Density, Viscosity, and Physical CO₂ Diffusivity of Novel Formulated Solvent N-Methyl-4-Piperidinol and 2-Amino-2-Methyl-1-Propanol for Carbon Capture

Teerawat Sema, Thanthip Kiattinirachara, Pipat Na Ranong, Pattaraporn Posoknistakul, and Ratana Jiraratananon

Abstract—**Amine based CO₂ capture is considered as one of the most effective technologies for mitigating global warming and climate change problems. The key of this technology is to use as highly effective solvent. In the present work, novel formulated MPDL-AMP solvent has been firstly introduced. Its essential data for determining and investigating the solvent performance as an alternative solvent for capturing CO₂ has not yet been reported. Therefore, density, viscosity, and physical CO₂ diffusivity of novel formulated MPDL-AMP solvent were determined in this work over ranges of concentrations and temperatures of 25%wt. MPDL/5%wt. AMP to 15%wt. MPDL/15%wt. AMP and 313 K to 333 K, respectively. The physical data reported in the present work are important for determining the optimum hydrodynamics of the fluid flow inside the absorption column as well as designing the height of the column through the kinetics and the mass transfer data. The results observed in the present work showed that the novel formulated MPDL-AMP solvent should be further investigated for its potential to be used as an alternative solvent for capturing CO₂.**

Index Terms—**Amine, CO₂, density, diffusivity, viscosity.**

I. INTRODUCTION

It is well known that carbon dioxide (CO_2) is the major greenhouse gas (GHG) responsible for global warming and climate change problems. In order to reduce the CO_2 emission from large point industrial source, carbon capture technology should be implemented. One of the very most promising and successful methods is amine based CO_2 absorption [1]. This statement has been confirmed by SaskPower Boundary Dam Carbon Capture Project (located in Saskatchewan, Canada), which is the world largest and the first commercial amine based CO_2 capture plant with 1.0 million tons of capturing CO_2 annually. Within the first few years of its operation, more than 2.0 million tons of CO_2 has been captured from the coal fired Boundary Dam power generation plant [2].

In the amine based CO_2 absorption, CO_2 is captured from feed gas by counter currently flowed reactive chemical solvent. The CO_2-rich solvent leaves from the bottom of absorber and is pumped to the stripper to discharge CO_2. The CO_2-lean solvent is then recycled to the absorber [3]. Typical amines used in the absorption are monoethanolamine (MEA), N-methyldiethanolamine (MDEA), 2-amino-2-methyl-1- propanol (AMP), and piperazine (PZ) [4]. Since each amine has its advantages and disadvantages, it has therefore been reported in the literature that one of the successive keys for this technology is to use a highly effective solvent. As a result, numbers of novel amines have been developed, synthesized, and screened [3].

At present, N-methyl-4-piperidinol (MPDL), a cyclical tertiary amine, shows great potential to use as an alternative solvent in substitution of the conventional amine. This is because MPDL possesses very high absorption capacity, reasonable absorption rate, and considerably low energy requirement for solvent regeneration [5], [6]. However, one of its major drawbacks is that MPDL has too slow CO_2 absorption rate comparing with industrial benchmarking MEA [6]. Therefore, MPDL is not suitable to use as a single solvent. Based on its very high absorption capacity and considerably low energy requirement for solvent regeneration [5], MPDL should be blended with highly reactive amine. It is expected that the blending two amines will enrich the advantages of each amine and encounter the disadvantages of one amine by another amine [4].

As a streically hindered primary amine, AMP is one of the most commonly used solvents because of its high reactivity with CO_2 [3]. Additionally, due to the sterically hindered effect, instable AMP-carbamate is formed after CO_2 absorption. The AMP-carbamate is easily hydrolyzed to bicarbonate and free AMP. The free amine can then react with CO_2 again. Thus, the absorption capacity of AMP is reported to be higher than MEA. Therefore, three novel formulated solvent of MPDL-AMP should be further investigate for its potential to use as alternative promising solvents in substation of industrial benchmarking MEA. The chemical structures of the four amines are presented in Table I.

Teerawat Sema is with the Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand and the Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok, 10330, Thailand (e-mail: teerawat.se@chula.ac.th).

Thanthip Kiattinirachara, Pipat Na Ranong, and Pattaraporn Posoknistakul were with the Department of Chemical Engineering, Faculty of Engineering, Mahidol University, Nakhon Pathom, 73173, Thailand (e-mail: thantip.kia@student.mahidol.edu, pipat.nar@student.mahidol.edu, pattaraporn.pos@mahidol.edu).

