Computer-Aided Integrated Design of Chemical Process for Diels-Alder Reaction

Ekkaphong Sangla-Iad, Suksun Amornraksa, and Danan S. Wicaksono

Abstract-The Diels-Alder reaction of anthracene and 4-phenyl1-1, 2, 4-triazoline-3, 5-dione (PTAD) in gas expanded solvents is studied in this work. The aim is to develop a computational tool to guide and aid engineers to implement systematic methods for integrated design of chemical process and reaction solvent. A methodology to identify the optimal solvent as well as the optimal mixture composition is presented. The preferential solvation model is used to predict the mixture properties of the solvent candidates: acetone, acetonitrile, and methanol. The model includes some parameters to be estimated using experimental data from the literatures. Aspen Plus and MATLAB are used as tools to perform simulation and estimation using Levenberg-Marquardt algorithm, respectively. Finally, a feasible simulated process which includes the results obtained from the estimation is proposed for this specific reaction. This work demonstrates an integration between model identification using experimental data and computer-aided process design.

Index Terms—Gas-expanded liquid solvent, solvatochromic parameter, Diels-alder reaction, preferential solvation model, model identification, process design.

I. INTRODUCTION

Solvents are important in the chemical industries. They can stimulate solubility of reactants in the reaction, control of reaction rates and temperature [1], etc. Generally, a certain volume of solute can be dissolved by solvent at a specified temperature. The solvatochromic parameters (α , hydrogen-bond donor (HBD) acidity; β , hydrogen-bond acceptor (HBA) basicity; π^* , dipolarity/polarizability), properties parameters of organic solvents, linear solvation energy relationship (LSER) and correction terms (δ , polarizability correction term; δ_H , Hildebrand solubility parameter; ξ , a coordinate covalency measure) have been studied by many researchers for decades [2]-[8].

The Diels-Alder reaction is an organic chemical cycloaddition. The basic construction of Diels-Alder reaction is conjugation between diene and substituted alkene (dienophile) to form a substituted cyclohexene system. A minimum number of π -bond is equal to one. When the diene and/or dienophile framework has one or more heteroatoms, this reaction of

cycloaddition (two or more unsaturated molecules (or parts of the same molecule) combine with the formation of a cyclic) is called a hetero-Diels-Alder reaction [9]. The Diels-Alder reaction is classified as a $[\pi 4_s + \pi 2_s]$ cycloaddition; The subscript 4 and 2 refer to the number of π -electrons involved in the electronic rearrangement (diene) and the number of atoms originating the unsaturated six-membered ring (dienophile) respectively. The Diels-Alder reaction has been studied by many researchers for years. They performed experiments to measure the solvatochromic parameters [10], [11] and established the preferential solvation model with correction term [12], [13]. The effect of pure and mixture solvents to the related characteristics of Diels-Alder reaction in the gas-expanded liquid has also been studied [1], [10].

In recent years, a promising alternative media for performing separations, extractions, reactions and other applications which is gas-expanded liquids (GXLs) has been explored by several research groups. In the past, the supercritical CO₂ could satisfy several green chemistry and engineering usages because CO₂, as a benign medium, has many advantages such as environmentally friendly, nontoxic, nonflammable, etc. However, the supercritical CO₂ is substituted with CO₂ gas-expanded liquids (CXLs) that are promising alternative media in chemical applications because of preferential properties of CO₂ gas-expanded liquids.

A GXL is a mixed solvent composed of a compressible gas (in this work is CO_2) dissolved in an organic solvent [14]. The beneficial properties of combination of dense CO_2 and organic solvents are improved permanent gas solubilities and mass transfer properties, enhanced solubility of solid and liquid solutes including homogeneous catalysts respectively [15]. The advantages of CXLs in process are ease to remove CO₂ from system, enhanced solubility of reagent gases (compared to liquid solvents), fire suppression capability of the CO₂ and milder process pressures (tens of bars) compared to supercritical CO₂ (hundreds of bars). The reaction advantages are higher gas miscibility compared to organic solvents at ambient conditions, enhanced transport rates due to the properties of dense CO2 and between 1 and 2 orders of magnitude greater rates than in neat organic solvent or supercritical CO₂. The environmental advantages are many replacement of organic solvents with environmentally benign dense-phase CO_2 [14]. Among them, the advantage of operating at medium pressure is the most attractive in economic term because it can save both capital costs and energy cost.

The specific reaction between anthracene and PTAD is used to study the solvatochromic parameters and correction terms because they can react easily or run conveniently in very dilute solution, due to the high reactivity of the

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Ekkaphong Sangla-iad and Suksun Amornraksa are with the Department of Mechanical and Process Engineering, The Sirindhorn International Thai-German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand (e-mail: mon_pet16@ hotmail.com, suksuna@kmutnb.ac.th).

