Investigation of Asphaltene under Subcritical Water Treatment

Pradip Chandra Mandal and Mohamad Azmi Bin Alias

Abstract—**The world reserves of conventional lighter oils are dwindling and being replaced by an increasing amount of heavy oils. High amount of heavy components such as asphaltene (AS) and coke in the crude oil nowadays makes it heavier. Heavy oil contains high amount of AS having less valuable in the refining process compares to the lighter oil that contains lighter component which is known as maltene (MA). Apparently, the traditional upgrading process of heavy oil which are coking, vis-breaking and solvent de-asphalthing have low efficiency and have high operation cost. This paper aims to extract MA, AS and coke from Saudi Arabian heavy oil under the standard room condition and to investigate the AS under subcritical water treatment process. The subcritical water experiments were conducted in an open breaker at a temperature of 100ºC, a pressure of 1 atm. and reaction times of 0-90 min. Experimental results revealed that the Saudi Arabian heavy oil contained 77.43 wt.% of MA, 16.93 wt.% of AS and 5.64 wt.% of coke. After the subcritical water treatment, the amount of MA was increasing with increasing reaction time and the amount of AS and coke were decreasing with increasing reaction time. Approximately 86.11% of MA was obtained at a temperature of 100ºC and a reaction time of 90 min. The subcritical water treatment was found to be potential to convert the heavy oil into the lighter oil.**

Index Terms—**Asphaltene, coke, crude oil, heavy oil, maltene, and subcritical water.**

I. INTRODUCTION

Upgrading of heavy oils is essential because the world reserves of conventional light oils are decreasing and being replaced by an increasing amount of heavy oils [1]-[6]. The total estimated reserve of heavy oil and bitumen in the world are approximately 6.2 trillion barrels [7], [8]. Petroleum density is generally expressed in terms of °API [9]. Heavy oil is basically one of the unconventional oil types which have API gravity approximately between 10º to 20º [10]. Reservoirs of heavy oil are vastly undeveloped for one good reason: their contents have been much more difficult — and therefore more costly — to produce, transport and refine than conventional oil and gas. Thus the need to develop technology to refine heavy oil into clean fuels is becoming acute; at the same time, environmental restrictions on both refining processes and refined products are becoming more stringent [7].

Heavy oil is composed of asphaltene (AS), maltene (MA) and coke [11]. Basically, the portion of the heavy oil which can be dissolved in the n-heptane (C_7H_{16}) is known as MA. On the other hand, the portion of the heavy oil which cannot be dissolved in the n-heptane, but easily dissolve in toluene ($C_6H_5CH_3$) is known as AS. AS are complex hydrocarbons [12] having 1) condensed aromatic hydrocarbons with side chain up to C30, 2) hetero-aromatic compounds with sulfur present in benzothiophene rings and nitrogen in pyrrol and pyridine rings, 3) bi- or polyfunctional molecules with nitrogen as amines, amides, and oxygen in groups, such as, ketones, armides, phenols, and carboxylic acids and 4) nickel and vanadium containing metal complexes with pyrrole nitrogen atoms in porphyrin ring structures. On the other hand, MA contain [12] 1) low molecular weight compounds which is a version of AS called resins, 2) aromatic hydrocarbons with or without O, N and S, 3) straight chain or cyclic unsaturated hydrocarbons called oleifins, 4) cyclic saturated hydrocarbons known as naphthenes, 5) straight or branch chain saturated hydrocarbons. The presence of AS will usually cause side effect to the production as well as refining processes. AS can easily deposit in the pipeline and directly it will cost some money to do the cleaning of the pipeline which is known as pigging. Moreover, the presence of AS in the crude oil will lead the stabilization of emulsion. In the refinery process, the valuable products such as petrol, diesel and kerosene are extracted from the MA of heavy oil.

The direct upgrading of heavy crudes is a difficult task. Distillation typically yields low levels of distillates, and the remaining residual oils cannot be added in significant amounts to fluid catalytic crackers because of their extraordinarily high levels of metals and conradson carbon residue (CCR). These metals and asphaltenic carbon fraction attach to the catalyst, thus obstructing the pores, destroying the activity of the active centers, and generating pressure drops [13]. A conventional solution for this has been coking, one of several thermal cracking processes, which has traditionally been the process of choice for upgrading heavy oils. Currently, the major heavy oil process used in United States refineries is delayed coking [14]. This process results in about 20-40% of very low-value precipitate (coke), creating potential disposal difficulties. The preferred alternative to delayed coking is a severe hydrotreatment process, which is significantly more expensive and produces only 50-60% of useful residual oil, the remainder being a high-sulfur fuel oil, which is becoming difficult to market without sulfur removal. Two other processes, visbreaking and solvent deasphalting, practiced mainly outside the United States, are equally inefficient and costly [15]. The key problem to share these processes is their inability to convert AS to oil; this flaw, results in the formation of coke, a product

of low value. Clearly, an alternative upgrading processes that can overcome the abovementioned drawbacks is desirable.

