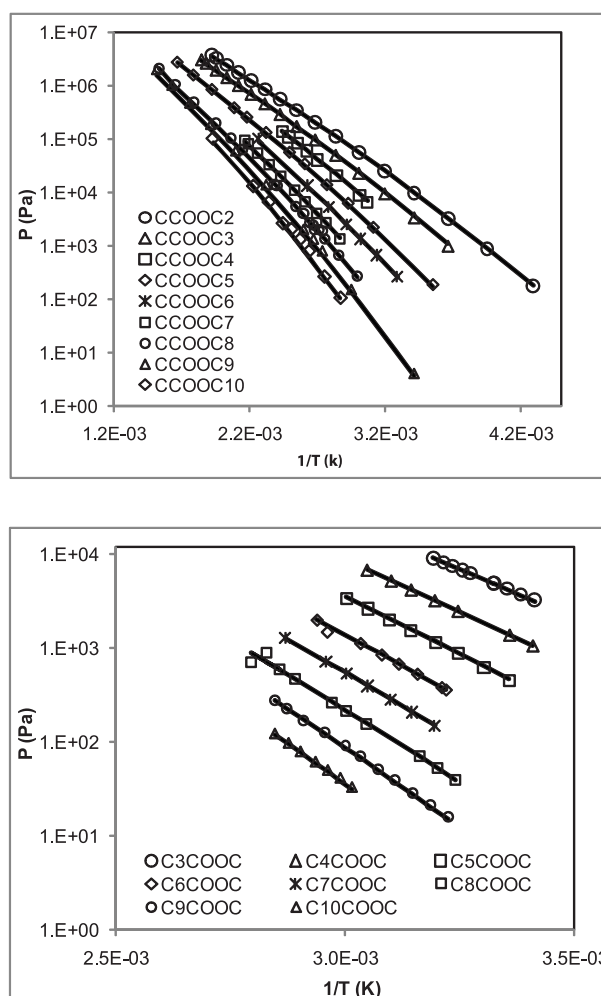


Fig. 2. Vapor pressure of the FAME ester. The symbols represent the experimental data [50], while the continuous curves correspond to the mGC-PC-SAFT description with the parameters estimated in this work

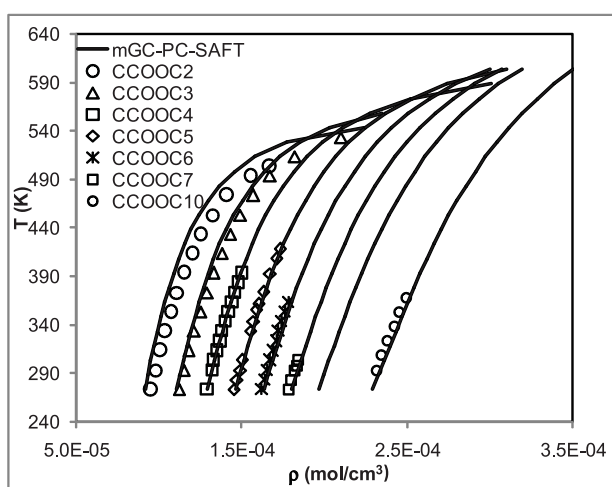


Fig. 3. Saturated liquid densities of the FAME esters. The symbols represent the experimental data [50], while the continuous curves correspond to the mGC-PC-SAFT description with the parameters estimated in this work

for FAME (an overview can be found at <http://www.ddbst.com/files/ddbsp/DDBSP-Biodiesel-2006.pdf>) and most of the better quality data on FAME vapour pressures are believed to be from Scott et al. [45], Rose and Supina [46], and van Genderen et al. [47]. The number of data points decrease with the increasing number of carbon atoms, due to difficulties in precise measurements of increasingly low pressures (e.g. the vapour pressure of methyl stearate at 316K is 9.96mPa [47]). Liquid density data can be found in the work of Pratas et al. [23, 48, 49].

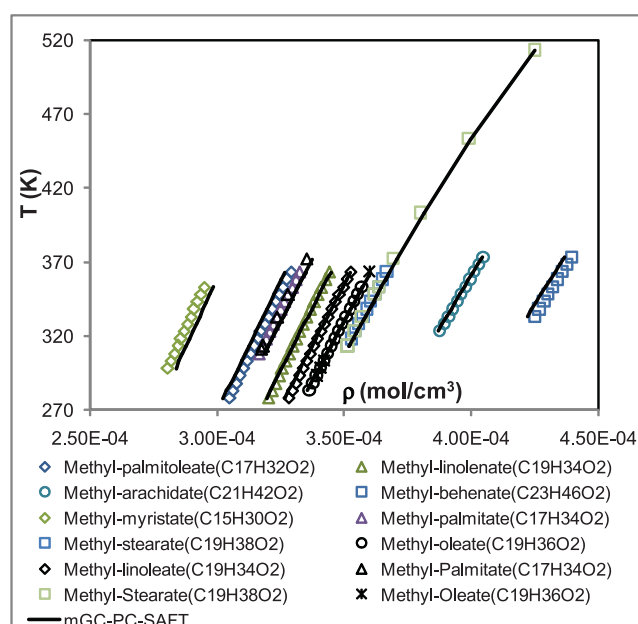
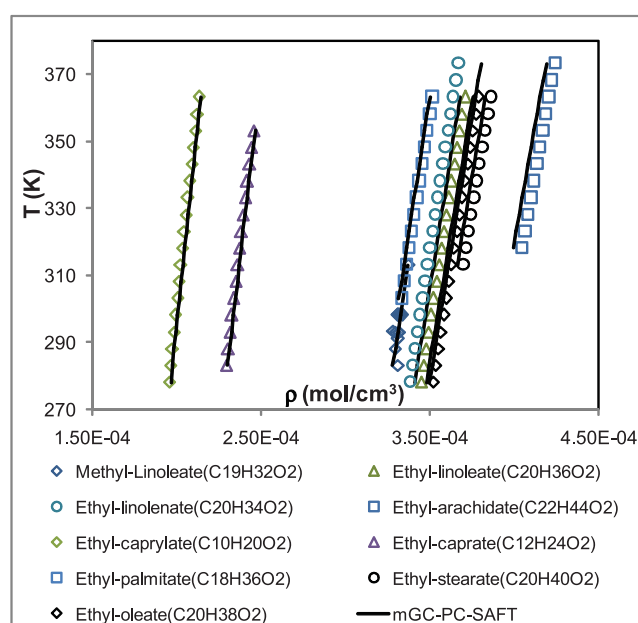
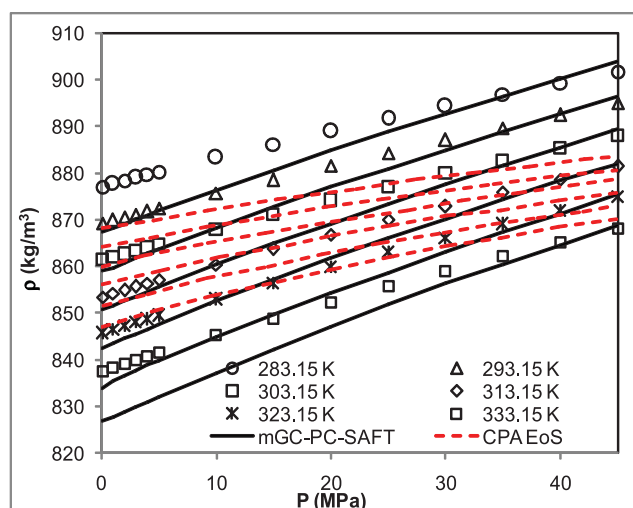


Fig. 4. Prediction of liquid density of alkyl esters series. The symbols represent the experimental data [23, 50], while the continuous curves correspond to the mGC-PC-SAFT prediction

Table 2. Prediction results of liquid density of some heavy esters. Experimental data are taken from [23, 50]

Compounds	T _{rang} (K)	$\rho_{\min}$ (mol/cm ³)	$\rho_{\max}$ (mol/cm ³)	AAD (%)	Npt
Methyl-caprylate (C ₉ H ₁₈ O ₂)	283 - 353	1.79E-04	1.92E-04	2.20	15
Ethyl-caprylate (C ₁₀ H ₂₀ O ₂)	278 - 363	1.96E-04	2.14E-04	0.58	18
Methyl-caprate (C ₁₁ H ₂₂ O ₂)	278 - 363	2.11E-04	2.29E-04	1.93	18
Ethyl-caprate (C ₁₂ H ₂₄ O ₂)	283 - 353	2.30E-04	2.46E-04	0.42	15
Methyl-laurate (C ₁₃ H ₂₆ O ₂)	283 - 353	2.44E-04	2.61E-04	1.59	15
Methyl-myristate (C ₁₅ H ₃₀ O ₂)	298 - 353	2.81E-04	2.95E-04	1.17	12
Methyl-palmitoleate (C ₁₇ H ₃₂ O ₂)	278 - 363	3.05E-04	3.29E-04	0.67	18
Methyl-palmitate (C ₁₇ H ₃₄ O ₂)	308 - 363	3.17E-04	3.32E-04	0.71	12
Ethyl-palmitate (C ₁₈ H ₃₆ O ₂)	303 - 363	3.34E-04	3.52E-04	0.51	13
Methyl-linolenate (C ₁₉ H ₃₄ O ₂)	278 - 363	3.20E-04	3.44E-04	0.12	18
Methyl-linoleate (C ₁₉ H ₃₄ O ₂)	283 - 313	3.31E-04	3.38E-04	0.37	13
Methyl-oleate (C ₁₉ H ₃₆ O ₂)	283 - 353	3.36E-04	3.57E-04	0.10	15
Methyl stearate (C ₁₉ H ₃₈ O ₂)	313 - 513	3.51E-04	4.25E-04	0.24	10
Ethyl-linolenate (C ₂₀ H ₃₄ O ₂)	278 - 373	3.39E-04	3.67E-04	3.50	20
Ethyl-linoleate (C ₂₀ H ₃₆ O ₂)	278 - 363	3.45E-04	3.71E-04	0.91	18
Ethyl-stearate (C ₂₀ H ₄₀ O ₂)	313 - 363	3.70E-04	3.86E-04	0.90	11
Methyl-arachidate (C ₂₁ H ₄₂ O ₂)	323 - 373	3.88E-04	4.05E-04	0.18	11
Ethyl-arachidate (C ₂₂ H ₄₄ O ₂)	318 - 373	4.05E-04	4.24E-04	1.26	12
Methyl-erucate (C ₂₃ H ₄₄ O ₂)	278 - 363	4.00E-04	4.29E-04	0.85	18
Methyl-behenate (C ₂₃ H ₄₆ O ₂)	333 - 373	4.25E-04	4.39E-04	0.68	9
Methyl-lignocerate (C ₂₅ H ₅₀ O ₂)	338 - 373	4.61E-04	4.74E-04	1.20	8


Fig. 5. Density isotherms for methyl laurate. Comparison between two models, (—) predicted by mGC-PC-SAFT (this work); (---) computed with CPA EoS [44]. Data taken from ref [44]

The relative deviations obtained on the vapor pressures and saturated liquid phase volumes for pure FAME are presented in Table 1. The T-P and T- ρ diagrams are given in Fig. 2. From this table, it appears that the mGC-PC-SAFT provide generally reasonable and comparable

correlations of pure esters VLE. The agreement between experimental and calculated vapor pressure is generally lower than 5% i.e. slightly better than the one obtained in previous work [40, 42].

PpT predictions results for pure heavy esters

PpT calculations of heavier compounds using the modified group contribution PC-SAFT without adjustment on experimental data is a pertinent test of the predictive character of the approach. The results obtained on several representative compounds are displayed in Figs. 4 - 5 and Table 2 along with those obtained by other methods for comparison.

For the prediction, very good agreements can be seen between the model and the experimental data for esters up to ethyl-arachidate (< 2%). The predictions are poorer for Ethyl-linolenate (C₂₀H₃₄O₂) (3.5%), but in fact they are quite reasonable if compared to those given by other predictive methods [40].