Ratana Jiraratananon is with the Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, Bangkok, 10140, Thailand (e-mail: ratana.jir@kmutt.ac.th).

TABLE I: CHEMICAL STRUCTURE OF AMINES (MPDL AND AMP) USED IN THE PRESENT WORK

Amine	Molecular weight (g/mol)	Chemical structure	Amine classification	CAS No.
MPDL	115.17		Cyclical tertiary amine	106-52-5
AMP	89.14		Sterically hindered primary amine	124-68-5

It is important to mention that in order to effectively design the hydrodynamics parameters (e.g., gas flow rate, liquid flow rate, and liquid to gas flow ratio) in the absorption column, the physical properties of the amine solvents (including density and viscosity) are required. Additionally, a determination of the reaction kinetics and mass transfer parameters (e.g., overall reaction rate constant, second-order reaction rate constant, enhancement factor, and mass transfer coefficient), density, viscosity and physical CO_2 diffusivity of the amine solvents are needed. Those reaction kinetics and mass transfer parameters are essential for designing the absorption column. Since the formulated MPDL-AMP solvent used in the present work is newly developed, the experimental data on its density, viscosity, and physical CO_2 diffusivity have therefore not yet been measured. Thus, the data reported in this work will be very useful for further studying on hydrodynamics of the solvents, kinetics and mass transfer of the CO_2 absorption, and designing the absorption column.

As discussed above, highly reactive amine (in this case, AMP) should be blended with MPDL to improve its CO_2 absorption kinetics or reactivity. Since 30% wt. total amine concentration is widely accepted to be generally used in the industry, the blended ratios of MPDL and AMP were then varied at 25/5%wt, 20/10%wt., and 15/15%wt., respectively. In the present work, the density and the viscosity were measured over a temperature range of 303-333 K, which is an actual absorber temperature in the industry.

II. EXPERIMENTAL SECTION

A. Chemicals

MPDL with a purity of 98% and AMP with a purity of 95% were obtained from Sigma-Aldrich, Switzerland. CO_2 with a purity of 99% were supplied by Linde (Thailand) PCL. All materials in this study were used as received without further purification.

B. Density

The density of MPDL based solvents were measured by a 25 mL adjusted Gay-Lussac pycnconometer (WINTEG Co., Germany). The operating temperatures of 303-333 K were controlled by a temperature controlled water bath (ISOTEMP2150, Fisher Scientific Inc., USA) with an operating range of 293-373 K and a temperature stability of ± 0.02°C. The pycnometer and the procedure of measuring solvent density were validated with pure MEA and 5.0 M MEA over temperature of 303-333 K as described in our previous work [6]. The results showed that the absolute average deviation percentages (%AADs) were 0.70% and 0.48%, respectively. Thus, it infers that the equipment and procedure used in the present work are accurate and can be used to determine the density of novel formulated MPDL-AMP solvent.

C. Viscosity

The kinematic viscosity of novel formulated MPDL-AMP solvent was measured by a capillary Cannon-Fenske Routine Viscometer (Cannon Instrument Co., USA). The variation of solvent's temperature was also controlled by a temperature controlled water bath (ISOTEMP2150, Fisher Scientific Inc., USA) with an operating range of 293-373 K and a temperature stability of ± 0.02°C. An experimental procedure was reported in our previous work [6]. It should be noted that the dynamic viscosity of the solvent can be calculated based on its density and kinematic viscosity. Additionally, the results showed that the dynamic viscosity of pure MEA and 5.0 M MEA well corresponded with the reference values [7]-[9] with AADs of 1.49% and 1.42%, respectively. Thus, it can be said that the equipment and procedure for measuring the dynamic viscosity was accurate and reliable.

D. Physical Diffusivity of CO_2

It is generally known that CO_2 reacts chemically with amine, thus the physical diffusivity of CO_2 cannot be measured directly. Typically, the physical diffusivity of CO_2 in aqueous amine solvent can be determined by N_2O analogy by measuring its physical N_2O diffusivity [4], [10]. The experiment can be done in laminar jet absorber [11]. However, the experiment is time-consuming and costly. In the present work, the physical diffusivity of CO_2 in novel formulated MPDL-AMP solvent were then calculated through its dynamic viscosity by modified Stokes-Einstein equation [10].

III. RESULTS AND DISCUSSION

A. Density of MPDL-AMP Solvent

The density of aqueous solutions of novel formulated MPDL-AMP was experimentally measured over a temperatures and MPDL/AMP blended ratios of 303-333 K and 25/5%wt.-15/15%wt., respectively. The results are presented in Table II and plotted in Fig. 1.