Subcritical water, the temperature and pressure below the critical temperature and pressure of water, technology could play a significant role not only in saving energy but also in converting wastes to valuable resources and/ or energy [16]. The use of hot water in thermal or steam oil recovery is well established for high viscosity oils [17]. Subcritical water as green treatment method has wide applications in various fields of green engineering and material cycling [18]. Such type of water has as a low electric constant and high ion production [19]. Many chemical reactions are catalyzed under the subcritical water condition [16] for hazardous organics, sewage sludge, wood wastes, meat and bone meal and in the synthesis of new materials. The most important parameter is to convert the heavy oil into lighter products by increasing the H/C ratio [20], [21]. Under subcritical conditions water could act as a hydrogen donor promoting hydrogen intake by the molecules. Very few research works have been conducted for extraction of asphaltene from heavy oil using subcritical water. Park and Son [22] in 2011 reported that bitumen conversion was 24% under subcritical water treatment at a temperature of 380oC, pressure of 30 MPa and a reaction time of 90 min. In addition, Daud et al. [23] in 2012 discovered that reactions of model compounds of heavy oils in supercritical water with the help of an oxidant would attack preferentially central rather than peripheral rings in polyaromatic structures to make them prone to subsequent cracking in that position. Deng *et al.* [24], [25] discovered that sub-critical water is capable of cracking kerogen (a mixture of organic chemical compounds) into low molecular weight hydrocarbons at relatively low temperatures. The comparison of the classical pyrolysis and the subcritical water extracts reflects that the subcritical water could extract mole long-chain alkanes from oil shale [25]. Moreover, the alkenes gradually transformed to alkanes in subcritical water.

The objective of this paper is to extract AS, MA and coke from Saudi Arabian heavy oil at standard room condition and investigate AS under subcritical water treatment for the first time.

II. EXPERIMENTAL SECTION

A. Materials

Crude oil/ heavy oil is a material of complex composition, the components of which largely differ in molecular weight, complex chemical structure (Fig. 1) and value of hydrophilic–lipophilic balance. Crude oil that was used in this study was collected from Saudi Arabia and used without further treatment. This crude oil was insoluble in water at normal environmental conditions. The solvents, n-heptane (purity: 99%) and toluene (purity: 99.9%), were purchased from WAKO pure chemicals industries Ltd., Japan and used without further treatment.

B. Extraction of AS

Crude oil/ heavy oil obtained from Saudi Arabia was precipitated by the addition of 40 volumes of n-heptanes to the bitumen as per the process described in Fig. 2. The initial weight of bitumen was approximately 25 g. The mixture was

stirred over about 6 h, allowed to stand for 16 h, and then centrifuged at 3500 rpm for 60 min. The AS was collected by filtering the samples using a membrane filter, dried in desiccators for one day at room temperature and then weighed. In order to determine the coke content in the heavy oil, toluene 40 times the weight of AS was added to each batch of dried AS. Then the same procedure was performed. The weight of the MA can be determined by subtracting the weight of the membrane filter from total weight. AS, MA and coke content of heavy oils are calculated by the following equations:

$$AS\ (wt\ \%) = \frac{wt\ of\ dried\ AS\ (g)}{wt\ of\ heavy\ oil\ (g)} \times 100. \quad (1)$$

$$Coke\ (wt\ \%) = \frac{wt\ of\ dried\ Coke\ (g)}{wt\ of\ heavy\ oil\ (g)} \times 100. \quad (2)$$