The comparison with other methods is not very easy since the different authors use different strategies

Table 3. Compositions of the Biodiesels Studied, in mass percentage. (S: soybean biodiesel, R: rapeseed biodiesel, P: palm biodiesel, SR: soybean + rapeseed biodiesel, PR: palm + rapeseed biodiesel, SP: soybean + palm biodiesel, SRP: soybean + rapeseed + palm biodiesel, Sf: sunflower biodiesel, GP and SoyA: soybean + rapeseed biodiesel)

Methyl-esters	Chemical formular	S	R	P	SR	PR	SP	SRP	Sf	GP	SoyA
C ₁₀	C ₁₁ H ₂₂ O ₂		0.01	0.03		0.02	0.01	0.01			
C ₁₂	C ₁₃ H ₂₆ O ₂		0.04	0.24	0.03	0.2	0.18	0.14	0.02	0.02	
C ₁₄	C ₁₅ H ₃₀ O ₂	0.07	0.07	0.57	0.09	0.54	0.01	0.38	0.07	0.13	
C ₁₆	C ₁₇ H ₃₄ O ₂	10.76	5.22	42.45	8.9	23.09	25.56	18.97	6.4	10.57	17.04
C ₁₆ :1	C ₁₇ H ₃₂ O ₂	0.07	0.2	0.13	0.15	0.17	0.11	0.14	0.09	0.13	
C ₁₈	C ₁₉ H ₃₈ O ₂	3.94	1.62	4.02	2.76	3.02	4.04	3.28	4.22	2.66	3.73
C ₁₈ :1	C ₁₉ H ₃₆ O ₂	22.96	62.11	41.92	41.82	52.92	33.13	42.51	23.9	41.05	28.63
C ₁₈ :2	C ₁₉ H ₃₄ O ₂	53.53	21.07	9.8	37.51	15.47	31.72	27.93	64.16	36.67	50.45
C ₁₈ :3	C ₁₉ H ₃₂ O ₂	7.02	6.95	0.09	7.02	3.08	3.58	4.66	0.12	7.1	
C ₂₀	C ₂₁ H ₄₂ O ₂	0.38	0.6	0.36	0.46	0.49	0.39	0.45	0.03	0.44	
C ₂₀ :1	C ₂₁ H ₄₀ O ₂	0.23	1.35	0.15	0.68	0.67	0.2	0.52	0.15	0.67	
C ₂₂	C ₂₂ H ₄₄ O ₂	0.8	0.35	0.09	0.46	0.24	0.32	0.33	0.76	0.45	
C ₂₂ :1	C ₂₂ H ₄₂ O ₂	0.24	0.19	0	0.12	0.09	0.12	0.14	0.08	0.12	
C ₂₄	C ₂₄ H ₄₈ O ₂		0.22	0.15			0.63	0.53			
Total		100	100	100	100	100	100	100	100	100	100

Table 4. Absolute Average Deviation between the measured density of biodiesel mixtures over the Temperature Range (278.15 to 363.15) K and those estimated by GCVOL Extension to High Pressures Models and comparing with the predicted results obtained by mGC-PC-SAFT. Experimental data are taken from ref. [49, 52 - 54]

Biodiesel mixture	T (K)	ρ (kg/ m ³)	GCVOL	mGC-PC-SAFT
S	278 - 363	832 - 894	0.52	0.23
R	278 - 363	831 - 893	0.74	0.43
P	278 - 363	823 - 893	0.47	0.53
SR	278 - 363	831 - 890	0.40	0.23
RP	278 - 363	827 - 890	0.30	0.50
SP	278 - 363	827 - 895	0.29	0.30
SRP	278 - 363	828 - 892	0.32	0.32
Sf	283 - 363	832 - 888	0.23	0.20
GP	283 - 363	830 - 888	-	0.11
SoyA	283 - 353	837 - 885	-	0.20

for group parameters regression on more or less wide compounds databases with or without mixtures and for different target systems, or apply their methods to compounds other than those investigated here, or give average deviations for data sets and data ranges different from those used in this study, or do not always give details on the database so true prediction cannot be distinguished from correlation.

As a matter of fact, the mGC-PC-SAFT deviations increase slightly with chain length but so do the deviations of the usual method which represent the best fit to the data with the given equation. It may be amazing

that in some cases, group contribution may give better liquid volume results than the direct fit of data [38]. But if one is reminded that both pressures and volumes are used for the fit, there is no contradiction, since the GC pressure deviations are greater and so are the overall deviations.

At least in the case of the work of Pratas et al. [44] was possible to give deviations for the liquid density on the same temperature and pressure ranges as a basis

for comparison on methyl-laurate, methyl-oleate and methyl-myristate (Fig. 5) and Table 5, mGC-PC-SAFT gives slightly better prediction than CPA EoS. The deviations may however appear slightly larger in the low pressure region, but in fact they are quite reasonable (maximum relative derivation is 1.94%) if compared to those given by other predictive methods [23, 51].

Biodiesel fuels PpT Prediction results and discussion

Here, pure predictions of liquid density of biodiesel (multi-component mixture) were made, which means that no binary interaction parameters were used

Table 5. Absolute Average Deviation for Biodiesel and Methyl Ester Densities at High Pressures Calculated with the CPA EoS and predicted with mGC-PC-SAFT. Experimental data are taken from ref. [44]

Component/ Biodiesel mixture	AAD %		
	CPA EoS		mGC-PC-SAFT
	$\rho(0.1 - 45 \text{ MPa})^*$	$\rho(0.1 - 45 \text{ MPa})^{**}$	$\rho(0.1 - 45 \text{ MPa})^{***}$
methyl-laurate	4.47	0.59	0.68
methyl-myristate	5.86	0.99	0.32
methyl-oleate	3.24	0.84	1.25
biodiesel S	-	0.79	0.43
biodiesel R	-	2.51	0.78
biodiesel P	-	1.13	0.50
biodiesel RP	-	1.07	0.43
biodiesel SR	-	0.82	0.42
biodiesel SP	-	1.25	0.43
biodiesel SRP	-	0.89	0.44

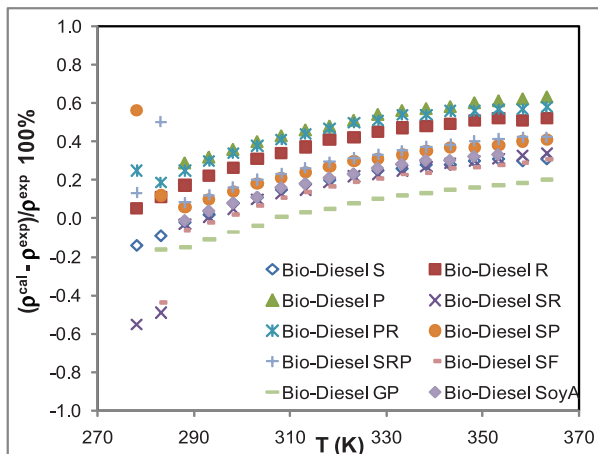


Fig.7. Absolute average deviation between experimental and predicted densities as a function of the temperature using mGC-PC-SAFT

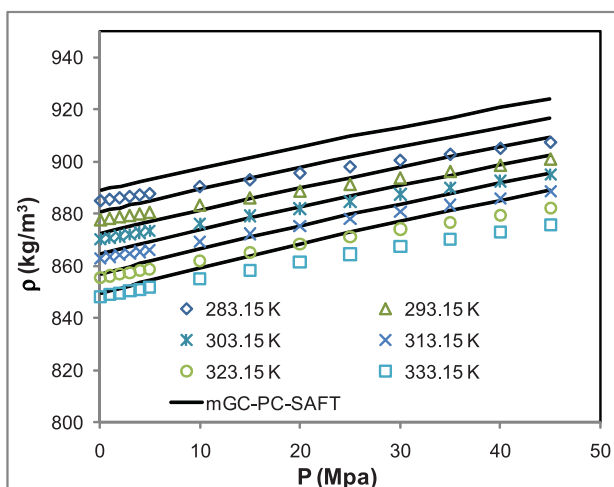
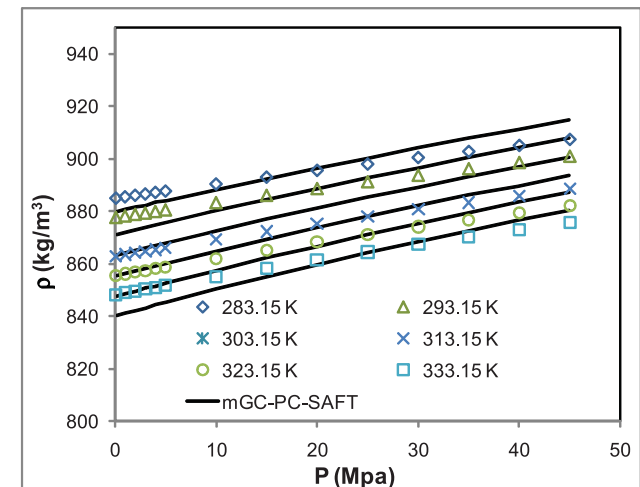


Fig.8. Density isotherms for rapeseed biodiesel (left) and palm biodiesel (right). The symbols represent the experimental data, while the continuous curves correspond to the mGC-PC-SAFT prediction

(*) with FAME CPA pure compound parameters from correlations; (**) with FAME CPA pure compound parameters correlated from pure component data. (***) pure prediction results.

($k_{ij} = l_{ij} = 0$). Various classes of biodiesel were investigated to test the validity of mGC-PC-SAFT applied to esters mixtures.

Table 3 reports methyl ester compositions for the biodiesels selected for this work. This information is of major importance because the fatty acid ester profiles of biodiesels determine their chemical and physical properties, such as densities [49].

To study the predictive ability of the mGC-PC-SAFT, the AAD for the predicted densities for each biodiesel were estimated according to equation 12. The AAD for each biodiesel studied are reported in Table 4 and 5, while the AAD of the individual data points for the 10 biodiesel samples are shown in Fig.7.

Detailed prediction results of 10 bio-diesel mixtures at atmospheric pressure are reported in Table 4 and prediction results of liquid density for 3 pure heavy methyl-esters and 7 bio-diesel mixtures at 0.1 - 45 MPa are grouped in Table 5. Very good predictions were obtained with mGC-PC-SAFT, with an AAD of about 0.50%, except in the case of methyl-oleate, unsaturated alkyl-ester. No significant differences between the results obtained with the GCVOL and mGC-PC-SAFT are observed (Table 4),

which may come as a surprise but can easily be justified by the similarity of the compounds in nature and size present in the biodiesels, resulting in similar concentration values regardless of the units adopted, resulting in a marginal

impact on the prediction (Fig.7).

The AAD for each biodiesel studied are reported in Table 4, while the relative deviation of the individual data points for the 10 biodiesel samples are shown on Fig.7.

Results from Pratas et al. [44] used CPA EoS to compute liquid density of biodiesel at high pressure showed in Fig.9 indicate that CPA EoS has a poorer performance for heavy ester and biodiesels at high pressure and high temperature, such as soybean biodiesel (Fig.9).

In most cases (Figs.8 - 11), mGC-PC-SAFT tends to over-predict mixture's density values at higher pressures (approach to the critical zone) and under-predict at low pressure region, this was the conclusion in very recent work by Burgess et al. [55] for PC-SAFT equation of state. Moreover, the pure-component mGC-PC-SAFT parameters of heavy compounds are predicted using the equations 7 - 10, belong to their chemical structure, that might effect the model's accuracy (the derivations are however smaller than 1%, Fig. 7). Although a correction term can be applied

to the ε/k parameter to make high pressure high temperature (HTHP) PC-SAFT pure-component density predictions, only slightly inferior to predictions with the original PC-SAFT parameters, but vapor-liquid equilibrium predictions with the original PC-SAFT parameters are clearly superior to predictions made with the HTHP parameters [55].

It was shown that representation of mixtures PTxy and pPT can be improved if the binary interaction parameters are taken into account [35, 56], for the sake of simplicity, all zero binary interaction parameters were assumed here, but remain acceptable results.

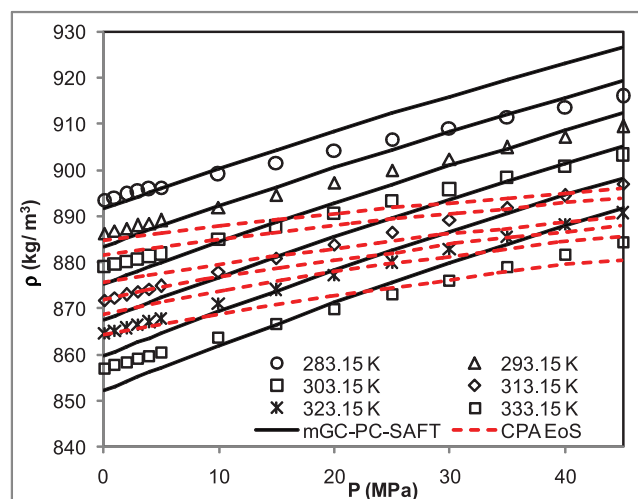


Fig.9. Density isotherms for soybean biodiesel. Comparison between two models, (—) predicted by mGC-PC-SAFT; (---) computed with CPA EoS [44]. Data taken from ref. [44]

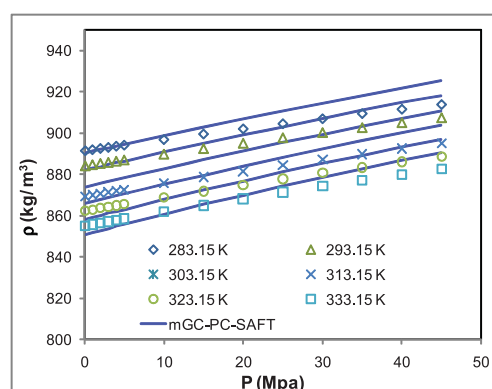
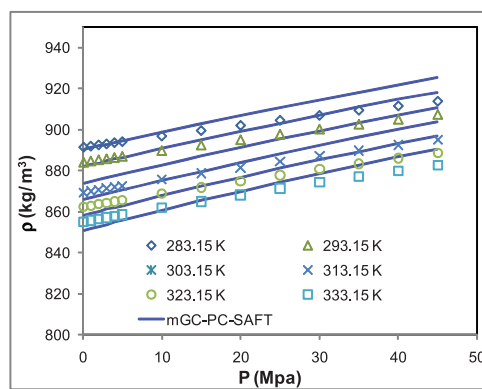


Fig.10. Density isotherms for soybean + rapeseed biodiesel (left) and rapeseed + palm biodiesel (right). The symbols represent the experimental data, while the continuous curves correspond to the mGC-PC-SAFT prediction. Data taken from ref. [44]

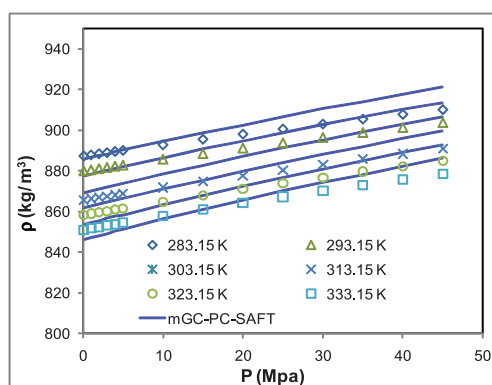
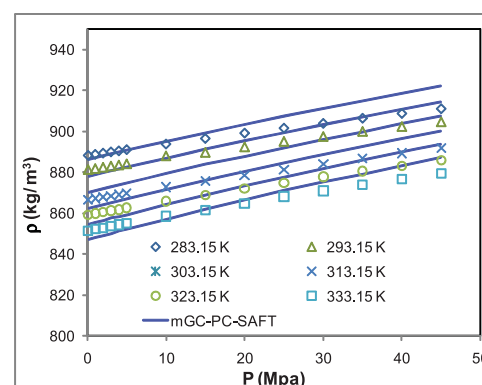


Fig.11. Density isotherms for soybean + palm biodiesel (left) and soybean + rapeseed + palm biodiesel (right). The symbols represent the experimental data, while the continuous curves correspond to the mGC-PC-SAFT prediction. Data taken from ref. [44]

Conclusions

PpT at atmospheric pressure and very high pressure of 10 biodiesel mixtures were predicted with mGC-PC-SAFT. Along with chemical group parameters determined from the PVT data of 10 first components of the alkyl-esters series, PpT densities were used to predict biodiesel densities based on information of their FAME compositions. It was shown that mGC-PC-SAFT is able to predict the liquid density of both pure heavy alkyl-esters and biodiesel with less than 2% deviation in general. In particular, mGC-PC-SAFT provides an uncertainty that is close to the experimental uncertainties of the experimental data and can thus be an interesting tool for the design of biofuels.