It can be seen from Table II and Fig. 1 that the density of aqueous solutions of MPDL-AMP decreased as temperature increased. This observation is in good agreement with the density of water, 30%wt. MEA, and 30% wt. AMP presented in the literature [8], [9]. Additionally, it can be found that the density of aqueous solutions of MPDL-AMP decreased as concentration of AMP decreased. This is because the density of pure AMP is lower than that of pure MPDL [6]. It should also be mentioned that the density of aqueous solutions of MPDL-AMP was found to be slightly lower than that of 30%wt. MEA and slightly higher than that of 30% wt. AMP. Based on this observation, it can be said that the novel formulated solvent of MPDL-AMP over a concentration range of 25/5%wt. to 15/15%wt. can be used for capturing CO_2 based on its density.

TABLE II: EXPERIMENTAL DENSITY OF AQUEOUS SOLUTIONS OF BLENDED MPDL-AMP

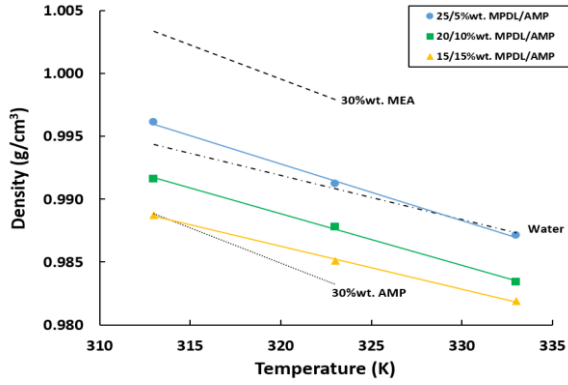| Temperature (K)	Density (g/cm³)		
	25/5%wt.	20/10%wt.	15/15%wt.
313	0.9961	0.9916	0.9887
323	0.9912	0.9878	0.9851
333	0.9871	0.9834	0.9819

Fig. 1. Density of aqueous solutions of MPDL-AMP at various concentrations and temperature; dots are the experimental data, solid lines are predicted data from the correlation developed in this work, and dash lines are literature data of MEA, AMP, and water [8], [9].

In the present work, a predictive correlation based on polynomial model was developed in order to predict the density of aqueous solutions of MPDL-AMP over ranges of concentrations and temperatures of investigation. The polynomial model can be written as:

$$\rho = A_0 + A_1C + A_2C^2 \tag{1}$$

where C is concentration of MPDL in the blended solvent (%wt.), and A_0, A_1, and A_2 are temperature dependent coefficients, which are a function of temperature (T) in Kelvin as shown in (2)-(4).

$$A_0 = a + bT + cT^2 \tag{2}$$

$$A_1 = a' + b'T + c'T^2 \tag{3}$$

$$A_2 = a'' + b''T + c''T^2 \tag{4}$$

By applying non-linear regression analysis, the constant parameters for the temperature dependent coefficients (A_0, A_1, and A_2) can be obtained and presented in Table III. The predicted results are showed in Fig. 1 as solid lines. It can be seen that the predicted results very well correspond with the experimental data with AAD of 0.46%.

B. Viscosity of MPDL-AMP Solvent

The measurement of liquid kinematic viscosity of aqueous solutions of novel formulated MPDL-AMP solvent was experimentally measured at various concentrations and temperatures. From the density data, the dynamics viscosity can be determined and presented in Table IV and Fig. 2. It can be observed that the viscosity of aqueous solutions of novel formulated MPDL-AMP solvent decreased as temperature increased over a temperature range of 313-333 K. The effect of temperature on the MPDL-AMP viscosity obtained in the present work is in good agreement with the

that of MEA, MDEA, and AMP reported in by Li and Lie [8]. Additionally, it can be found that the viscosity of aqueous solutions of novel formulated MPDL-AMP solvent increased as concentration of AMP in the blended solvent increased. This is due to the fact that the viscosity of pure AMP is higher than that of pure MPDL [6].

Additionally, by comparing the viscosity of the novel formulated MPDL-AMP solvent with that of conventional MEA, MDEA, and AMP at the same concentration of 30% wt., it can be found that the viscosity of novel formulated MPDL-AMP is higher than that of AMP, MDEA, and MEA, respectively. However, the viscosity of 30% wt. novel formulated MPDL-AMP is in the same range of that of 30%wt. AMP, which is the very well-known and highly effective solvent for capturing CO_2, as presented in Fig. 2. This indicates that the novel formulated MPDL-AMP solvents can be used for capturing CO_2 based on its viscosity.