Danan S. Wicaksono is with the AVT - Process Systems Engineering, RWTH Aachen University, Aachen, Germany (e-mail: Danan.Wicaksono@avt.rwth-aachen.de).

dienophile [16]. Fig. 1 shows the Diels-Alder reaction of anthracene and PTAD. The compressible CO_2 gas in GXL is postulated to act as a lewis-acid catalysis on PTAD in type of hetero-Diels-Alder reaction [10]. Fig. 2 shows the mechanism of Lewis acid catalysis by CO_2 on PTAD.



Fig. 1. Diels-alder reaction of anthracene and PTAD [10].



Fig. 2. Proposed mechanism of Lewis acid catalysis by CO2 on PTAD [10].

In this work, the first objective is to identify the optimal solvent, which gives the highest reaction rate constant, from three solvent candidates: acetone, acetonitrile, and methanol, as well as the optimal composition of the mixture between the solvent and CO_2 using theoretical prediction. The second objective is to design the process of the Diels-Alder reaction in the aforementioned gas-expanded solvent. The feasibility of the process design is verified by simulation using aspen plus V.7.3 using the predicted optimal solvent and its optimal mixture composition.

II. METHODOLOGY

A. Model and Solvent Identification

The solvation capability or solvation power of a solvent, which is the result of many different kinds of interaction mechanisms between the molecules of the solute and the solvent [13], has been widely classified into non-specific and specific solute/solvent interactions. The solvent effects are generally more complicated and often more specific than substituent effects and the polarity is the simple concept as a universally determinable and applicable of solvent characteristic [13]. The general form of multiparameter approach tales into account two or more aspects of solvation as shown below:

$$A = A_0 + b \cdot B + c \cdot C + d \cdot D + \dots \tag{1}$$

where A is the value of a solvent-dependent physicochemical property (log K, log k, etc.) in a given solvent and A_0 is the statistical quantity corresponding to the value of this property in the gas phase or in an inert solvent. B, C, D, and \ldots represent independent but complementary solvent parameters which account for the different solute/solvent interaction mechanisms. b, c, and d are the regression coefficients describing the sensitivity of property A to the different solute/solvent interaction mechanisms [13]. Another important treatment of the general form of multiparameter approach has been done and proposed by Kamlet, Abboud, and Taft (KAT) [5]. It is essential to consider non-specific and specific solute/solvent interactions separately. The later should be subdivided into solvent Lewis-acidity interactions (HBA solute/HBD solvent) and solvent Lewis basicity interactions (HBD solute/HBA solvent) [13]. The solvatochromic solvent parameters α ,

 β , and π^* are used in the KAT's equation that is called *"linear solvation energy relationships"* (LSER) as shown below:

$$A = A_0 + s\left(\pi^* + d\delta\right) + a\alpha + b\beta \tag{2}$$

where π^* is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. The π^* values are proportional to the dipole moment of the solvent molecule. The π^* scale was selected to run from 0 for cyclohexane to 1.0 for dimethyl sulfoxide. δ is a discontinuous polarizability correction term equal to 0 for non-chloro-substituted aliphatic solvents. 0.5for poly-chloro-substituted aliphatics and 1.0 for aromatic solvents. The δ parameter reflects the observation that differences in solvent polarizability are significantly greater between the three solvent classes than within the individual classes [5], [13]. α is a measure of the solvent hydrogen-bond donor (HBD) acidity. β is a measure of the solvent hydrogen-bond accepter (HBA) basicity. The regression coefficients a, b, d, and s measure the relative sensitivities of the solvent-dependent solute property of Ato the indicated solvent parameters [5], [13]. Reliable estimation of these parameters is important [17].

The KAT's equation can be extended by the introduction of two further solvent parameters (correction terms) i.e., the δ_H term and the ξ term [5], [13]. The extended equation from KAT as is shown below:

$$A = A_0 + s\left(\pi^* + d\delta\right) + a\alpha + b\beta + h\delta_H + e\xi \quad (3)$$

where δ_{H} parameter is the Hildebrand solubility parameter, a measure of the solvent/solvent interactions that are interrupted in creating a cavity for the solute (the cavity term). It is important when dealing with enthalpies or free energies of solution. ξ parameter is a coordinate covalency measure. This measure is interpreted as being approximate measure of the relative coordinate covalencies of the bonds which are formed between solute and solvent at the base centers of the solvent [13]. The value of ξ are equal to -0.20 for P = O bases (e.g., HMPT), 0 for C = O, S = O and N = O bases (arbitrary reference value), 0.10 for triple-bonded nitrogen bases (e.g., nitriles), 0.20 for single-bonded oxygen bases (e.g., ethers), 0.60 for sp²-hybridized nitrogen bases (e.g., pyridines) and 1.0 for sp³-hybridized nitrogen bases (e.g., amines) [5], [6], [13]. The advantage of KAT's equation is that it can be applied to many types of chemical reactions.