Two different modeling approaches were used to compare the prediction performance: the CPA EoS and mGC-PC-SAFT developed in this work. The first method presented an AAD slightly more important than that obtained with mGC-PC-SAFT, the modified GC combined with the PC-SAFT EoS was shown to predict biodiesel temperature and pressure dependent density with an OAAD of 1% while also providing information concerning the phase equilibria of the biodiesel systems. These results clearly showed that, provided that the biodiesel FAME composition is known, the predictive methods investigated here can be used to predict liquid density of biodiesel fuels in a wide range of temperatures and pressures.

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Effect of feedstock properties on the performance of ZSM-5 additive in catalytic cracking reaction

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 Nguyen Huu Trung, Dao Thi Thanh Xuan, Nguyen Hoai Thu
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Abstract

In this study, we present our recent laboratory experimental results regarding the application of ZSM-5 additive in catalytic cracking reactions. Our results show that the nature of feedstock significantly influences the performance of ZSM-5. For paraffinic feedstock, ZSM-5 additive not only increases propylene yield and gasoline octane but also improves the bottom cracking ability of Fluid Catalytic Cracking (FCC) catalysts. The conversion of paraffinic feedstock could increase up to 10wt% while that of aromatic feedstock remains almost unchanged upon the addition of ZSM-5 additive to the FCC catalyst. Mixing 5wt% of ZSM-5 additive with the FCC catalyst also results in increased propylene yields of 13wt% and 8wt% for paraffinic and aromatic feedstock, respectively. Our results can serve as guidance for refineries to flexibly control product yields by adjusting the processed feedstock or the amount of ZSM-5 additive used in the FCC unit.

Introduction

Propylene is one of the key products of refineries, particularly for those which integrate petrochemical plants such as a polypropylene (PP) plant. Due to the decline of crude oil resources, refineries are now facing the challenge of adapting their operation to a variety of feedstocks in which assuring a stable supply for downstream petrochemical plants such as the PP plant is a key issue. On the other hand, the continuous change in market demand also requires refineries to have certain operating flexibilities in order to maximize their profit. For example, depending on the relative prices of their main products such as gasoline, diesel, and propylene in the market, refiners often have to adjust the product slate to maximize the margin. Therefore, a flexible solution to adjust those product yields is of vital importance for refineries nowadays. Fig.1 shows the changing relative prices of the main refining products in the period of 2008 - 2011.

In order to adjust the propylene yields, it is quite common that ZSM-5 additive for catalyst is applied in FCC units, from which most of propylene in the refinery is produced [1]. ZSM-5 is a small pore (5 - 6Å) and high Si/Al (30 - 200) zeolite compared to those of Y zeolite (7 - 8Å

pore and Si/Al of 3 - 6). As a result, ZSM-5 selectively cracks the gasoline hydrocarbon (C5 - C12) to light olefins such as propylene and butene [2]. On the other hand, ZSM-5 also facilitates the isomerization of straight olefin to branched olefin in the gasoline fraction. The resulting effect is the improvement of light olefin yields and of gasoline octane at the expense of gasoline yield [3]. However, the effectiveness of ZSM-5 is largely dependent on the feedstock nature and the applied concentration. Therefore, in this study, we investigated the effect of feedstock properties and ZSM-5

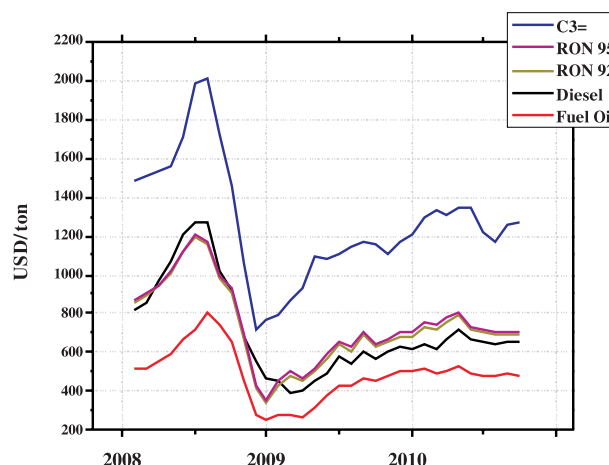


Fig.1. Relative price of different refining products in the period of 2008 - 2011

additive concentration on the product yields of catalytic cracking reactions. Our results can serve as guidance for refineries to flexibly control product yields by adjusting the processed feedstock or the amount of ZSM-5 additive used in FCC units.

Experiment

FCC catalyst and ZSM-5 additive samples are commercial products obtained from Grace Davison. The feedstocks were obtained by distillation of different commercial crude oils, from which the residue fraction (370°C+) was collected. The main properties of the FCC catalyst, ZSM-5 additive and feedstocks are shown in Table 1 and 2, respectively. Four feedstocks used in this study show different properties ranging from very paraffinic (AR1, AR2) to aromatic in nature (VGO2) as can be seen by some main properties such as aniline point and wax content.

The FCC catalyst and ZSM-5 additive were separately steam deactivated for 12 hours at 816°C prior to the cracking experiment. The properties of deactivated catalyst and ZSM-5 additive are shown in Table 3. For the cracking experiments, the FCC catalyst/ZSM-5 blends (~ 10g each) were prepared by mechanical mixing of deactivated FCC catalyst and ZSM-5 additive. The concentration of ZSM-5 in the blend was varied between

0 - 20wt% by changing the amount of ZSM-5 additive in the mixture.

Cracking experiments were performed by a fixed bed short contact time Micro Activity Test (SCT-MAT) designed and built by Grace Davison. All experiments were performed at the temperature of 560°C and the same catalyst/oil ratio with the amount of feed and time-on-stream were kept constant at 1.75g and 12s, respectively. Gaseous cracking products were analyzed by Refinery Gas Analysis Gas Chromatography (GC RGA) according to ASTM D-1945-3 standard, whereas Simulated Distillation Gas Chromatography (GC SIMDIS) and carbon analyzer were used for the liquid fraction and for coke analysis according to ASTM D-2887 and ASTM E-1915 standards, respectively. The gasoline octane was calculated from the detailed hydrocarbon analysis (DHA) performed by Gas Chromatography (GC DHA). The conversion is defined as:

Conversion = 100% - LCO (%) - HCO (%) where:

LCO is Light Cycle Oil, which is the liquid fraction with the boiling point in the range from 216 - 360°C;

HCO is Heavy Cycle Oil, which is the liquid fraction with the boiling point above 360°C.

Results and Discussion

The effects of ZSM-5 concentration on the propylene yield in cracking products and the conversion of 4 different FCC feedstocks are shown in Fig. 2 and 3, respectively. It is clear that upon the addition of ZSM-5 to the FCC catalyst, a large increase of propylene yield is observed for all feedstocks. The maximum increase is obtained at the ZSM-5 concentration of 5wt%, at which propylene yield increases by 13wt% for paraffinic feedstocks (AR1, AR2) and 8wt% for aromatic feedstock (VGO2). The higher increase of propylene yield for paraffinic feedstock is due to the fact that the gasoline fraction in the cracking products of paraffinic feedstock contains higher olefin content (42%) compared to that (23.6%) of aromatic feedstock as shown in Table 3. Since the cracking rate of olefin on ZSM-5

Table 1. FCC catalyst and ZSM-5 additive properties

Catalyst	FCC catalyst	ZSM-5 additive
Zeolite surface area, m ² /g	131.22	136.59
Matrix surface area, m ² /g	116.06	22.97
P ₂ O ₅ , %wt	-	8.88
RE ₂ O ₃ , %wt	0.99	-
Al ₂ O ₃ , %wt	56.35	24.02
Unit cell size, Å	24.57	-
ZSM-5, wt%	-	50.00
Pore volume, cc/g	0.25	0.09
Average particle size, µm	62.80	77.90
Attrition Index	4.85	1.20

Table 2. Feedstock properties

Feedstock	VGO 1	VGO 2	AR 1	AR 2
Density at 15°C (g/ml)	0.8983	0.9104	0.9158	0.9176
API°	25.90	23.80	22.90	22.60
Conradson carbon, wt%	0.06	0.23	4.37	2.03
Wax, wt%	24.29	13.13	35.60	42.80
Aniline point, °C	97.00	86.00	121.40	118.60

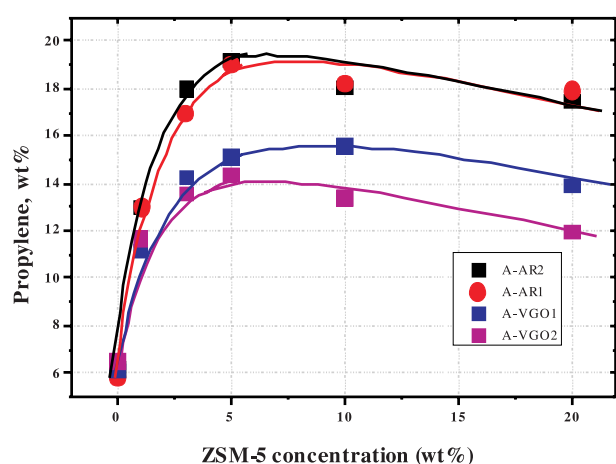


Fig.2. Propylene yield in cracking products of different FCC feedstocks as a function of ZSM-5 additive concentration in FCC catalyst/ZSM-5 blend

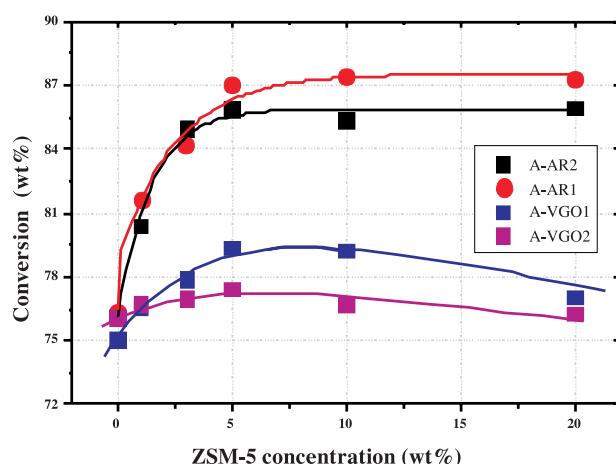


Fig.3. Conversion of different FCC feedstocks as a function of ZSM-5 additive concentration in FCC catalyst/ZSM-5 blend

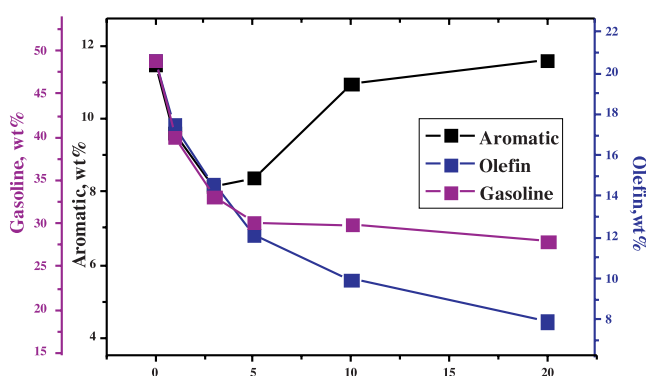


Fig.4. Gasoline aromatic and olefin yields (AR2 feedstock) as a function of ZSM-5 additive concentration in FCC/ZSM-5 blend

is faster than the other hydrocarbon types, this leads to a higher increase of propylene yield [4, 5]. At the ZSM-5 concentration higher than 5wt%, the propylene yields

start decreasing due to other competing reactions on ZSM-5 such as oligomerization or aromatization of propylene. Both oligomerization and aromatization of light olefin on ZSM-5 catalyst have been observed, however, the oligomerization is facilitated at high pressure and low temperature while the latter is favored at low pressure and high temperature. At the reaction temperature of 560°C in this case, therefore, aromatization is much more favorable than oligomerization. This is supported by the fact that the aromatic content in the gasoline fraction increases quickly when the ZSM-5 concentration exceeds 5wt% as shown in Fig.4.

The effect of ZSM-5 on the conversion also depends on the nature of the feedstock. As shown in Fig.3, the conversion of paraffinic feedstock (AR2) could increase up to 10wt% at ZSM-5 concentration of 5wt%, while that of aromatic feedstock (VGO2) remains almost unchanged upon addition of ZSM-5 additive to the FCC catalyst. In the ZSM-5 concentration range between 5 - 20wt%, the conversion of paraffinic feedstock remains constant, whereas that of aromatic feedstock starts decreasing. The increase of conversion upon addition of ZSM-5 to FCC catalyst is a surprising result since it is usually believed that ZSM-5 does not affect the conversion in the cracking reaction due to its small pore structure which prevents the large hydrocarbon molecules in LCO, HCO fraction from diffusing into the pore and reaching the reactive sites. This can be seen in Fig. 6; as the ZSM-5 concentration increases, the gasoline yield decreases quickly while there is a slight decrease in LCO and HCO yields. The HCO yield starts increasing at the ZSM-5 concentration of 3wt% due to the diluted active matrix content in the catalyst mixture at increasing ZSM-5 concentration, which leads to a lower bottom cracking ability. In the other words, for aromatic feedstock, the reactivity on ZSM-5 is in the order: Gasoline > LCO > HCO. The LCO and HCO fraction of aromatic feedstock contains mainly the aromatic hydrocarbon, which is too large to get into the pore of ZSM-5.