TABLE III: CONSTANT PARAMETERS FOR THE TEMPERATURE DEPENDENT COEFFICIENT USED IN DENSITY ESTIMATION

Temperature dependent coefficient	Constant parameter	
A_0	a	3.5047
	b	-0.0151
	c	0.00002
A_1	a'	-49.3445
	b'	0.3052
	c'	-0.00047
A_1	a''	229.6017
	b''	-1.4274
	c''	0.0022

TABLE IV: EXPERIMENTAL DYNAMICS VISCOSITY OF AQUEOUS SOLUTIONS OF BLENDED MPDL-AMP

Temperature (K)	Viscosity (mPa.s)		
	25/5%wt.	20/10%wt.	15/15%wt.
313	2.3166	2.3965	2.4313
323	1.7293	1.7766	1.8191
333	1.3400	1.3652	1.4108

In order to predict the dynamics viscosity of the novel formulated MPDL-AMP solvent over range of concentration and temperature used in the present work, the predictive correlation based on polynomial model was developed. According to the results presented in Table IV and Fig. 2, it can be seen that the viscosity is a function of both amine concentration and temperature. Thus, in this work, the predictive correlation was then expresses as a function of both amine concentration and temperature as shown in (5).

$$\mu = B_0 + B_1C + B_2C^2 \tag{5}$$

where C is concentration of MPDL in the blended solvent (%wt.), and B_0, B_1, and B_2 are temperature dependent coefficients, which are a function of temperature in Kelvin as shown in (6)-(8).

$$B_0 = d + eT + fT^2 \tag{6}$$

$$B_1 = d' + e'T + fT^2 \tag{7}$$

$$B_2 = d'' + e''T + f''T^2 \qquad (8)$$

By applying non-linear regression analysis, the constant parameters for the temperature dependent coefficients (B_0, B_1, and B_2) can be obtained and presented in Table V. The predicted results are showed in Fig. 2 as solid lines. It can be seen that the predicted results very well correspond with the experimental data with AAD of 1.23%.
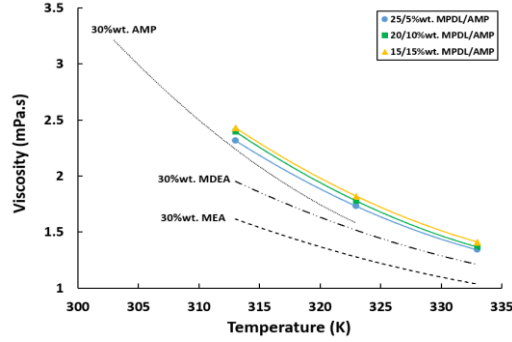

Fig. 2. Dynamics viscosity of aqueous solutions of MPDL-AMP at various concentrations and temperature; dots are the experimental data, solid lines are predicted data from the correlation developed in this work, and dash lines are literature data of MEA, MDEA, and AMP [8].

TABLE V: CONSTANT PARAMETERS FOR THE TEMPERATURE DEPENDENT COEFFICIENT USED IN VISCOSITY ESTIMATION

Temperature dependent coefficient	Constant parameter	
B_0	d	115.0143
	e	-0.65879
	f	0.000952
B_1	d'	140.6003
	e'	-0.71528
	f'	0.00091
B_1	d''	-506.211
	e''	2.49554
	f''	-0.00302

C. Physical CO$_2$ Diffusivity in MPDL-AMP Solvent

In this work, the physical diffusivity of CO_2 in aqueous solutions of novel formulated MPDL-AMP were calculated from its dynamics viscosity through the modified Stokes-Einstein equation as can be written as (9).

$$D_{CO_2-MPDL-AMP}\,\mu_{MPDL-AMP}^{0.8} = D_{CO_2-water}\,\mu_{water}^{0.8} \qquad (9)$$

where $D_{CO_2-MPDL-AMP}$ is physical diffusivity of CO_2 in aqueous MPDL-AMP solutions (m^2/s), $D_{CO_2-water}$ is physical diffusivity of CO_2 in water (m^2/s), $\mu_{MPDL-AMP}$ is dynamics viscosity of aqueous MPDL-AMP solutions (mPa.s), and μ_{water} is dynamics viscosity of water (mPa.s).