The two solvent-exchange processes can be characterized by two preferential solvation parameters; $f_{2/1}$ and $f_{12/1}$. They indicate the trend of the indicator dye (I) to be solvated by solvents S2 and S12 with reference to solvation by solvent S1 [12], [13], [18]. The preferential solvation parameters are defined as:

$$f_{2/1} = \frac{\left(x_2^S / x_1^S\right)}{\left(x_2^0 / x_1^0\right)^2} \tag{4}$$

$$f_{12/1} = \frac{\left(x_{12}^{s} / x_{1}^{s}\right)}{\left(x_{2}^{0} / x_{1}^{0}\right)}$$
(5)

where x_1^S , x_2^S , and x_{12}^S are the mole fraction of solvents S1, S2, and S12 in the solvation shell of the indication dye, respectively. x_1^0 and x_2^0 are the mole fractions of the two solvents S1 and S2 in the bulk binary solvent mixture.

The general preferential solvation equation of a binary solvent mixture is transformed to solvatochromic property of the mixture is called "Y". This equation relates with α , β or π^* value [1], [18] as shown below:

$$Y = \frac{Y_1 \left(1 - x_2^0\right)^2 + Y_2 f_{2/1} \left(x_2^0\right)^2 + Y_{12} f_{12/1} \left(1 - x_2^0\right) x_2^0}{\left(1 - x_2^0\right)^2 + f_{2/1} \left(x_2^0\right)^2 + f_{12/1} \left(1 - x_2^0\right) x_2^0}$$
(6)

where Y_1 and Y_2 are the solvatochromic properties in the pure solvents (S1 and S2). Another parameter, Y_{12} is the solvatochromic property in solvent S12, which is formed by the interaction of the two solvents S1 and S2 in the microsphere of solvation [1].

Firstly, the pure solvatochromic parameters and correction terms are gathered e.g., from the literatures. These parameters are then used to predict the solvatochromic parameters and correction terms of the mixture using the preferential solvation model. The solvatochromic parameters and correction terms in the preferential model of mixture are related to the pure solvent parameter $(Y_1 \text{ and } Y_2)$ and the mixture solvent parameters (Y_{12} , $f_{2/1}$, and $f_{12/1}$). The corresponding parameter in the preferential solvation model is substituted with the appropriate pure parameter for each solvent candidate (Y_1 and Y_2) such as in CO₂ expanded acetone, acetonitrile, and methanol; Y_1 = solvatochromic parameters of pure acetone [8], acetonitrile [8], and methanol [8], respectively and Y_2 = solvatochromic parameters of pure CO₂ [19]-[20]. The composition of x_2^0 is substituted by composition of CO2-expanded acetone, acetonitrile, and respectively. methanol. Subsequently, the mixture parameters $Y_{12}, f_{2/1}$, and $f_{12/1}$ are estimated from the data of CO_2 expanded acetone at 40 °C [11], acetonitrile at 40 °C [10], and methanol at 40 $\,^{\circ}$ C [11]. Lastly, the solvatochromic parameters and correction terms of mixture are used in LSER equation (KAT's equation) to predict mixture properties of interest (mixture kinetic parameter such as k, $\ln k$, $\log k$, etc.). The data of solvatochromic parameters and correction terms of the mixture of the solvent candidates and CO₂ gas have to be collected and/or estimated in order to identify the optimal composition of the optimal CO2-expanded solvent which gives the highest rate constant. These data are used to estimate the parameters of the preferential model. The nonlinear regression of Levenberg-Marquardt algorithm [21] in MATLAB are applied to estimate the paramaters to predict the solvatochromic parameters of CO2-expanded acetone, acetonitrile, and methanol. A diagram outlining the algorithmic framework which employs the preferential solvation model and the LSER equation is shown below:



Fig. 3. Algorithmic framework.