$$MA\ (wt\ \%) = 100 - wt\ \%\ of\ AS - wt\ \%\ of\ coke. \quad (3)$$
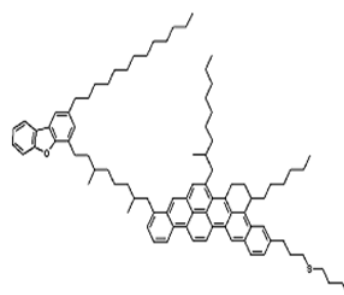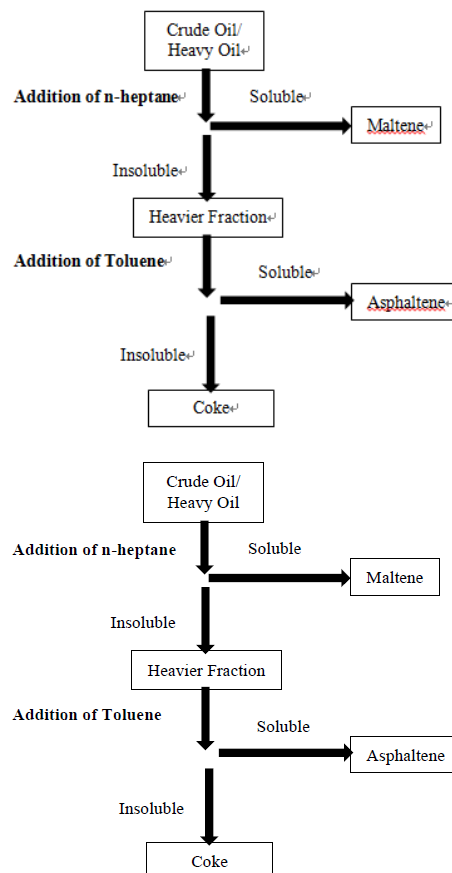

Fig. 1. Chemical structure of typical AS.

Fig. 2. AS extraction process from crude oil/ heavy oil.

C. Experimental Procedures

The detail experimental procedures are shown in Fig. 3. Three samples of heavy oil were taken in three different

beakers. Sufficient amount of water was then added into all the samples so that the process environment cannot evaporate all water. The samples were heated in the water bath for 30 min, 60 min and 90 min at a temperature of 100°C. After the specified time, the beaker was removed from the water bath and cooled in open air.

D. Analytical Procedures

The procedure of product separation and analysis are shown in Fig. 2. All the measurements used in this study were based on weight basis. The error margin of the acquired data is less than 2%, with 95% confidence.
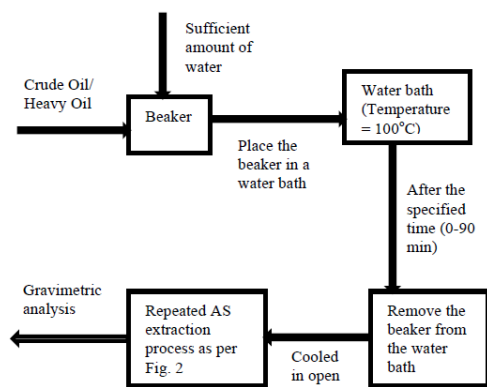

Fig. 3. Experimental procedure.

III. RESULTS AND DISCUSSION

AS content of heavy oil depend on the source of heavy oil. The heavy oil used in this study was obtained from Saudi Arabia, Middle East. Watanabe *et al.* in 2010 [11] have showed that Canadian oil sand bitumen contain 90 wt.% of MA and 10 wt.% of AS. Strausz of the University of Alberta disclosed that the AS content of the Alberta oil sand bitumen in the range of 16-25% [26]. This work revealed that Saudi Arabian heavy oil contains 77.43 wt% of MA, 16.93 wt.% of AS and 5.64 wt.% of coke (Fig. 4). So, Saudi Arabian heavy oil contains approximately 14% more AS than Canadian oil sand bitumen. In addition, Saudi Arabian heavy oil contains almost equal amount of AS that Alberta oil sand bitumen contain. Coke is the solid carbonaceous material present in heavy oils. The carbon to hydrogen ratio of coke is close to infinity. The coke reduces the market value of heavy oil. Iqbal *et al.* in 2008 [21] disclosed that the crude oil should have less and negligible amount of coke. The presence of 5.64 wt.% of coke in Saudi Arabian heavy oil make this a low value crude compare to Canadian oil sand bitumen. Seizing this coke from heavy oil or convert the same into valuable MA is the important issue to increase lighter oils of heavy oils.