On the other hand, the order of reactivity on ZSM-5 of paraffinic feedstock is quite different (HCO > LCO ≈ Gasoline) as shown in Fig. 5. Here the result indicates that the HCO fraction is consumed more rapidly than the Gasoline and LCO fractions as ZSM-5 concentration increases. As a result, a large increase of conversion is observed for paraffinic feedstock upon addition of ZSM-5 to FCC catalyst. This opposite effect observed on paraffinic feedstock is due to the fact that the HCO

fraction of paraffinic feedstock contains a high amount of long, straight chain paraffins with small kinetic diameter, which can more easily penetrate into the small pore of ZSM-5 than their aromatic counterparts [5, 6]. The higher reactivity of HCO fraction, compared to that of LCO and Gasoline fractions, is reasonable since the longer the length of the hydrocarbon molecule, the faster it is cracked on zeolite [7]. The HCO yield starts increasing at ZSM-5 concentration of 5wt% which again is again due to the dilution effect mentioned above.

Our results are also in agreement with Dupain et al.'s study [6], in which cracking of highly paraffinic Fischer-Tropsch (FT) wax was investigated. They observed that the FCC catalyst/ZSM-5 blend displays higher reactivity than that of FCC catalyst for the cracking reaction of highly paraffinic FT wax [6]. This is due to the fact that HCO range olefins, which are produced by pre-cracking on the FCC catalyst, are crackable on ZSM-5 and there is a synergy effect between FCC catalyst and ZSM-5 additive.

Table 4 shows the effect of ZSM-5 additive on the gasoline octane in cracking product of 4 different feedstocks. Aromatic feedstock (VGO2) shows a larger improvement of gasoline octane ($\Delta\text{RON} = 3.4$) compared to that ($\Delta\text{RON} = 1.37$) of paraffinic feedstock (AR2) when ZSM-5 concentration increases from 0 to 5wt%. The rate of gasoline octane increase, however, is similar for all feedstocks in the ZSM-5 concentration region of 5 - 20wt%. The larger octane enhancement of aromatic feedstock compared to that of paraffinic feedstock can be explained from the difference in gasoline components. By adding

ZSM-5 at 5wt%, the aromatic content of the gasoline fraction in cracking products of aromatic feedstock (VGO2) increases by a factor of 1.37 (from 38.79 - 53.04), while that of paraffinic feedstock (AR2) only increases by a factor of 1.19 (from 23.38 - 27.85%). As a result, the effect of ZSM-5 addition on the gasoline octane improvement for aromatic feedstocks is more profound than that for paraffinic feedstocks.

Conclusions

Our results have shown that using ZSM-5 additive for FCC catalyst could improve the propylene yield and gasoline octane for all feedstocks investigated. ZSM-5 additive was found to be the most effective on paraffinic feedstock as both propylene yield and conversion are significantly increased upon addition of ZSM-5 to the FCC catalyst. At ZSM-5 concentration of 5wt%, the propylene yield and conversion could increase by 13wt% and 10wt%, respectively. Particularly, the effect of ZSM-5 on bottom (HCO) cracking ability of FCC catalyst for paraffinic feedstock, observed in this study, is unprecedented. The fact that ZSM-5 could improve propylene yield and conversion of paraffinic feedstock at the same time is a very beneficial effect for refineries. In contrast, it was found that gasoline octane improvement by ZSM-5 is higher for aromatic feedstocks compared to that of paraffinic feedstocks. To further clarify the mechanism by which cracking of paraffinic feedstock is enhanced by addition of ZSM-5 to FCC catalyst, synthetic feedstocks with varied paraffinicity can be prepared by mixing

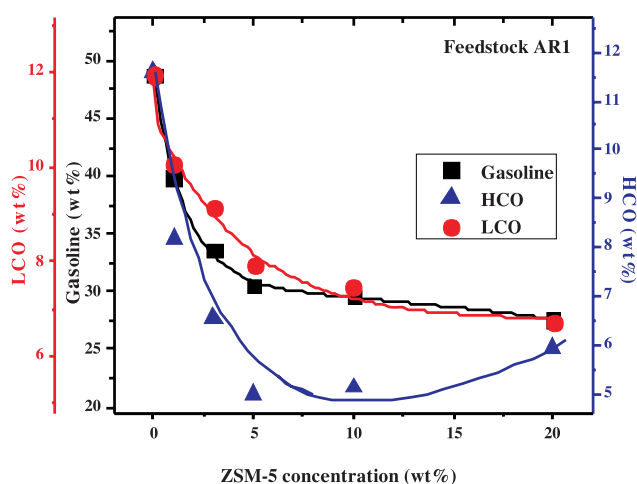


Fig.5. Main cracking products of paraffinic feedstock (AR1) as a function of ZSM-5 additive concentration in FCC catalyst/ZSM-5 blend

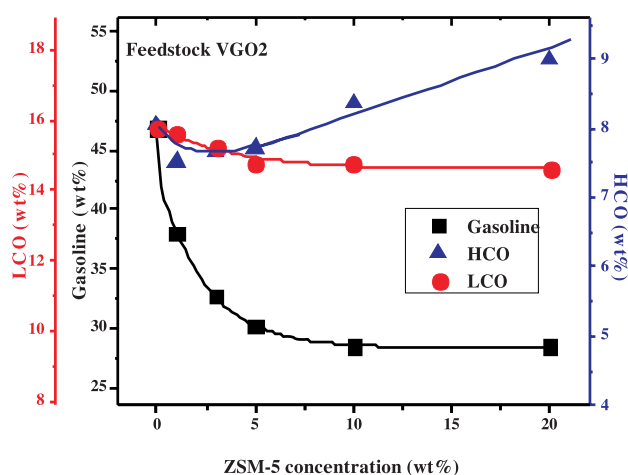


Fig.6. Main cracking products of aromatic feedstock (VGO2) as a function of ZSM-5 additive concentration in FCC catalyst/ZSM-5 blend

Table 4. Gasoline octane and composition in cracking products of 4 feedstocks at different ZSM-5 additive concentration

Additive, wt%	Conversion, wt%	Dry gas, wt%	Propylen, wt%	LPG, wt%	Gasoline, wt%	LCO, wt%	HCO, wt%	Coke, wt%
A-AR1								
0	76.42	2.65	5.88	19.96	48.79	11.95	11.58	4.87
1	81.67	3.15	13.02	33.24	39.94	10.08	8.18	5.04
3	84.24	4.11	17.02	40.70	33.61	9.15	6.54	5.51
5	87.06	5.30	19.11	45.40	30.47	7.92	4.97	5.56
10	87.39	6.70	18.30	44.75	29.56	7.45	5.11	6.05
20	87.31	7.96	17.97	45.82	27.62	6.71	5.93	5.58
A-AR2								
0	76.17	2.46	6.19	20.65	48.99	11.88	11.86	3.79
1	80.45	2.94	13.05	33.31	40.07	10.54	8.94	3.83
3	84.97	4.26	18.01	42.95	33.07	8.66	6.31	4.38
5	85.88	5.20	19.24	45.90	30.09	8.53	5.54	4.37
10	85.39	6.52	18.11	44.26	29.84	8.56	5.98	4.45
20	85.95	8.00	17.50	45.21	27.96	7.51	6.48	4.46
A-VGO1								
0	75.10	2.34	6.11	19.74	50.14	14.48	10.33	2.60
1	76.57	2.80	11.21	28.91	42.02	13.64	9.69	2.56
3	77.88	3.76	14.29	34.45	36.79	13.04	8.99	2.59
5	79.40	4.38	15.17	36.83	35.12	12.44	8.09	2.78
10	79.24	6.01	15.59	38.53	31.50	12.16	8.51	2.90
20	77.05	6.77	13.94	36.95	30.38	11.97	10.90	2.66
A-VGO2								
0	76.08	3.30	6.54	20.91	46.93	15.77	8.06	4.65
1	76.76	4.04	11.69	29.19	38.07	15.62	7.52	5.18
3	77.01	5.30	13.62	33.09	32.72	15.25	7.65	5.61
5	77.44	6.40	14.40	35.14	30.16	14.76	7.72	5.46
10	76.76	7.69	13.41	35.02	28.49	14.78	8.37	5.27
20	76.32	8.18	12.00	34.55	28.50	14.60	8.99	4.81

the above feedstocks with model compounds such as n-paraffin mixture (C32 - C40). The synthetic feedstocks cracking will be carried out using the ZSM-5 additive/FCC catalyst mixture, the results of which may reveal a greater insight into the role of ZSM-5 in paraffinic feedstock cracking mechanism.

The maximal ZSM-5 concentration which should be used for those four feedstocks with the selected FCC

catalyst is about 5wt% because above this concentration, there is no further improvement in terms of propylene yield as well as conversion. Depending on the processed feedstock and refinery objectives, the refiner can flexibly control the product yields by changing the ZSM-5 additive concentration in the unit in the range between 0 and 5wt%. The exact ZSM-5 concentration, however, must be determined by detailed economic evaluation for the whole refinery.

Table 3. Conversion and products yields of 4 feedstocks at different ZSM-5 additive concentration

Additive, wt%	RON	Paraffin	Isoparaffin	Aromatic	Naphthene	Olefin
A-AR1						
0	89.52	7.73	24.80	21.96	4.73	40.78
1	90.81	8.43	20.58	23.16	3.35	44.48
3	91.50	9.73	19.00	26.68	2.64	41.94
5	91.74	10.29	19.56	26.91	2.37	40.88
10	92.67	10.96	18.59	33.17	2.78	34.50
20	95.00	10.00	16.75	39.54	2.26	31.45
A-AR2						
0	91.28	5.96	23.59	23.38	5.02	42.05
1	91.48	7.06	21.33	24.04	3.92	43.65
3	92.28	8.50	19.71	24.66	2.95	44.17
5	92.65	9.18	19.93	27.85	2.63	40.41
10	94.22	9.30	17.92	36.64	2.75	33.40
20	95.49	9.26	18.63	41.38	2.41	28.32
A-VGO1						
0	92.68	4.20	23.54	32.50	6.60	33.17
1	93.55	4.47	23.86	36.52	5.99	29.17
3	93.94	4.96	24.66	38.39	5.11	26.88
5	95.02	5.06	23.69	41.44	4.19	25.62
10	96.07	5.23	21.83	46.45	4.18	22.31
20	97.96	4.97	19.58	53.11	3.16	19.19
A-VGO2						
0	92.70	4.13	27.64	38.79	5.83	23.61
1	94.30	4.22	24.91	45.42	5.62	19.83
3	95.10	4.52	23.80	49.98	5.04	16.66
5	96.10	4.49	22.56	53.04	4.58	15.33
10	97.50	4.21	20.67	58.17	3.87	13.07
20	99.20	3.81	18.15	63.40	3.14	11.49

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Establishment of a methodology for determination of the strength condition of fixed offshore jacket structures in deepwater, based on probabilistic model and reliability theory, and its application in Vietnamese sea conditions

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Abstract

Exploitation of oil and gas fields in deepwater is an increasing tendency worldwide; this requires the installation of production platforms with high safety in the most unfavorable conditions. This has encouraged new approaches to description of the environmental conditions by statistical modelling, then establishment of appropriate methods for structural analysis and design of deepwater platforms, from fixed jacket to anchored floating platforms.

In the framework of this paper, the authors present the methodology for expressing the strength condition by a probabilistic model for estimate of the safety based on reliability theory, in order to analyse fixed platform jacket structure in deepwater aimed to be applicable in Vietnamese sea conditions from 200 - 400m depth. The paper content is developed from authors' research results in the National research Project KC.09.15/06-10.

1. Introduction

1.1. Overview of the development of fixed offshore jacket platforms in deepwater

The increasing demands of oil and gas exploitation in deepwater from 1,000 - 3,000m has created the strong motivation to push technical and technological improvement in the aim to design and install various offshore platform types in deepwater capable of being operated safely in more severe natural conditions, and furthermore to ensure product cost acceptable in comparison with that exploited in shallow fields.

The evolution of oil and gas exploration and exploitation at greater water depth has been increasing day by day, especially in the first decade of the 21st century, as presented in Fig.1.

There is a tendency of developing various offshore platform types in water depths over 1,000ft (328m), in which there are 7

fixed steel platforms installed in deepest water worldwide, as given in Fig.2 and Table 1 [1].