B. Process Simulation

In this work, the process of the Diels-Alder reaction of anthracene and PTAD in the optimal CO₂-expanded solvent is simulated using aspen plus V.7.3. The proposed process design contains a CSTR reactor, mixers (input and CO₂ recycle), separators (crystallizer and CO₂ feedback separator), and a pressure changer (valve). CSTR reactor is used normally with a mixture of solid and liquid. However, this reaction consists of solid, liquid, and gas. Therefore CO₂ is compressed into the liquid solvent (acetone) at 7.85 MPa. In this pressure, the CO_2 comes to be liquid that expands in acetone around 0.95 (XCO₂) [22]. The previously obtained information on the predicted highest rate constant as well as the corresponding solvent and the composition of CO₂-expanded solvent are used in the design. The reaction in the simulation consists of three phases: solid, liquid, and gas. The solid phase is anthracene, PTAD, and the product after crystallization. The liquid phase is the optimal solvent and the gas phase is the co-solvent i.e., CO₂.

III. RESULT AND DISCUSSION

A. Model and Solvent Identification

The LSER equation of gas-expanded liquids as reaction solvents in Diels-Alder reaction [10] is used to calculate the kinetic parameter ($\ln k$ value) of the mixture of CO₂-expanded acetone, acetonitrile, and methanol when the corresponding solvatochromic parameters of the mixture that have been already identified. This LSER equation is shown below:

$$\ln k = 1.9 - 4.68\alpha + 1.58\beta - 2.62\pi^* \tag{7}$$

The solvatochromic parameters of the mixture of CO₂-expanded acetone, acetonitrile, and methanol can be calculated because the parameters in preferential model of those mixture $(Y_{12}, f_{2/1}, \text{ and } f_{12/1})$ can only be identified. Therefore, the kinetic parameter $(\ln k \text{ value})$ of the mixture of acetone, acetonitrile, CO₂-expanded and methanol, respectively are calculated only. The correction terms of the mixture can help to increase the prediction accuracy of the kinetic parameter of the mixture. These parameters can be added into the KAT's equation resulting in the extended equation (i.e., (3)). However, we limit our study to the solvatochromic parameters (α , β , and π^*) of the mixture of CO₂-expanded acetone, acetonitrile, and methanol in Diels-Alder reaction.

The solvent candidates are acetone, acetonitrile, and methanol that mix with CO_2 gas in Diels-Alder reaction of anthracene and PTAD. It is desirable to obtain the highest rate constant by selecting the optimal solvent and the optimal mixture composition. The composition (in molar fraction) of acetone of approximately 0.05 ($XCO_2 = 0.95$) is identified as the optimal mixture composition for the CO_2 -expanded liquid of the Diels-Alder reaction of anthracene and PTAD. The highest rate constant is predicted to be $2.363s^{-1}$. The accuracy of the LSER equation to predict the reaction rate constant of the Diels-Alder reaction in gas-expanded liquid has been experimentally verified by a previous study [10]. The study concludes that the prediction of the LSER equation has good agreement with the experimental data.

B. Process Simulation

Some estimated values or property values are required for Aspen Plus V.7.3 to perform the simulation; such as the composition of the mixture of acetone with CO₂, property values of PTAD, mass flow rate for each stream, etc. Some of them are not in the databank of Aspen Plus V.7.3; for instance, property values of PTAD, property values of product ($C_{22}H_{15}N_3O_2$ or 8,9,10,11-dibenzo-4-phenyl-2,4,6-triaza[5,2,2,0] tricycloundeca-8,10-diene-3,5-dione), etc. Therefore, we obtained or estimated these values from other sources such as the literatures. In order to initiate the simulation, the substances have to be properly defined in aspen plus V.7.3. Unfortunately, some substances required in this simulation are not in aspen plus V.7.3 databank i.e., PTAD, product (solution), and product (solid). Therefore, they are defined in aspen plus V.7.3 using User Defined function.

The NRTL method is used to solve this simulation in aspen plus V.7.3 and CO_2 is set to Henry component. CPIG (Ideal gas heat capacity polynomial), CPSPO1 (Aspen solid heat capacity polynomial), and VSPOLY (Aspen solids volume polynomial) property values of PTAD, product (solution), and product (solid) are required from aspen plus V.7.3. The temperature T = 40 °C, pressure = 7.85 MPa, Vapor-liquid = valid phases, volume = 1 m³, and type of reaction = equilibrium are assumed in CSTR (continuous stirred-tank reactor) setting. The temperature T = 10 °C, pressure P = 0.5 bar, solid product = C₂₆H₂₁N₃O₅ (C₂₂H₁₅N₃O₂ + C₃H₆O +CO₂), and anthracene = solvent are assumed in crystallizer setting. The outlet pressure = 1 bar is assumed in valve setting.