As presented in Fig. 3, the physical diffusivity of CO_2 in aqueous solutions of MPDL-AMP solvent decreased as concentration of AMP in the blended solvent increased. This is because as the concentration of AMP in the blended solvent increased, the solvent viscosity increased as shown in Table IV and Fig. 2. It is more difficult for CO_2 to physically diffuse through the higher viscosity solvent, thus the physical

diffusivity of CO_2 was then found to be decreased. Additionally, it can be seen that the physical diffusivity of CO_2 in aqueous solutions of MPDL-AMP is much lower than that of water because the viscosity of MPDL-AMP solvent is much higher than that of water. For the effect of temperature, it can be seen from Fig. 3 that the physical diffusivity of CO_2 increased as temperature increased. It can be reasoned that at elevated temperature, the viscosity of solvent decreases and there is higher driving force for CO_2 diffusing through the solvent.
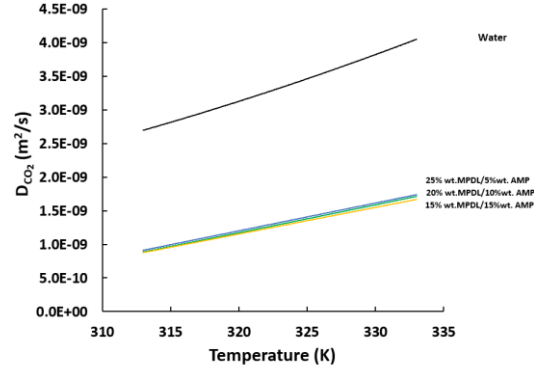

Fig. 3. Physical diffusivity of CO_2 in aqueous solutions of MPDL-AMP obtained from the present work and that of water obtained from the literature [10].

IV. CONCLUSION

In the present work, density, viscosity, and physical CO_2 diffusivity of novel formulated MPDL-AMP solvents were investigated. The density and the viscosity were experimentally measured over ranges of concentrations and temperatures of 25%wt. MPDL/5%wt. AMP to 15%wt. MPDL/15%wt. AMP and 313 K to 333 K, respectively. The physical diffusivity of CO_2 in novel formulated MPDL-AMP solvent was calculated based on its measured viscosity using the modified Stokes-Einstein Equation. It was found that both amine concentration and temperature affected density, viscosity, and physical CO_2 diffusivity of the MPDL-AMP solvent. Additionally, it should be mentioned that the density and the viscosity of novel formulated MPDL-AMP solvent were found to be in the same ranges of conventional ammines used in CO_2 capture process. Therefore, based on its density and viscosity, the novel formulated MPDL-AMP solvent can be considered as a potential alternative solvent to be further investigated for CO_2 capture applications.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

TS is the corresponding author for this work, he initiated the original concept of this work by blending MPDL with AMP and designed all experimental procedures, planning, and experimental conditions. TS also analyzed the data and wrote the paper. TK and PN conducted the experiment during their Bachelor's degree under the supervision of TS. PP and RJ reviewed the manuscript. All authors had approved the final version.

References

[1] D. Bostick, T. Stoffregen, and S. Rigby, *Final Techno-Economic Analysis of 550 MWe Supercritical PC Power Plant CO₂ Capture with Linde-BASF Advanced PPC Technology*, Linde LLC, Murray Hill, NJ, United State, 2017.

[2] K. Stephenne, "Start-up of world's first commercial post-combustion coal fired CCS project: Contribution of Shell Cansolv to SaskPower Boundary Dam ICCS project," *Energy Procedia*, vol. 63, pp. 6106-6110, 2014.

[3] A. L. Kohl and R. B. Nielsen, *Gas Purification*, 5th ed. Houston, USA: Gulf Publishing, 1997.

[4] T. Sema, A. Naami, Z. Liang, H. Shi, A. V. Rayer, K. Z. Sumom. P. Wattanaphan, A. Henni, R. Idem, C. Saiwan, and P. Tontiwachwuthikul, "Solvent chemistry: Reaction kinetics of CO₂ absorption into reactive amine solutions," *Carbon Management*, vol. 3, pp. 201-220, 2012.

[5] M. Xiao, D. Cui, L. Helei, P. Tontiwachwuthikul, and Z. Liang, "A new model for correlation anfd prediction of equilibrium CO₂ solubility in N-methyl-4-piperidinol solvent," *AIChE Journal,* vol. 63, pp. 3395-3403, 2017.

[6] T. Sema, W. Khuenkaew, and O. Sirirathonsud, "Kinetics of CO₂ absorption in novel tertiary N-methyl-4-piperidinol solvent," *International Journal of Greenhouse Gas Control*, vol. 90, p. 102796, 2019.