1.2. Characteristics of deepwater jacket structure design

The design of jacket structures in a deepwater has some differences from structures in shallow water, such as situated far offshore, environmental conditions and jacket structure configurations. The main characteristics of jacket structure design in deepwater are presented below [2]:

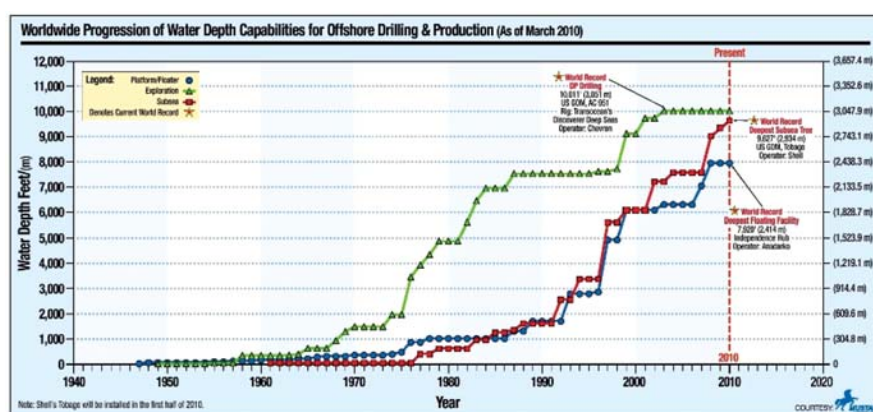


Fig.1. The worldwide progression of water depth capabilities for drilling and production (as of March 2010) [1]

- Basic frequency of jacket structure increases rapidly with water depth, resulting from the larger dynamic effect of the wave loads.
- The dynamic effect may be increased if the wave length is too larger than the distance between the legs of the jacket structure.
- In calculating internal forces of jacket elements it is necessary to take into account the axial bending effect of pipe elements subject to great axial forces (that leads to increase the element stress), and the vortex effect from current and wave passing through pipe elements (that creates periodic dynamic stresses resulting in the increase of the stress values in structural elements and maybe also local fatigue failure).
- Deepwater structures require the use of modern models and analytical methods giving high exactitude, this ensures safe operation of the offshore structures. This requires the use of the probability model for describing environmental conditions and to analyse strength as well as fatigue of jacket structure by reliability theory methods [4, 5].

The establishment of a methodology for expressing the strength condition of jacket structure based on the reliability as mentioned in the point 4 is the main content of the presentation below.

1.3. Some main problems of the methodology

- Description of random wave action on the jacket;
- Random dynamics of the jacket structure;
- Expressing structural strength condition by the probabilistic model and reliability theory.

2. Random wave loads

In each sea state, the motion of random surface waves is considered as a zero-mean stationary stochastic process, and described by surface wave spectra, $S_{\eta\eta}(\omega)$, typically, they are Pierson-Moskowitz (P-M) wave

spectrum, JONSWAP spectrum. Hence, the velocity and acceleration spectrum can be determined. The distribution function of wave height then may be defined based on the wave spectrum bandwidth, either narrow or broad band or any other band type.

The wave load spectral density function is used for analysis of structure subjected to random wave action. A typical structure is presented below to illustrate the method of determining wave load spectral function acting on the structure.

The random wave load acting on unit length of vertical fixed column, circle cross-section (A) with diameter D, is determined based on Morison's equation of linear form [2]:

$$F(t) = \frac{1}{2} \rho D C_D \sqrt{\frac{8}{\pi}} \sigma_{v_x} v_x + \rho C_I A a_x \quad (1)$$

Where: ρ : Sea water density; C_D and C_I - drag and inertial coefficients;

v_x and a_x : Horizontal velocity and acceleration of water particle, as stationary random processes with their spectral densities $S_{v_x} v_x$ and $S_{a_x} a_x$;

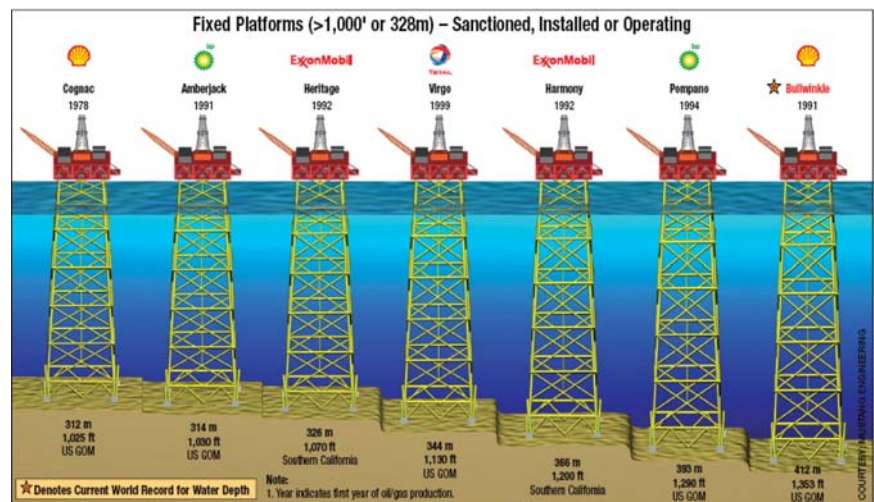


Fig.2. The seven deepest water worldwide fixed platforms

Table 1. Fixed platforms in the deepest water worldwide

No	Platform name	Year	Water depth (m)	Sea zone	Operator
1	Cognac	1978	312	GOM	Shell
2	Amberjack	1991	314	GOM	BP
3	Heritage	1992	326	South. Cali.	ExxonMobil
4	Virgo	1999	344	GOM	Total-Fina-Elf
5	Harmony	1992	366	South. Cali.	ExxonMobil
6	Pompano	1994	393	GOM	BP
7	Bullvinkle (*)	1991	412	GOM	Shell

(*) Maximum water depth at present time

σ_{v_x} : Standard deviation of random process v_x , determined by the variance of velocity v_x as follows:

$$\text{Var}(v_x) = \sigma_{v_x}^2 = \int_0^\infty S_{v_x v_x}(\omega) d\omega$$

From (1), we obtain the wave load spectrum:

$$S_{FF}(\omega) = \frac{2(\rho D C_D \sigma_{v_x})^2}{\pi} S_{v_x v_x}(\omega) + (\rho C_I A)^2 S_{a_x a_x}(\omega) \quad (2)$$

The expression (2) can be written by the new form below, taking into account the relationship between $S_{a_x a_x}(\omega)$, $S_{v_x v_x}(\omega)$ and $S_{\eta\eta}(\omega)$:

$$S_{FF}(\omega) = \left[\frac{2(\rho D C_D \sigma_{v_x})^2}{\pi} + (\rho C_I A)^2 \omega^2 \right] \left(\omega \frac{\text{ch}(ky)}{\text{sh}(kd)} \right)^2 S_{\eta\eta}(\omega) \quad (3)$$

Where $S_{\eta\eta}(\omega)$ is surface wave spectrum.

In the general case, the wave load acting on the diagonal elements with the circle cross-section of jacket structure, taking into account the structural displacement, Morison's equation (1) is written by the vector form, depending on the relative velocity vector of water particles (v) and structure, and on the relative acceleration vector of water particles (a) and structure, where $C_I = 1 + C_m$, C_m is added coefficient, and the relative acceleration calculated only with the term corresponding to C_m [16].

3. Random dynamics problem of the jacket structures

3.1. Problem of single-degree-of-freedom structure

The governing equation of single-degree-of-freedom problem is given by [2]:

$$M \ddot{u} + C \dot{u} + K u = F(t) \quad (4)$$

Where: M , C and K : Mass, damping coefficient and stiffness of structure;

$F(t)$: Random acting on the structure;

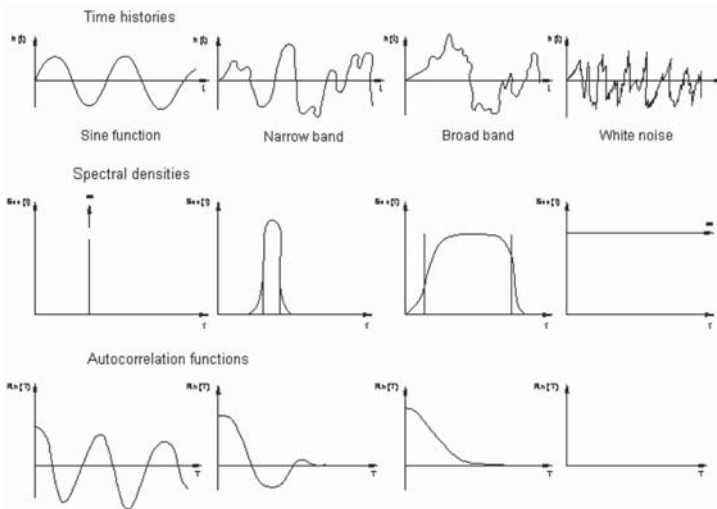


Fig. 3. The relationship between stationary random $h(t)$, correlation function, and spectral density function for various spectral bandwidths

$u(t)$: Displacement, ie. Structural response.

Let $R_{FF}(\tau)$ be the autocorrelation function of stationary random process $F(t)$, and using the Fourier transformation for $R_{FF}(\tau)$, we obtain:

$$R_{FF}(\tau) = \int_{-\infty}^{\infty} S_{FF}(\omega) e^{i\omega\tau} d\omega \quad (5)$$

Where: $S_{FF}(\omega)$: Spectral density of random process $F(t)$, can be considered as Fourier image of the autocorrelation function $R_{FF}(\tau)$, given by:

$$S_{FF}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} R_{FF}(\tau) e^{-i\omega\tau} d\tau \quad (6)$$

The pair of Eq. (5) and (6) is called Khintchine-Wiener expression; it plays the important role in the methodology of random dynamics problems. The relationship (6) allows transferring the original problem with the autocorrelation of time variable (t) to the new problem with the spectral density of the frequency variable (ω). This new problem can be favourably solved. The forms of this transformation are expressed in Fig. 3.

Using once again the Khintchine - Wiener expressions for random process $u(t)$, [in taking into account of the linear system (4), $u(t)$ is also a stationary random process], we obtain:

$$R_{uu}(\tau) = \int_{-\infty}^{\infty} S_{uu}(\omega) e^{i\omega\tau} d\omega \quad (7)$$

$$\text{and } S_{uu}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} R_{uu}(\tau) e^{-i\omega\tau} d\tau \quad (8)$$

Solving the problem (4) based on the spectral theory, one gets the important result which permits determination of the structural response spectrum density function, $S_{uu}(\omega)$ [2]:

$$S_{uu}(\omega) = |H(i\omega)|^2 S_{FF}(\omega) \quad (9)$$

Where:

$H(i\omega)$ - Transfer function of the SDOF structure subjected to stationary random loads: it is the complex function as follows

$$H(i\omega) = \frac{1}{(K - M\omega^2) + iC\omega} \quad (10)$$

$|H(i\omega)|$: Module of the transfer function determined by

$$|H(i\omega)| = \frac{1}{[(K - M\omega^2)^2 + (C\omega)^2]^{1/2}} \quad (11)$$

$$\text{Either: } |H(i\omega)| = \frac{1}{K} \frac{1}{[(1 - \Omega^2)^2 + (2\xi\Omega)^2]^{1/2}} \quad (12)$$

$$\text{Or: } |H(i\omega)| = \frac{1}{M} \left[(\omega_1^2 - \omega^2)^2 + (2\xi\omega)^2 \right]^{1/2} \quad (13)$$

Where: $\Omega = \frac{\omega}{\omega_1}$; $\omega_1 = (K/M)^{1/2}$: Natural angular frequency of structure;

$$C = 2\xi M; \quad \xi = \frac{C}{2\sqrt{KM}}: \text{Damping ratio.}$$

Hence, square of the transfer function is evaluated by:

$$|H(i\omega)|^2 = \frac{1}{K^2} \left[(1 - \Omega^2)^2 + (2\xi\Omega)^2 \right] \quad (14)$$

From (9) one can conclude: The spectral density of output (response of the structure) equals the product of spectral density of input (load) and square of the transfer function module (Fig. 4).

The variance of structural response can be determined by formula:

$$\sigma_u^2 = R_{uu}(0) = \int_0^\infty S_{uu}(\omega) d\omega = \int_0^\infty |H(i\omega)|^2 S_{FF}(\omega) d\omega \quad (15)$$

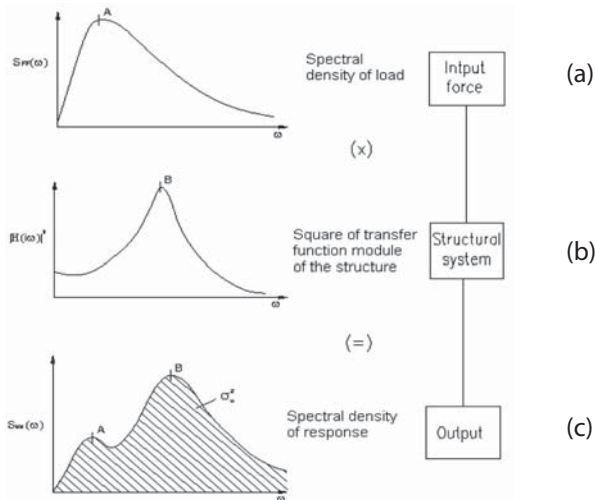


Fig.4. Relationship between load spectrum density and response spectrum density, by Eq.(9)

The transfer function $H(i\omega)$ still has meaning as a Response-Amplitude Operator (RAO), which can be used in Eq.(9) giving new form [2]:

$$S_{uu}(\omega) = [RAO]^2 S_{\eta\eta}(\omega) \quad (16)$$

3.2. Problem of multi-degree-of-freedom structure

The governing equation of the multi-degree-of-freedom (MDOF) problem for the jacket structure is performed as the principle of finite element method, and has the form developed from the SDOF problem:

$$M \ddot{U} + C \dot{U} + K U = F(t) \quad (17)$$

Where:

M: Mass matrix of structure, including added mass;

C: Matrix of structural and hydrodynamic damping coefficient;

K: Stiffness matrix of structure;

F(t): Vector of random wave loads, calculated using the linearised Morison's equation with absolutely rigid structure model;

U, $\dot{U}$ and $\ddot{U}$: Vectors of displacement, velocity and acceleration at structural nodes.

Using the mode superposition method as in the deterministic dynamics problem, the procedure of solving the random dynamics problem (17) in the frequency domain is given as follows:

1) Establishment of modal matrix: ϕ (n x n).

2) Change of variable from $U(t)$ to $Y(t)$ basing on ϕ :

$$U(t) = \phi Y(t) \quad (18)$$

The meaning of Eq.(18) is to express the structural response $U(t)$ by modes of structure ϕ .