Fig. 5 depicts the variation of composition of heavy oil after subcritical water treatment. It was seen that the weight percentage of MA was increasing with increasing reaction time at a fixed temperature and pressure indicating that subcritical water was capable to produce more MA. This behavior was a good agreement with the study conducted by Park and Son [22]. If the reaction time is longer than the 90 min, the MA production will increase and attain an optimal production at a specific reaction time under the experimental condition. On the other hand, the weight percentage of AS

and coke were decreasing with increasing reaction time. This was because with increasing reaction time some AS and coke was converted into MA. Thus subcritical water can convert AS and coke into valuable MA.
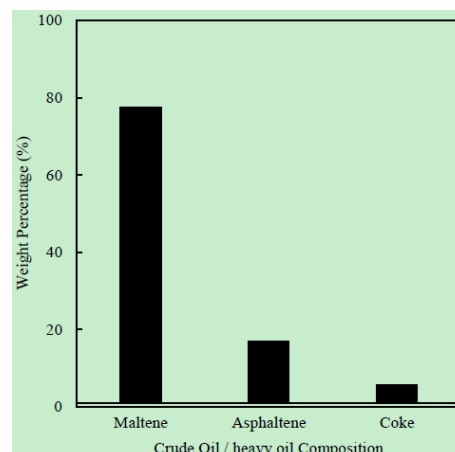

Fig. 4. Composition of Saudi Arabian heavy oil at standard room condition.

Golombak and Ineke [27] in 2013 disclosed that the hot water can pyrolytically crack the long molecular weight structures. Literature revealed that the hydrothermal reaction mechanism depends on water density: the reaction is controlled by the ionic reaction mechanism at high water density and low temperature; whereas the free radical reaction mechanism is prevalent at low water density and high temperature [28]-[30]. Thus, reactions of heavy oil with subcritical water can be described by ionic reaction mechanism. In addition, the dipolar nature of water implies a charge separation on the molecules and this itself is associated with the dissociation of water. The cage effect (the mechanism in which the properties of a molecule are affected by its surroundings), water attack on the molecule species or thermolysis [28], and the change in the phase behavior would decide the role of subcritical water. Upgrading heavy oil using the subcritical water requires a balance to be found between (1) dissolving the heavy oil component within this novel medium determined by dielectric constant and (2) cracking heavy oil simultaneously by using the enhanced $[H^+]$ and $[OH^-]$ present in subcritical water. Since MA is increasing with increasing reaction time heavy oil is converting into MA via a cracking mechanism. Then the following reaction can be believed:

$$HO_{(l)} \leftrightarrow HO_{(aq)} \xrightarrow{[H^+]+[OH^-]} MA_{(aq)} \leftrightarrow MA_{(l)} \qquad (4)$$
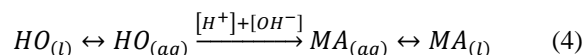
The symbol *HO* represents heavy oil. The respective subscripts (*l*) and (*aq*) refer to the hydrocarbon components present as pure water-insoluble liquid as found at ambient condition and dissolved in water under subcritical conditions. The ions, $[H^+]$ and $[OH^-]$, are the respective concentrations of hydrogen and hydroxide ions arising from dissociation of water as [27]:

$$H_2O \leftrightarrow H^+_{(aq)} + OH^-_{(aq)} \qquad (5)$$
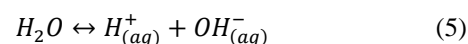
Heavy organics, in general, will be more soluble than MA. Thus the MA will form separate phases from water more

easily. As the more soluble heavy oils are cracked, then more heavy oil dissolves. Thus, it is not necessary to operate at temperature and pressure levels where the dielectric constants are at the low level of pentane solubility. The subcritical acetone level is sufficient for maximizing water dissociation.
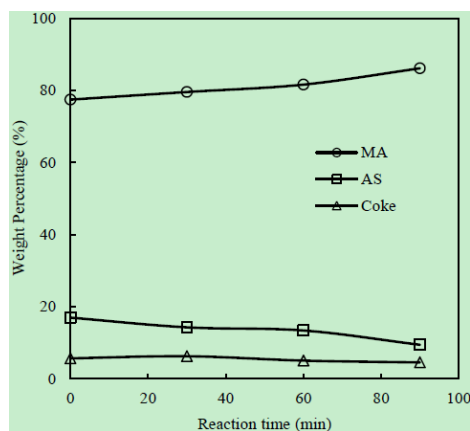

Fig. 5. Variation of composition of heavy oil after subcritical water treatment.

