The Application of an Incorporated Rate-Equilibrium Model for the Production of Pyrethroid Compound Process

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The pyrethroid-class compound has been produced in multiphase reactor which contains immiscible liquid phases. The reactants, products, and catalysts are partitioned within. These conditions allow novel synthesis paths, higher yields, and faster reactions, as well as facilitate production separation. A systematic modelling framework of three modules has been developed to describe phase equilibria, reactions, mass transfer, and material balances of such processes. The resulting mathematical model contains a few rate parameters to be regressed to a minimum of time-dependent data. In addition to describing the behaviour of such systems, predictions can be made of the effectiveness in rates and ultimate amounts of product formation with different feed scheme for further optimizing of this complex system operation.

1. Introduction

The pyrethroid-class compound is a man-made organic compound, which has similar structure to natural pyrethrin, used as insecticide (Thatheyus and Gnana Selvam, 2013). Pyrethroid is produced by reaction of cyclic aldehyde, organic acid, and inorganic salt. The reaction is carried out in a liquid-liquid aqueous-organic biphasic system; at which aldehyde, acid chloride, the Pyrethroid-class product, and side products remain in organic phase while an inorganic salt ion is being transferred from the aqueous phase (Umemura and Hirohara, 1989). Although pyrethroid is one of the most efficient insecticides without harmful effect toward human, the chemical production pathway of them are usually undisclosed or patented such as the work of Coelho et al. (2015).

In this work, the chemical production of the pyrethroid-class compound which are being used in the industrial scale are being studied. In order to describe the phenomena related to the reaction in multiple liquid phases, the developed framework for modelling of the multiphase reacting systems (Anantpinijwatna et al., 2016) has been applied. The multiphase reacting system has broad range of application area including the manufacture of petroleum-based products, the production of chemicals, pharmaceuticals, and agro-bio products. Some important examples, which are similar to the production of pyrethroid, include: (1) a reductant-free production of phenol using phase transfer catalysis (PTC) technique (Long et al., 2018); (2) a production of biodiesel combining the multiphase reactor with bifunctional catalyst (Borges et al., 2017); (3) a long-chain olefins alkylation reaction of benzene catalyzing by ionic liquid (Qiao et al., 2008); (4) a surfactant-assisted asymmetric synthesis of *p*-chlorobenzaldehyde with multiphase reactor (Aljbour et al., 2009). In these systems, multiple phases are created by the immiscibility between co-exist solvents such as aqueous/organic, where the reactants and catalysts (including phase-transfer catalysts) can exist in different liquid phases, allowing novel synthesis paths as well as higher selectivity, conversion, and yield. Furthermore, after the reaction, reactants, catalyst and products may end up in different liquid phases, making the separation tasks easier.

The reactor designs and operation decisions such as temperature, resident time, reactants feeding strategy, agitator shape, size, and speed, as well as reactor size and shape will influence production capacity and production rate. Modelling of this system could offer an efficient way to help analysis and development of the process in order to find the optimum reactor design and operation. The mathematical model must include all phenomena mentioned above. Based on the mentioned reaction mechanism, the reactor model was developed through the step-by-step framework, the parameters are identified and tested against measured data in a lab scale reactor with constant interfacial area. From the model-data mismatch, the reaction mechanism was

adjusted and the model performance was improved. However, while the current model was able to competently predict Pyrethroid-class production rate, a better match of the data or the reaction mechanism are needed to improve the model so that it could be used to understand the reactor performance and behavior. Also, based on the improved understanding, better operation of the reactor could be proposed