3) Establishment of dynamic equations with variable $Y(t)$: Substituting (18) in Eq.(17), then product at left of all terms and ϕ^T , one gets

$$\phi^T M \phi \ddot{Y} + \phi^T C \phi \dot{Y} + \phi^T K \phi Y = \phi^T F(t) \quad (19)$$

Note that the damping matrix C is often recognised as depending on M and K with the form [2]:

$$C = \gamma_1 M + \gamma_2 K \quad (20)$$

Where: γ_1 and γ_2 are damping constants.

For offshore structures the damping matrix, including hydrodynamic damping, can be received by [2]:

$$C = \gamma_1 M = 2\xi M; \quad \xi \approx (0,05 \div 0,1) \omega_1$$

Owing to the perpendicularity of modes, Eq. (19) can be transferred to new form:

$$M' \ddot{Y} + C' \dot{Y} + K' Y = F'(t) \quad (21)$$

Where:

$M' = \phi^T M \phi$: Generalised mass matrix, diagonal matrix;

$$M' = \begin{bmatrix} M'_1 & 0 & \dots & 0 \\ 0 & M'_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & M'_n \end{bmatrix};$$

$C' = \phi^T C \phi$: Generalised damping matrix, diagonal matrix;

$K' = \phi^T K \phi$: Generalised stiffness matrix, also diagonal matrix;

$$C' = \begin{bmatrix} C'_1 & 0 & \dots & 0 \\ 0 & C'_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & C'_n \end{bmatrix}; K' = \begin{bmatrix} k'_{11} & 0 & \dots & 0 \\ 0 & k'_{22} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & k'_{nn} \end{bmatrix};$$

$F'(t)$: Generalised random load vector ($n \times 1$);

$Y(t)$: Generalised random displacement vector ($n \times 1$).

4) Independent SDOF equation system:

Expanding the differential matrix equation (21) we receive n independent differential equations, in which each equation has the typical form of the SDOFs dynamics equation as follows:

$$M'_j \ddot{Y}_j + C'_j \dot{Y}_j + K'_{jj} Y_j = F'_{j(t)} \quad (22)$$

Where:

$$F'_j(t) = \phi_{j1} F_1(t) + \phi_{j2} F_2(t) + \dots + \phi_{jn} F_n(t); j = \overline{1, n} \quad (23)$$

With F_k ($k = 1, n$) is the k^{th} order element of random load vector.

5) Define the spectral densities of generalised loads: $F'_j(t)$, ($j = 1-n$): basing on the random process theory one gets the following expression with full form of spectral density of $F'_j(t)$:

$$S_{F'_j F'_k}(\omega) = \sum_{r=1}^n \sum_{s=1}^n \phi_{jr}(\omega) \phi_{ks}(\omega) S_{F_r F_s}(\omega); (j = \overline{1, n}; k = \overline{1, n}) \quad (24)$$

If neglecting the correlation between wave loads F_r and F_s ($r \neq s$), ie. $S_{F_r F_s} \approx 0$, then Eq.(24) has the new simple form:

$$S_{F'_j F'_k}(\omega) = \sum_{r=1}^n \phi_{jr}(\omega) \phi_{kr}(\omega) S_{F_r F_r}(\omega); (j = \overline{1, n}; k = \overline{1, n}) \quad (25)$$

For the case $j = k$, from (25) we have:

$$S_{F'_j F'_j}(\omega) = \sum_{r=1}^n \phi_{jr}^2(\omega) S_{F_r F_r}(\omega) \quad (26)$$

6) Determine the transfer function in generalised coordinate system

The complex transfer function of generalised coordinate j ($j = 1, n$) for the SDOF system equation (22):

$$H_j(i\omega) = \frac{1}{K'_{jj} - M'_j \omega^2 + i C'_j \omega} \quad (27)$$

Hence, the module of transfer function (27) has form:

$$|H_j(\omega)| = \frac{1}{\sqrt{(K'_{jj} - M'_j \omega^2)^2 + (C'_j \omega)^2}} \quad (28)$$

These densities can be easily defined by the same way as for the SDOF system problem:

$$S_{Y_j Y_k}(\omega) = H_j^*(i\omega) H_k(i\omega) S_{F'_j F'_k}(\omega) \quad (29)$$

$$j = (1, n); k = (1, n)$$

Where:

$H_j^*(i\omega)$: Complex conjugate of the function $H_j(i\omega)$ (27);

$S_{F'_j F'_k}(\omega)$: Cross spectral density of two generalised loads (24).

7) Determine response spectral densities of the n -DOF system

The relationship between response $U_j(t)$ and generalised coordinates $Y_1(t), Y_2(t), \dots, Y_n(t)$ is given from matrix (18) by the general formula below:

$$U_j t = \phi_{j1} Y_1 t + \phi_{j2} Y_2(t) + \dots + \phi_{jn} Y_n(t); j = \overline{1, n} \quad (30)$$

Hence, one obtains the displacement spectral densities of n -DOF structure of the original problem (17) with the full form:

$$S_{u_j u_j}(\omega) = \sum_{r=1}^n \sum_{s=1}^n \phi_{jr}(\omega) \phi_{js}(\omega) S_{Y_r Y_s}(\omega); (j = \overline{1, n}) \quad (31)$$

Considering as $S_{Y_j Y_j}(\omega) = S_{Y_r Y_r}^*(\omega)$, so Eq.(31) has new form :

$$S_{u_j u_j}(\omega) = \sum_{r=1}^n \phi_{jr}^2(\omega) S_{Y_r Y_r}(\omega) + 2 \sum_{r=2}^n \sum_{s=1}^{r-1} \phi_{jr}(\omega) \phi_{js}(\omega) \text{Re}\{S_{Y_r Y_s}(\omega)\}; (j = \overline{1, n}) \quad (32)$$

Where: $\text{Re}\{*\}$: Real part of the complex function (29).

In practical analysis and design with acceptable exactitude, the terms of cross spectral densities between generalised coordinates in Eq.(32) are often neglected, so one has the new shorter form:

$$S_{u_j u_j}(\omega) = \sum_{r=1}^n \phi_{jr}^2(\omega) S_{Y_r Y_r}(\omega) \quad (33)$$

The variance of jacket structure response (ie. square of the displacement standard deviation) is determined based on the spectral density function (33) as follows:

$$\begin{aligned} \sigma_{u_j}^2 &= \int_0^\infty S_{u_j u_j}(\omega) d\omega = \int_0^\infty \sum_{r=1}^n \phi_{jr}^2(\omega) S_{Y_r Y_r}(\omega) d\omega \\ &= \sum_{r=1}^n \int_0^\infty \phi_{jr}^2(\omega) S_{Y_r Y_r}(\omega) d\omega \end{aligned} \quad (34)$$

3.3. Evaluate the spectral densities of internal forces and stress of the jacket structure

The main purpose of random dynamics problem of the jacket structure (17) is already performed, that is to determine the structural joint spectral density by either (32) or (33).

However, in order to realize the strength problems of structures by the reliability theory, as presented below, it is necessary to determine the spectra of internal forces, then stresses at jacket structural typical positions.

The total force vector (F_T) acting on all structural jacket joints depended on their displacements $U(t)$ with the algebraic relationship, is determined from Eq. (17):

$$F_T(t) = K \cdot U(t) = F(t) - [M \ddot{U} + C \dot{U}] \quad (35)$$

We can find then the internal forces and stresses with algebraic relationship also of the total loads $F_T(t)$.

The calculation procedure can be realized by starting from the structural spectrum by (31) or (32), $S_{u_i u_j}(\omega)$, for obtaining the total force spectrum, $S_{F_T F_T}(\omega)$, then internal force spectrum and finally one sets the maximum stress (σ_m) spectrum of all typical structural points necessary for the strength checking, $S_{\sigma_m \sigma_m}(\omega)$.

From spectrum $S_{\sigma_m \sigma_m}(\omega)$, the standard deviation of maximum stress is given by

$$\sigma_{\sigma_m \sigma_m}(\omega) = \left[\int_0^\infty S_{\sigma_m \sigma_m}(\omega) d\omega \right]^{1/2} \quad (36)$$

This standard deviation is main parameter of the distribution function of random maximum stress at points under consideration, used later for the structural reliability assessment in strength checking.

4. Strength checking of jacket structure in deepwater zone

4.1. Strength checking of jacket structures by probability model basing on reliability

The structural reliability in strength condition at typically dangerous positions of the jacket structure is given under the probability form as follows [4], [5]:

$$P = \text{Prob}(R \geq S) = \text{Prob}(Z = R - S \geq 0) \quad (37)$$

Where:

R = Strength of material, with its probabilistic density function (PDF), f_R ;

S = Random maximum stress of checking point, with its PDF, f_S ;

P = Reliability in strength condition at checking point.

From reliability (37), one can receive the failure probability at the point under consideration:

$$P_f = 1 - P = \text{Prob}(Z = R - S < 0) \quad (38)$$

The safety condition by structural reliability is expressed by:

$$P = \text{Prob}(Z = R - S \geq 0) \geq [P] \quad (39)$$

or

$$P_f = 1 - P < [P_f] \quad (40)$$

Where:

$[P]$: Permissible (or acceptable) reliability;

$[P_f]$: Permissible (or acceptable) reliability of failure.

From Eq. (37) and (38) we see that $Z = R - S$ is the safety zone of strength condition, also the random variable with its PDF, f_Z .

Fig. 5 is the diagram of PDF of three random variables R , S and $Z = R - S$, and failure probability described by the shaded area of the f_Z curve.

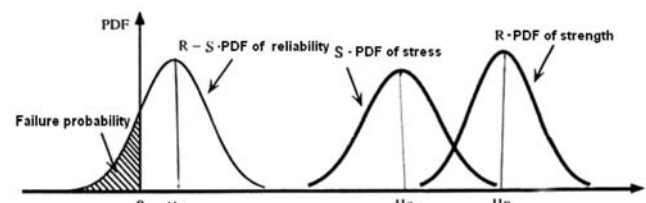


Fig.5. PDF diagram of the random variables R , S and $Z = R - S$

Note that in Eq. (37) the maximum stress, S , at the strength checking point, is the total stress consisting of two components, in which only the second one (S_2) is random variable:

$$S = S_1 + S_2 \quad (41)$$

Where:

S_1 : Stress at the point under consideration due to deterministic loads, with constant value;

S_2 : Maximum stress, $\sigma_{\max}$, of zero-mean random process, $\sigma(t)$, due to random waves.

The distribution function of random process of stress S_2 is determined based on the bandwidth of its spectrum, $S_{\sigma_m \sigma_m}(\omega)$ either narrow or broad as well as any band. The distribution function of total maximum stress S in Eq. (41), f_S , can be given based on the distribution function of random stress S_2 . From the distribution functions f_{S_2} and f_R (of material strength), we obtain the distribution function $Z = R - S$, so called f_Z , (Fig. 5).

The structural reliability is still expressed by the reliability index as follows:

$$\beta = \frac{\mu_Z}{\sigma_Z} = \frac{\mu_R - \mu_S}{\sqrt{\sigma_R^2 - \sigma_S^2}}; \quad (42)$$

and the structural safety is still estimated by its reliability index with the expression:

$$\beta \geq [\beta] \quad (43)$$

Where:

μ_R, μ_S and μ_Z : Mean value of random variables R, S and Z, with $\mu_S = S1$ [see Eq. (41)];

σ_R, σ_S and σ_Z : Standard deviation of random variables R, S and Z;

$[\beta]$: Permissible (or acceptable) reliability.

4.2. Safety checking of structures by the deterministic model based on maximum probability value

If there is not now regulation in design standards using the reliability theory for structural strength checking, one can transfer the reliability model to the deterministic model based on probabilistic theory for obtaining the approximate maximum stress value of random variable $\max \sigma(t)$.

In the case of narrow band spectral density of stress, $\sigma(t)$, of the checking point, $S_{\sigma\sigma}(\omega)$, the random variable $\max \sigma(t)$ has Rayleigh distribution function, and the approximate maximum stress value in N stress cycles of the extreme sea state is approximately evaluated by the following formula [2]:

$$\sigma_{\max} = \sqrt{M_0} \cdot \sqrt{2 \ln(N)}; \quad (44)$$

Where:

$$M_0 = \int_0^{\infty} S_{\sigma\sigma}(\omega) d\omega; N = \frac{T^*}{T_Z} = \frac{T^*}{2\pi} \sqrt{\frac{M_2}{M_0}};$$

with: $S_{\sigma\sigma}(\omega)$: Spectral density of the stress random process $\sigma(t)$;

T^* (sec): Duration of the extreme sea state, normally used with 3 or 6hrs for a storm;

$$T_Z = 2\pi \sqrt{\frac{M_0}{M_2}} \text{ (sec): Mean zero-upcrossing period of}$$

random process $\sigma(t)$, depending on the k^{th} -order spectral moments, M_k , eg. M_0 for $k = 0$, M_2 for $k = 2$.

5. Application to deepwater condition in Nam Con Son basin

In our country today, the fields are being exploited in up to just 150m water depth. In the future, the strategy objective of the Petrovietnam Group is to exploit oil and gas fields in deepwater zones of over 200m depth on the Vietnam continental shelf [10], [11].

In the previous research by the same authors on choosing the appropriate solution for jacket structure in 200m deepwater conditions at the Nam Con Son basin based on the deterministic wave load model, research results were presented in a paper in the Petrovietnam Journal Vol. 6/2010 [18].

The research methodology application of this paper is realized for a concrete jacket structure in deepwater zone of Vietnam sea. In order to compare favorably between the „rough” models for deterministic wave and the more exact model for random wave, the same jacket structure installed in the same natural environmental conditions in the Nam Con Son basin is used.