The believed Reaction pathways of AS decomposition under subcritical water treatment are presented in Fig. 6. The reaction mechanism can be divided into two main parts based on the experimental data. First, AS and coke decomposed into AS core, and MA during the reaction. A part of AS core was then converted into MA either by chain scission or by hydrogenation reaction. Second, a part of AS core was converted into MA and coke either by decomposition of AS core or by addition reactions. The first reaction mechanism was faster than the second reaction mechanism due to the increasing trend of MA and decreasing trend of AS and coke.
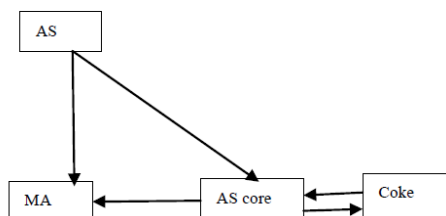

Fig. 6. Reaction pathways of AS decomposition under subcritical water treatment.

IV. CONCLUSION

Based on the experimental results, it was seen that Saudi Arabian heavy oil contains 77.43 wt.% of MA, 16.93 wt.% of AS and 5.64 wt.% of coke. In addition, Saudi Arabian heavy oil contains approximately 14% more AS than Canadian oil sand bitumen. The subcritical water treatment at temperature of 100°C and reaction time of 90 min showed that the higher amount of MA (86.11%) and the less amount of AS (9.40%) were produced by the action of subcritical water. Thus, subcritical water was active during experiments for producing MA. It was believed that AS and coke could be decomposed into MA for producing low molecular weight hydrocarbons. It is clearly concluded that the subcritical water is able to turn the heavy oil into the lighter oil as a green environmental protection technology.

REFERENCES

[1] P. C. Mandal, Wahyudiono, M. Sasaki, and M. Goto, "Non-catalytic vanadium removal from vanadyl etioporphyrin (VO-EP) using a mixed solvent of supercritical water and toluene: A kinetic study," *Fuel*, vol. 92, pp. 288-294, 2012.

[2] C. W. Hung and J. Wei, "The kinetics of porphyrin hydrodemetallation. 1. Nickel compounds," *Ind. Eng. Chem. Process Des. Dev.*, vol. 19, pp. 250-256, 1980.

[3] C. W. Hung and J. Wei, "The kinetics of porphyrin hydrodemetallation. 1. Vanadyl compounds," *Ind. Eng. Chem. Process Des. Dev.*, vol. 19, pp. 257-263, 1980.

[4] B. J. Smith and J. Wei, "Deactivation in catalytic hydrodemetallation 1. Model compound kinetic studies," *J. Catal.*, vol. 132, pp. 1- 20, 1991.

[5] A. J. Garcia-Lopez *et al.*, "Hydrodemetallation (HDM) kinetics of Ni-TPP over Mo/Al$_2$O$_3$-TiO$_2$ catalyst," *Catal. Today*, vol. 107-108, pp. 545-550, 2005.

[6] G. P. Dechaine and M. R. Gray, "Chemistry and associated of vanadium compounds in heavy oil and bitumen, and implications for their selective removal," *Energy Fuels*, vol. 24, pp. 2795-2808, 2010.

[7] P. C. Mandal, M. Goto, and M. Sasaki, "Removal of Nickel and vanadium from heavy oils using supercritical water," *J. Jpn. Petrol. Inst.*, vol. 57, no. 1, pp. 18-27, 2014.

[8] R. C. Schucker, "Heavy oil upgrading process," U.S. Patent 6524469, February 25, 2003.

[9] R. G. Santos, W. Loh, A. C. Bannwart, and O. V. Trevisan, " An overview of heavy oil properties and its recovery and transportation methods," *Braz. J. Chem. Eng.*, vol. 31, no., 3, pp. 571-590, 2014.

[10] J. G. Speight, *The Chemistry and Technology of Petroleum*, 4th ed. New York: CRC Press, Boca Ratan, 2007.

[11] M. Watanabe, S. N. Kato, S. Ishizeki, H. Inomata, and R. L. Smith Jr., "Heavy oil upgrading using high density water: A basic study," *J. Supercrit. Fluids*, vol. 53, pp. 48-52, 2000.

[12] HOSC. (May 2015). More about the chemistry of asphaltenes and maltenes. *Heavy oil science center*. [Online]. Available: http://www.lloydminsterheavyoil.com/asphaltenes2.htm

[13] P. Trambouze, J. P. Euzen, P. Bergez, and M. Claveau, "Process for deasphalting a hydrocarbon oil," U.S. Patent 4816140, March 28, 1989.

[14] A. M. Hooper and G. M. Sieli, "Do heavy oil upgrades make sense for small refineries?" *World Refining*, pp. 1-4, December 2000.