Fig. 4 shows the possible process simulation block diagram that includes the stream name for each process line. The solid product of $C_{26}H_{21}N_3O_5$ is separated from crystallizer that means this process simulation is possible to produce solid product from the Diels-Alder reaction in CO_2 -expanded acetone when anthracene and PTAD as reactants. In other words, CO_2 in this process which is removed by separator and crystallizer can be recycled to the reactor. Small amount of CO_2 input is required to make up for the CO_2 loss in the process.

IV. CONCLUSION

The preferential solvation model is used to predict the solvatochromic parameters of the mixture. However, this work studies only the solvatochromic parameters of the mixture of CO₂-expanded acetone, acetonitrile, and methanol. In addition, some parameters (Y_{12} , $f_{2/1}$, and $f_{12/1}$) of the preferential solvation model are estimated from the experimental data using Levenberg-Marquardt algorithm. Hence, the kinetic values are estimated only for CO₂-expanded acetone, acetonitrile, and methanol. The solvatochromic parameters of mixture for other solvents except acetone, acetonitrile, and methanol are not considered in this work. The composition (in molar fraction) of acetone of approximately 0.05 is identified as the optimal mixture composition for the CO₂-expanded liquid to produce the highest rate constant of the Diels-Alder reaction of anthracene and PTAD. This composition results in the predicted highest rate constant i.e., 2.363 s⁻¹.

Aspen plus V.7.3 is used to simulate and to verify the feasibility of the proposed process design. This simulation uses the results from the model and solvent identification. From the simulation result, the solid product can be separated from crystallizer indicating the feasible process simulation. However, the solid product from the simulation is a combination of $C_{22}H_{13}N_3O_2 + C_3H_6O$ and CO_2 , instead of a pure $C_{22}H_{13}N_3O_2$. This is because the product from crystallizer is formed from solution containing $C_{22}H_{13}N_3O_2 +$ C_3H_6O and CO_2 . The advantage of this process is the 100% recycling of CO₂ from the process that is fed back into initial step of process. An integration between model identification using experimental data and computer-aided process design is demonstrated in this work. Some estimated parameters are used in this simulation. These parameters influence the accuracy of the simulation and the reliability of the assessment on the feasibility of the proposed process design.



Fig. 4. Block diagram of process simulation.

In the future, laboratory experiments can be performed to validate the theoretical prediction. Other simulators can also be used to verify the possible process design that is simulated in this study using aspen plus 7.3.

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Ekkaphong Sangla-Iad was born on 25th May 1988 at Suphan Buri, Thailand. He graduated in the bachelor's degree of chemical engineering in 2010 from Department of Chemical Engineering, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand. Subsequently, he has continued the master education in chemical and process engineering program at the Sirindhorn International

Thai-German Graduate School of Engineering (TGGS), King Mongkut's University of Technology North Bangkok, Bangkok, Thailand. In summer 2011, he performed the student project in topic of a study of force response in pellets of herbal spa salts by using Discrete Element Method (DEM) via computer simulation at the Sirindhorn International Thai-German Graduate School of Engineering (TGGS), King Mongkut's University of Technology North Bangkok, Bangkok, Thailand. Afterwards, he practiced the internship in topic of heat recovery optimization of Heat Recovery Steam Generator (HRSG) and using heat lost from air cooler outlet to pre-heat raw material header in neutralization unit. These works were operated at Cognis Thai Co., Ltd. (Now BASF (Thai) Ltd.), Chonburi, Thailand.

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Suksun Amornraksa was born in Thailand. He obtained a master degree and Ph.D. degree in chemical engineering from Imperial College, UK. He has worked as a researcher for the SCG Chemicals Company for six years, responsible for process improvement, environmental performance and energy efficiency improvement of olefins production process. Currently, he is working as a lecturer at the department

of Mechanical and Process Engineering, The Sirindhorn International Thai-German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok, Thailand. His main research interests are process and product design, and novel processes for production of chemicals from conventional and unconventional feedstocks.



Danan S. Wicaksono was born in Jakarta, the capital city of Indonesia. He completed his undergraduate study in chemical engineering at Bandung Institute of Technology, Indonesia with a distinction (cum laude). He earned a Master of Engineering (MEng) degree in chemical engineering from National University of Singapore, Singapore assisted by a scholarship from

AUN/SEED-Net and Japan International Cooperation Agency. He continued his study at Carnegie Mellon University, United States of America and graduated with a Master of Science (MS) degree in chemical engineering and a GPA of 4.00 out of 4.00. He is presently working towards a doctoral degree at RWTH Aachen University, Germany supported by a Marie Curie Initial Training Network fellowship. His main research interest is in the field of mathematical optimization.