5.1. Geometric shape of the fixed jacket structure installed in deepwater zone of Nam Con Son basin

The jacket structure configuration in 200m water depth of Nam Con Son basin as the same one presented in

Table 2. Overall configuration of the jacket structure

Parameter	Jacket of 200m depth	Parameter	Jacket of 200m depth
Top Dimension	22 x 48m	Slope	I = 1/10
Number of wells	16	Largest distance between two diaphragms	30m
Number of Risers	4	Smallest distance between two diaphragms	20m

Table 3. Preliminary selection of jacket members, piles, and construction method

Main parameters	Jacket of 200m depth	Main parameters	Jacket of 200m depth
Legs	From ϕ 3000 x 4 to ϕ 1067 x 25.4	Brace system	K and X form braces
Braces	From ϕ 813 x 20.6 (at bottom) to ϕ 508 x 15.9 (jacket top)	Construction method	Load out by skidding to barge, transportation to the sea site installation by launching
Pile diameter	ϕ 1219	Piling solution	Vertical skirt piles connected by under-water welding

the published paper [18], has main parameters given in Table 2, Table 3 and Fig. 6.

5.2. Main results of the strength problem

Some typical calculation results are presented below basing on the API standard (API - RP 2A WSD) [7], and using professional software SACS (specified for offshore structures by spectral method).

5.2.1. Natural frequencies and dynamic coefficient

Three first periods (s)	Dynamic coefficient
T1 = 2.7 (DY)	1.14
T2 = 2.1 (DX)	
T3 = 1.5 (RZ)	

5.2.2. Main results of the strength problem (in comparing with the deterministic model)

- Strength checking of some typical elements
- Strength checking of some typical joints

5.3. Conclusion

- The member at the bottom bay and top pile have highest ratio of used material; this is the appropriate distribution of internal forces in the jacket structure.

- The used material ratio in calculation by the random model is a little greater than by the deterministic model [18], noting that the random model gives the calculation results more exactly than the deterministic model;

- The used material ratio of some members and joints has values of 1,05 and 1,07; this means that their behaviour is exploited in maximum and permissible also by current API standard.

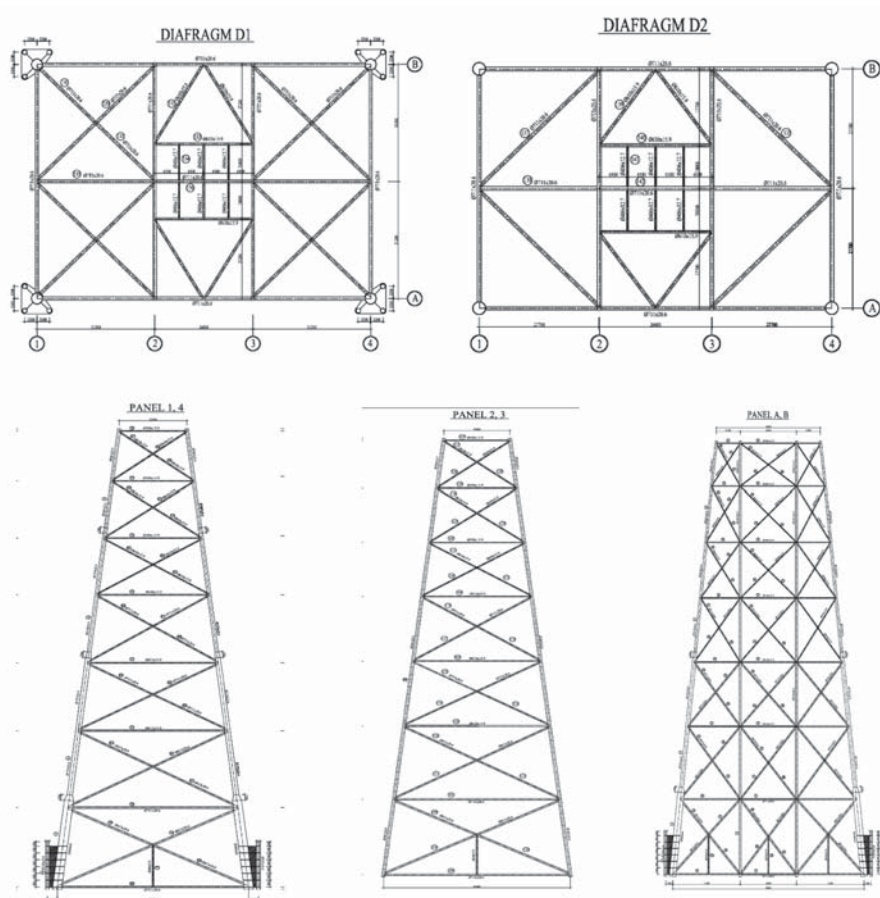


Fig.6. Layout of the jacket structure chosen with 213m height, chosen for 200m water depth zones

Element	Position	Used material ratio	
		Deterministic dynamic model	Ramdom dynamic model
469 - 293	Bottom bay braces	0.96	1.02
195 - 295	Pile	1.05	1.07

Joint	Location	Used material ratio	
		Deterministic dynamic model	Ramdomdynamic model
62	Second bay (from seabed) Face x = -13m	0.96	1.03
63	Second bay (from seabed) Face x = 13	0.97	1.05

- Almost jacket members have the used material ratio values less than 1.0, except the element 195 - 295 with value of 1.05, but it is acceptable for API standard.

- The jacket structure configuration above chosen with 200m water depth in specified sea zone satisfied

entirely technique condition (strength safety of structure) as well as economic condition (saving material volume as using in maximum the permissible used material ratio values).

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PETROVIETNAM NEWS

Produce first oil from Junin 2 project, Venezuela

On 26th September 2012, first oil flowed from PM-24 well, C-102 well head platform, Junin 2 project Venezuela, earmarking an important milestone in PVEP's operations in the overseas market. Junin 2 project is currently operated by Petromacareo, a joint venture between Corporación Venezolana del Petróleo S.A. (CVP), a member of the Venezuelan National Oil Company PDVSA and PVEP. PM-24 is the first oil well to be drilled by a joint venture company recently established in the Junin area, Orinoco oil belt.

The Mixed Company Petromacareo was then set up to produce and upgrade oil at the Block Junin 2, on an area of 247,77km² with reserves of about 36 billion barrels of oil in place. The plateau production of the Mixed Company is expected to reach around 200,000 barrels of oil per day. The duration of the Mixed Company shall be 25 years, extendable for a further maximum 15 years in accordance with Venezuelan laws.



This first oil production was achieved by Petromacareo after nearly 2 years of operation. Photo: PVEP

This first oil production was achieved by Petromacareo after nearly 2 years of operation, thanks to both sides' efforts and effective cooperation. Until now, a lot of project milestones have been passed. The putting into production of PM-24 is PVEP's early success in this project and is expected to be a prefix to reach its bigger target of production in years to come.

Tran Thu

The 10th ASCOPE Conference & Exhibition will be hosted by Petrovietnam for the first time



Dr. Nguyen Quoc Thap - Vice President & CEO of Petrovietnam chaired press conference in Malaysia. Photo: PVN

The 10th ASCOPE (ASEAN Council on Petroleum) Conference & Exhibition (ASCOPE C & E) entitled "Innovation and Cooperation - The way forward", will take place in Ho Chi Minh City from 28th to 30th November, 2013. Hosted by Petrovietnam for the first time, this event is expected to showcase about 300 exhibitors and approximately 500 conference delegates.

Leading companies of the oil and gas industry will also be there exhibiting up-to-date tools and technologies for oil and gas exploration, production and transportation, equipment for energy resources metering and control, automatic process control systems, integrated operational systems for plant management, software,

innovative projects for oil and gas facilities construction, a wide variety of fittings, protective equipment, services for oil and gas complexes, etc. As a meeting place, the event has always promoted new connections between different industry players, strengthened and brought the existing cooperation to a higher level. Besides, deploying state-of-the-art equipment and techniques is an imperative in such a competitive industry. The event therefore will focus on technological breakthroughs in related areas.

The conference in particular brings a unique opportunity to effectively discuss burning issues of the oil and gas industry. The Presidents and CEOs of all ASEAN national oil companies are expected to make keynote speeches during the conference and they will be joined by a host of other senior executives from the region's oil industry. Together, they will provide a timely insight into the ASEAN petroleum business, challenges to be faced, strengths to be enhanced and solutions to be applied. In addition, there will be a technical conference for the region's petroleum engineers. By gathering leading industry speakers from around the globe, the ASCOPE conference expects to bring an invaluable update for engineers based in ASEAN.

Hoang Son

First gas from offshore Lan Do field



First gas from Lan Do field in Block 06.1. Photo: Minh Huyen

TNK Vietnam, a fully owned subsidiary of TNK-BP, announced that the Company has successfully produced the first gas from the Lan Do field in Block 06.1, about 360km offshore south of Ba Ria - Vung Tau Province in Vietnam. Lan Do wells were opened for gas production on 7th October 2012. "Lan Do is the first offshore field development project in the past 10 years for the team in Vietnam, and the first ever for TNK-BP Group" - Hugh McIntosh, TNK Vietnam General Director said.

The two vertical sub-sea wells in a water depth of 185m from Lan Do field are now tied back to Lan Tay Platform in Block 06.1, through 28km of single 12 inch flow line and umbilical, enabling TNK Vietnam to produce gas

from the existing infrastructure. The Lan Do field, which has a maximum production design capacity of 5Mmscmd (175Mmscfd), is expected to bring two billion cubic metres (70 billion cubic feet) of gas to market annually.

Alexander Dodds - TNK-BP Executive Vice President for Upstream said: "The development of our offshore fields is of massive significance in terms of TNK-BP's long-term strategic development. This first gas at Lan Do field opens a new phase in the life of our Company. We have effectively delivered our first offshore drilling project in TNK-BP's history, thereby proving that the Company has all that is required to undertake such sophisticated and complex projects. The experience we've gained will allow TNK-BP to successfully participate in the development of other offshore oil and gas projects in the future".

The Lan Do field development project started in 2010 and became intensive from the beginning of this year, with successful completion of drilling operations in April, umbilical installation in June, flow line installation in July, and mechanical completion and well test at design flow rate in October. The project was delivered without any lost-time incidents, on time and within budget.

Minh Huyen

PVEP becomes a shareholder at Block 67 in Peru

On 10th October 2012, the Completion Ceremony for the Sales and Purchase Agreement relating to Block 67 in Peru between Petrovietnam Exploration Production Corporation (PVEP) and Perenco SA took place in Ha Noi.

PVEP and Perenco, who has a 95% interest for the petroleum contract at Block 67, signed the Sales and Purchase Agreement on 21st June 2012. After nearly 4 months, the two sides carried out the necessary procedures to finalize the transaction. PVEP is now a shareholder in Perenco Peru Limited. Block 67 is situated in the Marañon basin's North West in Peru. PVEP has also just completed its purchase of interests at Block 39 via a transaction with Burlington Resource in August 2012. PVEP now adds its third project in Peru, bringing its international assets portfolio up to 20 with 65 in total.

PVEP's decision to invest in two potential projects with adjacent geographical locations will make a joint



The completion ceremony for the sales and purchase agreement relating to Block 67 in Peru. Photo: PVEP

development plan both viable and efficient. PVEP's participation in this venture marks another success in its overseas expansion strategy. The Corporation hopes that this project will soon be put into commercial production thus spearheading future investment plans.

Thu Huong

VPI has licensed doctoral level training in Petroleum Engineering

On 21st August 2012, the Ministry of Education and Training has issued Decision No.3165/QĐ-BGDĐT allowing Vietnam Petroleum Institute (VPI) to accredit the Petroleum Engineering doctoral program (code 62 52 06 04). This is the first doctoral program to be conducted by a training unit from Petrovietnam. It is a three-year program for master degree holders majoring in related engineering fields.

Doctoral students attending the program will be provided with scientific theories of oil and gas exploration and production, from analyzing sedimentary basins, researching the structure, mechanism of formation, storage, preservation, and destruction of hydrocarbon traps, to calculating potential reserves, recoverable reserves, reservoir modeling, production engineering and

simulation. Moreover, graduate students will have the opportunity to apply the skills and knowledge acquired into their researches and practical operations.

The doctoral training program is an important forward step in the 34-year development of VPI, particularly when VPI is focusing on being a specialized academy combining research, training and application, thus becoming a central scientific unit of all business activities of Vietnam oil and gas industry. At the same time, VPI strives to continuously improve the training of highly-qualified human resources for the oil and gas sector as well as for the country, contributing to the implementation of one of the three breakthrough solution measures of the Accelerating Strategy of the Vietnam National Oil and Gas Group.

Nguyet Trang

PPS launches FSO/FPSO operation & management services abroad

Recently, PTSC Production Services (PPS) held the 10th anniversary ceremony of its establishment and received the 3rd Grade Labor Medal from the Vietnam President. Starting from supplying services to Floating Production Storage & Offloading (FPSO) Ruby Princess operated by PCVL & developing geological survey by ROV (Remotely Operated Vehicle, PPS has so far supplied, operated & managed 10 FSO/FPSO (three of them in operation abroad) and hundreds of ad-hoc and survey services.

In the last 10 years, PPS achieved a turnover of VND 7,100 billion, contributing VND 1,500 billion to the State's budget. Especially, with hundreds of staff, skilled & highly qualified engineers plus modern and synchronous equipment system, PPS has become a leading provider of O & M services and workforce to FPSO/FSO. Mr. Nguyen Hung Dung - General Director of PTSC stated:

"With ceaseless efforts of the whole employees and staff, PPS has now become a leading unit of providing crude oil reserve and floating storage services in Vietnam. We are step by step affirming our position and prestige in the international market".

Pursuing the development and growth strategy of Petrovietnam and PTSC, PPS has been taking firm steps in the process of promoting services overseas, especially in Malaysia. The effective co-operation through operation and maintenance between PPS in particular and PTSC in general with Malaysian partners like PCVL, MISC, Talisman Malaysia, Yinson, etc, is highly appreciated by customers. In addition, the establishment of joint ventures to invest new FSO/FPSO like Bien Dong FSO, Lam Son FPSO, etc, proves that PPS has won the trust of partners and customers through its services as well as its correct business strategy and sustainable development objectives in the future.