[7] R. M. DiGuilio, R. J. Lee, S. T. Schaeffer, L. L. Brasher, and A. S. Teja, "Densities and viscosity of the ethanolamine," *Journal of Chemical and Engineering Data*, vol. 37, no. 2, pp. 239-242, 1992.

[8] M. H. Li and Y. C. Lie, "Densities and viscosities of solutions of Monoethanolamine + N-methyldiethanolamine + Water and Monoethanolamine + 2-Amino-2-methyl-1-propanol + Water," *Journal of Chemical and Engineering Data*, vol. 39, no. 3, pp. 444-447, 1994.

[9] B. P. Mandal, M. Kumdu, and S. S. Bandyopadhyay, "Density and viscosity of aqueous solutions of (N-Methyldiethanolamine + Monoethanolamine), (N-Methyldiethanolamine + Diethanolamine), (2-Amino-2-methyl-1-propanol + Monoethanolamine), and (2-Amino-2-methyl-1-propanol + Diethanolamine," *Journal of Chemical and Engineering Data*, vol. 48, no. 3, pp. 703-707, 2003.

[10] G. F. Versteeg and W. P. Van Swaaij, "Solubility and diffusivity of acid gases (carbon dioxide, nitrous oxide) in aqueous alkanolamine solutions," *Journal of Chemical and Engineering Data*, vol. 33, no. 1, pp. 29-34, 1988.

[11] T. Sema, M. Edali, A. Naami, R. Idem, and P. Tontiwachwuthikul, "Solubility and diffusivity of N₂O in aqueous 4-(diethylamino)-2-butanol solutions for use in postcombustion CO₂ capture," *Industrial and Engineering Chemistry Research*, vol. 51, no. 2, pp. 925-930, 2012.

Teerawat Sema received Ph.D in engineering from the University of Regina, Regina, SK, Canada in 2012. Dr. Sema holds an international master of science in petrochemical technology from the Petroleum and Petrochemical College, Chulalongkorn University, Thailand since 2008 and a bachelor of engineering in petrochemical and polymeric materials with first class honor from Faculty of Engineering and Industrial Technology, Silpakorn University, Thailand in 2006.

He is presently working as a full-time lecturer at Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Thailand. From August 2017 to December 2018, he was appointed as a full-time lecturer at Department of Chemical Engineering, Faculty of Engineering, Mahidol University, Thailand. Up to present, 26 peer-reviewed international papers have been published in a field of Gas Separation and Purification and Carbon Capture Technology. His research interest includes high efficiency CO₂ separation and purification with reactive solvents, heat and mass transfer with chemical reactions, and intelligent and knowledge-based systems.

Pipat Na Ranong holds a bachelor of engineering in chemical engineering with second class honor from Mahidol University, Thailand in 2019.

He is currently a master's degree student in chemical engineering at Graduate School of Engineering, Kobe University, Kobe, Japan. His research interest is chemical catalytic process for energy and environment applications and carbon capture technologies.

Thanthip Kiattinirachara holds a bachelor of engineering in chemical engineering with second class honor from Mahidol University, Thailand in 2019.

She presently is a master's degree student in chemical engineering at Department of Chemical Engineering, Chulalongkorn University, Thailand. Her research interest is multiphase-flow in micro-reactor and carbon capture technologies.

Pattaraporn Posoknistakul received a Ph.D in biomaterial sciences from University of Tokyo, Tokyo, Japan in 2017. Dr. Posoknistakul holds master of engineering in pulp and paper technology from Asian Institute of Technology, Pathum Thani, Thailand from 2013 and bachelor of engineering in Nano Technology from Chulalongkorn University from 2011.

She is recently a full-time faculty at Department of Chemical Engineering, Faculty of Engineering, Mahidol University, Thailand. Since 2013, 8 international peer-reviewed papers have been published. Her research interest covers lignin degradation and valorization, lignocellulose pretreatment and characterization, and biomass conversion and biorefinery.

Ratana Jiraratananon received Ph.D in chemical engineering from the University of New South Wales, Australia in 1980. She also holds master of applied science in chemical engineering from the University of New South Wales, Australia since 1977 and bachelor of science in chemical engineering with honor from Chulalongkorn University, Thailand since 1974.

She presently is a full-professor in chemical engineering at the Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, Bangkok, Thailand. Up to present, hundreds of papers have been published in the international recognized journals. Her research interest covers membrane technology and mass transfer in chemical engineering applications.