[15] S. Zhao, C. Xu, X. Sun, K. H. Chung, and Y. Xiang, "China refinery tests asphaltenes extraction process," *Oil & Gas Journal*, vol. 108, no. 12, pp. 52-59, 2010.

[16] O. Tavakoli and H. Yoshida, "Application of sub-critical water technology for recovery of heavy metal ions from the wastes of Japanese scallop patinopecten yessoensis," *Science of the Total Environment*, vol. 398, pp. 175-184, 2008.

[17] M. R. Gray, *Upgrading Petroleum Residues and Heavy Oils*, New York: Marcel Dekker, 1994.

[18] F. S. Asghari and H. Yoshida, "Kinetics of the decomposition of fructose catalyzed by hydrochloric acid in subcritical water: Formation of 5-hydroxymethylfurfural, levulinic, and formic acids," *Ind. Eng. Chem. Res.*, vol. 46, pp. 7703-7710, 2007.

[19] K. Tomita and Y. Oshima, "Stability of manganese oxide in catalytic supercritical water oxidation of phenol," *Ind. Eng. Chem. Res.*, vol. 43, no. 24, pp. 7740-7743, 2004.

[20] M. Oballa, *Catalytic Hydroprocessing of Petroleum and Distillates*, 1st ed. CRC Press, 1994, pp. 1-480.

[21] R. Iqbal, Anshumali, O. Eng, and P. Niccum, "Heavy oil and bitumen upgrading," U.S. Patent 7381320, June 3, 2008.

[22] J. H. Park and S. H. Son, "Extraction of bitumen with sub- and supercritical water," *Korean J. Chem. Eng.*, vol. 28, no. 2, pp. 455-460, 2011.

[23] A. R. M. Daud, J. L. Pinilla, P. Arcelus-Arrillaga, K. Hellgardt, R. Kandiyoti, and M. Millan, "Heavy oil upgrading in subcritical and supercritical water: studies on model compounds," *American Chemical Society, Division of Energy and Fuels Preprints*, vol. 57, no. 2, pp. 22, 2012.

[24] S. Deng, Z. Wang, Q. Gu, F. Meng, J. Li, and H. Wang, "Extracting hydrocarbons from Huadian oil shale by sub-critical water," *Fuel Process. Technol.*, vol. 92, no. 5, pp. 1062-1067, 2011.

[25] S. Deng, Z. Wang, Y. Gao, Q. Gu, X. Cui, and H. Wang, "Sub-critical water extraction of bitumen from Huadian oil shale lumps," *J. Anal. Appl. Pyrol.*, vol. 98, pp. 151-158, 2012.

[26] O. P. Strausz. (May 2015). The chemistry of the Alberta oil sand bitumen. [Online]. Available: https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/22_3_MONTREAL_06-77_0171.pdf

[27] M. Golombok and E. Ineke, "Oil mobilization by subcritical water processing," *J. Petrol. Explor. Prod. Technol.*, vol. 3, pp. 225-263, 2013.

[28] P. C. Mandal, T. Shiraishi, Wahyudiono, M. Sasaki, and M. Goto, "Kinetics and reaction pathways for heptylbenzene decomposition in supercritical water," *J. Chem. Eng. Jpn.*, vol. 44, no. 7, pp. 486-493, 2011.

[29] S. wang, Y. Guo, L. Wang, Y. Wang, D. Xu, and H. Ma, "Supercritical water oxidation of coal: Investigation of operating parameters' effects, reaction kinetics and mechanism," *Fuel Process. Technol.*, vol. 92, pp. 291-297, 2011.

[30] Y. Guo, S. Z. Wang, D. H. Xu, H. H. Ma, and X. Y. Tang, "Review of catalytic supercritical water gasification for hydrogen production from biomass," *Renew. Sust. Energ. Rev.*, vol. 14, no. 1, pp. 334-343, 2010.

Pradip C. Mandal graduated from Bangladesh University of Engineering and Technology (BUET) in 1998 and received his PhD degree in chemical engineering from Kumamoto University, Japan in 2011. From 2001 to 2014, he worked at Titas Gas Transmission and Distribution Co. Ltd. Currently, he is a lecturer at the Department of Chemical Engineering, Universiti Teknologi PETRONAS (UTP), Malaysia. His research interests are in heavy oil upgrading, extraction and methane capture. He is a member of IEB, IJET, and JOAE.

Md. Azmi B. Alias received his BE degree in petroleum engineering from Universiti Teknology PETRONAS (UTP) in 2014. Currently, he is searching industrial job. His research interest is in heavy oil upgrading.