Khanh Linh

PTSC Marine supplies service vessels to Thang Long JOC



PTSC Marine and Thang Long JOC signed a supply agreement. Photo: PTSC

On 5th October 2012, PTSC Marine and Thang Long Joint Operating Company (Thang Long JOC) signed a supply agreement for services vessels. Accordingly, PTSC Marine will supply one 10,760 BHP service vessel valued at VND 42.49 billion and one 8,080 BHP service vessel valued at VND 36.1 billion, both vessels will serve drilling activities for Thang Long JOC for a period of 100 days (starting from early October 2012).

Being a leading provider of service vessels in Vietnam and in the region, PTSC in the past years has joined with Thang Long JOC to supply production timely services and safely of the highest effectiveness. The signing of the supply agreement of services between Thang Long JOC and PTSC Marine once again affirms prestige, trust in the good co-operation and traditional relationship between both sides.

Nguyen Oanh

PVE organized the 1st Science and Technologies Conference

Petrovietnam Engineering Corporation (PVE) and the Faculty of Geology and Petroleum of the Polytechnic University of Ho Chi Minh City joined to organize the 1st Science and Technologies Conference in 2012. The conference went well with much exciting participation, as well as many practical speeches concerning research in the oil and gas design engineering consultancy from PVE's experts and researchers and lecturers from the Polytechnic University of Ho Chi Minh City.

PVE's leaders have placed great importance on scientific and technological activities, and considered such activities as the main factors to lead PVE to continuing success and sustainable development. PVE has also initiated the scientific research campaign in order to take advantage of ideas to innovate the production and business activities, to hold evaluation meetings for such scientific and technological activities and to report applied scientific research of PVE's staff members.

With the success of this conference, PVE plan to organize the next conference with the topic "Application of science and technologies in the oil and gas design



Dinh Co Gas Processing plant. Photo: PVE

engineering consulting industry" with more highly qualified scientific research reports. Specifically, among such reports shall be research on technologies applied in the design engineering activities of PVE, including technologies on LNG storage and distribution; technologies on offshore oil/gas exploitation for drilling platforms, exploiting platforms and process platforms; condensate producing technologies, innovative oil refinery plants in the world...

Nguyen Nam

PTSC to meet investors

On 3rd October 2012, Petroleum Technical Services Corporation (PTSC) organized a meeting with investors including investment funds, local and foreign companies and etc. The meeting aims to help them to timely and fully capture information relating to the business and production activities of PTSC.

At the meeting, leaders of PTSC announced its business and production results in the first 9 months and the plan for the last 3 months in 2012. Despite the negative impacts of the global and Vietnamese economy and uncertainty of oil markets PTSC still remains

its key services. In the first 9 months of 2012, PTSC achieved a total turnover of VND 20,500 billion, equivalent to 117% as planned, pre-tax profit of VND 950 billion. It is expected that the target in the last 3 months of 2012 is VND 5,000 billion and pre-tax profit of VND 90 billion.

Apart from providing information related to business and production activities in 2012, leaders of PTSC also answered questions of investors relating to its wide range of services, development orientation, projects under implementation and information about chartered capital increase to VND 4,467 billion.

Minh Phuong

PVD Training receives ABS Certificates of Service Recognition

PVD Training is honored to announce that they have recently been awarded the Certificate of Service Recognition in Self Contained Breathing Apparatus (SCBA) category by ABS Register. This certificate aims to recognize that PVD Training's services of SCBA have been audited and met the set standards in Marine and Offshore Classification.

The American Bureau of Shipping (ABS) is a classification organization that promotes marine safety through the development of standards called ABS Rules. These Rules form the basis for assessing the design and construction of new vessels and the integrity of existing vessels and marine structures.

The approval grants PVD Training the authority to carry out a wide range of technical services for SCBA including but not limited to survey, inspection, repair & maintenance, refill and certification services in compliance with ABS guidelines and standards. Furthermore, as the authorized service provider of ABS, PVD Training's personnel are trained and certified by ABS society to qualify for the service implementation of SCBA.

Thuy Hang



OIL & GAS GLOBAL MARKET

Oil prices

Although worldwide oil and gas production in the first half of 2012 was stable, and the supply was higher than the demand (Table 1), the global oil prices in this period were characterized by a high fluctuation during the transient months between the first and the second quarters. From January to March the prices of crude oils continued the augmented trend established in the fourth quarter of 2011. Spot prices for dated Brent increased by about 15USD/bbl during the first quarter of 2012 and averaged 125USD/bbl in March. The WTI price increased at a high rate, thus the difference between these two principal bench mark oils shortened considerably. Prices began to weaken in April and the slide accelerated in May and the slow-down in the oil price continued in the next months. In August oil prices increased again. Going by the current trades, oil average prices are hovering about 100USD/bbl, but many analysts believe that it will be higher in the second half of 2012 and in the first quarter of 2013.

For a short-term prediction, the combination of a sustained loss of most North African and Iranian exports, the risk of increased tensions in different regions of the globe and the effect of other factories mentioned above, could cause oil prices to spike, at least temporarily. The magnitude of upward price pressure will depend on the duration of loss of supply and on the willingness and the ability of suppliers to make up for the shortfall. However with the depreciation of the USD we believe that, in real terms, oil prices will be far lower than levels seen in the early 1980s, when the OPEC basket reached the highest in its real value. Although risks remain high for price volatility and an oil price spike, all international forecasts for the next few months are more optimistic that the market will be relatively balanced, given the current state of global oil markets.

The price of gasoline at the pump is determined by various complicated factors and a whole range of issues which include the supply and demand of crude oil along with factors such as inflation, local taxes and changes in currency valuations. A typical breakup of the per litre gasoline price would be as follows: price of crude oil (68%), refining costs (10%), state taxes (10%), distribution and marketing costs (5%), profit margins (7%).

Referring to the gas market, Asian LNG demand is expected to hold up in the future. With Asian LNG, buying in the past times was moderate, now all eyes are on how demand will pan out this winter. The drop in demand in the summer has pushed down spot LNG prices from about USD18 per million Btu in early June to just over USD13 per million Btu in August and according to WGI price assessments term prices have also fallen - if less markedly, as they are oil-indexed-to around USD16/Mmbtu. Existing buyers are now reviewing winter stockpiling, which typically starts around October. Some support for the market should come from the start-up of new regional import terminals. Moreover, signs are that Japan won't restart many of its nuclear reactors progressively after the March 2011 Fukushima disaster. While the government remains concerned about the economic impact of the nuclear closure - the need to import substitute LNG and oil pushed Japan into its first annual trade deficit since 1976 in the months to March 2012 - expectations are that Tokyo may adopt a zero - nuclear option when it finally unveils its new mid - to long term energy policy.

China's net gas imports from Turkmenistan via the Central Asia pipeline hit 6.95 billion cubic meters in the first half of 2012, up almost 50% from 4.67 Bcm in the same period last year. Domestic gas production, meanwhile, totaled 58.2Bcm in the first half, up 12.6% year-on-year.

India is seeking LNG to offset lower domestic output which slumped 10.3% in the first half of 2012 to 22.2Bcm. More winter demand could also emerge in SouthEast Asia, where LNG import terminals in Thailand, Indonesia and Malaysia are operating below capacity. Over the first half, NorthEast Asian LNG importers Japan, South Korea, Taiwan, and China which account for the bulk of Asian gas demand - bought 75.9 million tons of LNG, up 13.8% from a year earlier. The number of Atlantic Basin cargos doubled to 160 as traders took advantage of higher Asian prices.

Further on, Asian gas demand is expected to continue growing. Consultancy Facts forecasts that consumption will increase by 4% a year from 2010 to 2030 to reach 19Bcf/d (1.2trillion cubic meters per year), or roughly two-thirds of the global total, largely led by the power generation sector.

Other factors such as oil and gas global and regional production and trade activities in the first half of year 2012 are sufficiently stable. The majority of oil and gas companies continue to invest greatly in exploration, production and processing of these valuable energy resources and their sustainable profit.

2013 oil demand

According to EIA forecast, 2013's global oil demand growth will be slightly higher in comparison with 2012. Worldwide liquids fuels consumption will rise by 800,000b/d this year and by 900,000b/d in 2013, according to the latest outlook from the Energy Information Administration. In last month's short-Term Energy Outlook (STEO), EIA projected that global oil demand would climb 700,000 b/d during both 2012 and 2013.

In its latest STEO, EIA sees China, the Middle East, Central and South

America and other countries outside of the Organization for Economic Cooperation and Development accounting for nearly all consumption growth. Projected OECD liquid fuels consumption will decline by 430,000b/d in 2012 and by 130,000 b/d in 2013.

EIA expects that OPEC members will continue to produce more than 30 million b/d of oil over the next 2 years to accommodate the projected increase in worldwide oil consumption and to counterbalance supply

Table 1. World oil balance

No.	Demand/Supply (MMb/d)	2012 - 1 st quarter	2011 - 4 th quarter	2010 - 4 th quarter
1	DEMAND			
1.1	Total OECD	45.67	46.05	46.96
	US & Territories	18.58	18.90	19.49
	Canada	2.21	2.28	2.23
	Mexico	2.11	2.16	2.07
	Japan	5.28	4.81	4.57
	South Korea	2.31	2.30	2.35
	France	1.80	1.75	1.86
	Italy	1.30	1.43	1.56
	United Kingdom	1.54	1.57	1.61
	Germany	2.27	2.41	2.54
	Other OECD Europe	6.76	6.94	7.27
	Australia & NewZealand	1.51	1.50	1.42
1.2	Total non OECD	42.49	42.29	41.09
	China	10.12	9.82	10.00
	FSU	4.69	4.76	4.54
	Non OECD Europe	0.74	0.77	0.75
	Other Asia	10.37	10.28	9.95
	Other non OECD	16.57	16.66	15.84
	TOTAL DEMAND	88.16	88.34	88.05
2	SUPPLY			
2.1	Total OECD	22.59	22.37	21.83
	US	10.83	10.65	9.94
	Canada	3.94	3.86	3.64
	Mexico	2.94	2.94	2.95
	North Sea	3.35	3.33	3.75
	Other OECD	1.53	1.59	1.55
2.2	Total non OECD	29.78	30.14	30.68
	FSU	13.41	13.30	13.36
	China	4.32	4.21	4.42
	Other non OECD - non OPEC	12.05	12.63	12.90
2.3	OPEC (Includes Angola)	36.31	35.73	35.14
	TOTAL SUPPLY	88.68	88.24	87.65

Source: Oil and gas journal, September 12, 2012

disruption. Projected OPEC oil production will increase by 900,000b/d in 2012 and then remain flat in 2013 as non-OPEC supply growth rises and stocks increase slightly.

EIA has said that Iran's oil production will fall by 1 million b/d by the year end from an estimated output of 3.6 million b/d at year end 2011, and by an additional 200,000b/d next year not only due to sanctions, but also due to the country's inability to make the investments necessary to offset natural production decline from existing wells. Non-OPEC production is forecast to increase by 600,000b/d this year and by 1.3 million b/d in 2013. The area with the most growth will be North America, where production will climb by 940,000b/d this year and by 440,000b/d next year.

EIA expects that Kazakhstan, which will commence commercial production in the Kashagan field next year, will increase its total production by 200,000b/d in 2013. In Brazil, output is projected to rise by 140,000b/d in 2013, with increased output from its offshore, pre-salt oil fields.

Forecast production also will rise in China, Russia, and Colombia over the next 2 years, while production declines in Mexico and the North Sea, according to the STEO [Oil and gas journal, August 13, 2012].

Global LNG supply to tighten through 2014

Global gas trends through the first-half of 2012 show that the LNG market for the next 5 years will increasingly tighten and residual volumes left for Europe will shrink. Thereafter, the market will loosen, according to a recent

commodities research note from Trevor Sikorski and Miswin Mahesh of Barclays Research, part of Barclays Bank PLC.

The analysts estimate that the LNG available specifically for Europe will fall to about 15 million tonnes/year (tpy) by 2014, from 2012 levels of 46 million tpy, before beginning to return to current levels when large Australian trains ramp up production and US exports of LNG begin. Europe, said the analysts, will continue to rely on pipelines to meet natural gas needs.

One of the notable trends in the global gas market this year, they said, has been the redirecting of LNG away from Europe towards Asia: European takes are down by 33% year-upon-year in the first - half of 2012; 50% in the UK alone. Asian takes, on the other hand, are up by 16% year-upon-year.

Asian demand, stoked by additional demand from Japan and new regasification in China, India, and others, has pulled gas away from Europe, which is seeing lower demand and greater competition to LNG from pipeline supply.

While these trends will persist for the rest of the year, the global gas trade's future is "colored by a large number of moving pieces". On the supply side are large LNG liquefaction projects: coal seam gas projects in Australia, the potential for North American shales production to be exported, and projects in new basins just being explored - East Africa, East Mediterranean.

On the demand side, the current trend is for Asian markets to take more and more LNG, reinforced by several large regasification projects under development as Japan seeks to replace much of its nuclear power. China and India look to natural gas to help diversify their energy mix and moderate their dependence on coal.

In Europe, said the analysts, the "potential golden age" of gas has some-what stalled as relative pricing no longer favors natural gas in power generation and the number of newly build natural gas-fired electric power projects begin to stall as the "uptake of renewable power generation tips the region's power markets into capacity oversupply".

Ha Phong

Table 2. *Nymex us gas futures*

Contract month	August 31, 2012 (USD/MMBtu)	August 27, 2012 (USD/MMBtu)
October 2012	2.799	2.673
November 2012	2.963	2.865
December 2012	3.220	3.144
January 2013	3.357	3.285
February 2013	3.375	3.303
March 2013	3.364	3.292
April 2013	3.357	3.286
May 2013	3.392	3.326
June 2013	3.434	3.370
July 2013	3.473	3.408
August 2013	3.492	3.428
September 2013	3.495	3.433

Source: WGI September 5, 2012