2. Framework and generic equations

The framework for modelling of the multiphase reactor consists of three modules; incorporating with generic property and process models as shown in Figure 1 (Anantpinijwatna et al., 2016). The initial steps are collecting information on the system and classifying the species and reactions. In this step, physico-chemical properties of the species are retrieved from a database or estimated by an appropriate method such as the group contribution approach of Kim et al. (Kim et al., 2016). The final result is a problem-specific model generated through different combinations of the equations obtained from three modules.
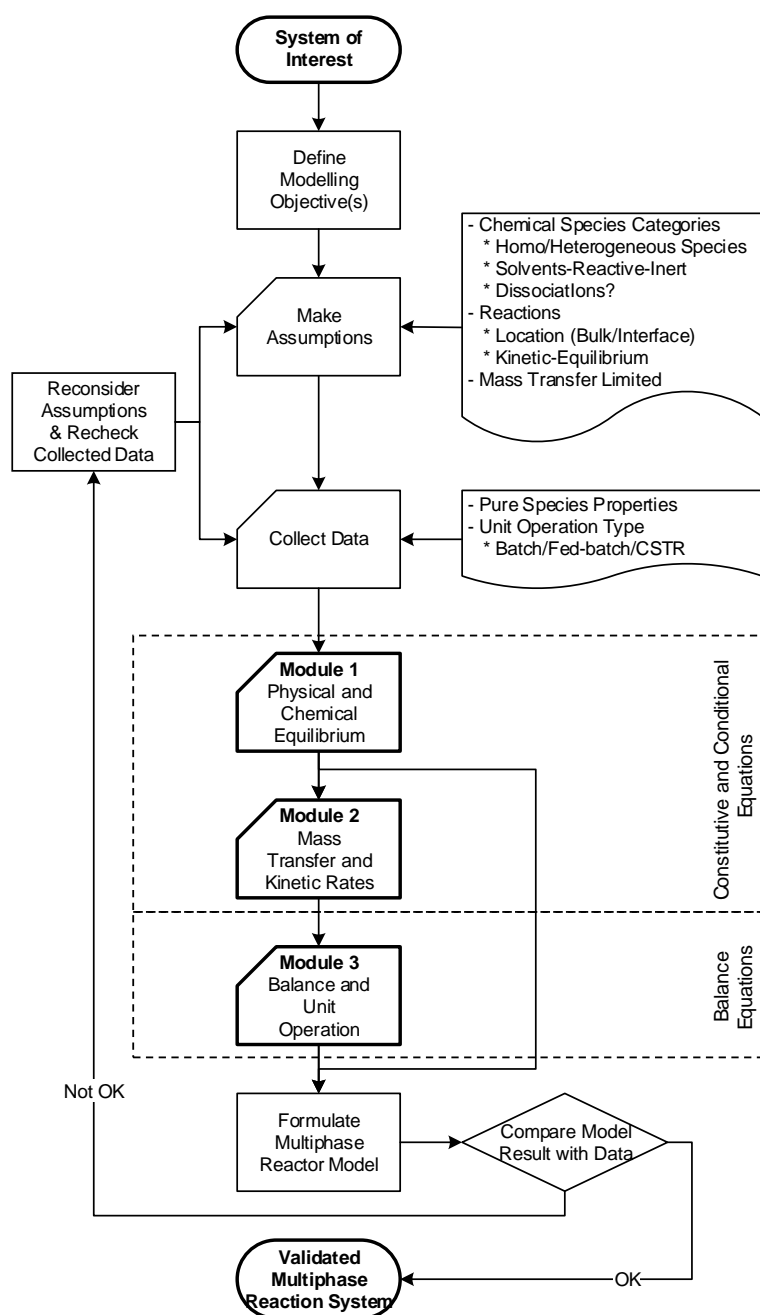
Figure 1: Framework for modelling of the multiphase reacting systems

Module 1 describes phase equilibrium of heterogeneous species. This yields the partition coefficient of each heterogeneous species, P_i, defined as the ratio of the phase mole fractions of the species. Phase equilibrium relations with a pure component standard state, give Eq(1).

Module 2 develops relations for the reaction rates and mass transfer rates through the interface. Our generic rate model, based on non-elementary reaction rate laws, is given by Eq(2); while the equilibrium constant ($K_{Eq,j}$) is calculated from the Gibbs energies of formation.

Module 3 develops the mass balances of the reactive species in the particular reactor system. The generic balance equations connect with the rate equations through extents of reaction, as in Eq(3).

If dissociated species are present, Eq(4) is used to initialize amounts of cation and anion species. Then, the generic balance equation for species i in phase α is formulated as Eq(5).

$$P_i \equiv \frac{x_i^\beta}{x_i^\alpha} = \frac{\gamma_i^\alpha}{\gamma_i^\beta} \tag{1}$$

$$R_j = k_j S \left(\prod_i \left(C_i \gamma_i \right)^{\varepsilon_{ij}^>} - \frac{\prod_i \left(C_i \gamma_i \right)^{\varepsilon_{ij}^<}}{K_{Eq,j}} \right) \tag{2}$$

$$\frac{d\xi_j}{dt} = R_j V_j \tag{3}$$

$$N_{i\pm}^0 = \sum_k \left(N_{ik}^0 + N_{ki}^0 \right) \tag{4}$$

$$N_i^\alpha = N_i^0 + \sum_j \nu_{ij} \xi_j + F_i^0 t - F_i t - N_i^\beta \tag{5}$$

Depending on the reactor type, the inlet and outlet flows can be zero (batch), a continuous function (CSTR), or a pulse function (Semibatch).

Once the mathematical model equation set is established, any undetermined parameters must be regressed to data or estimated. Typically, the rate constants are unknown, so reactant and product evolution measurements are needed. Such experiments can also validate the rate law and mass transfer assumptions. Phase equilibrium parameters may also be obtained from data, but estimation methods, such as group contributions, can also be used for activity coefficients and other thermodynamic properties. When the relations are formulated, different design and analysis problems can be solved, depending on the specifications of known and unknown variables, as well as of the substances involved.

3. Application

3.1 General process description

Production of pyrethroid-class compound, as shown in Figure 2, start with three reactants, sodium cyanide (NaCN), acid chloride (AC), and cyclic anhydride (RA). Initially, the AC is transferred between the organic phase and the interface for the reaction to produce pyrethroid. It can also react with trace of water in the organic phase, producing acid hydroxide (AOH), which undertaken further reaction to product acid anhydride (AA). The AA is then hydrolyzed back to AOH and partitioned between the organic and the aqueous phases. The AOH in the aqueous phase dissociates and transfer to the interface for the pyrethroid production reaction. While, the cyclic aldehyde (RA) is reacted with cyanide ion (CN⁻) and produced cyano-cyclic compound (RCN⁻), which also transfer to react at the interface.

3.2 Model construction

A mathematical model has been constructed for the production of the pyrethroid-class compound a multiphase batch reactor described above.

In module 1, partitioning of the 9-heterogeneous species: AC, AO⁻, AOH, H_2O, RA, OH⁻, RCN⁻, HCl, and P are expressed as generic species i in Eq(6).

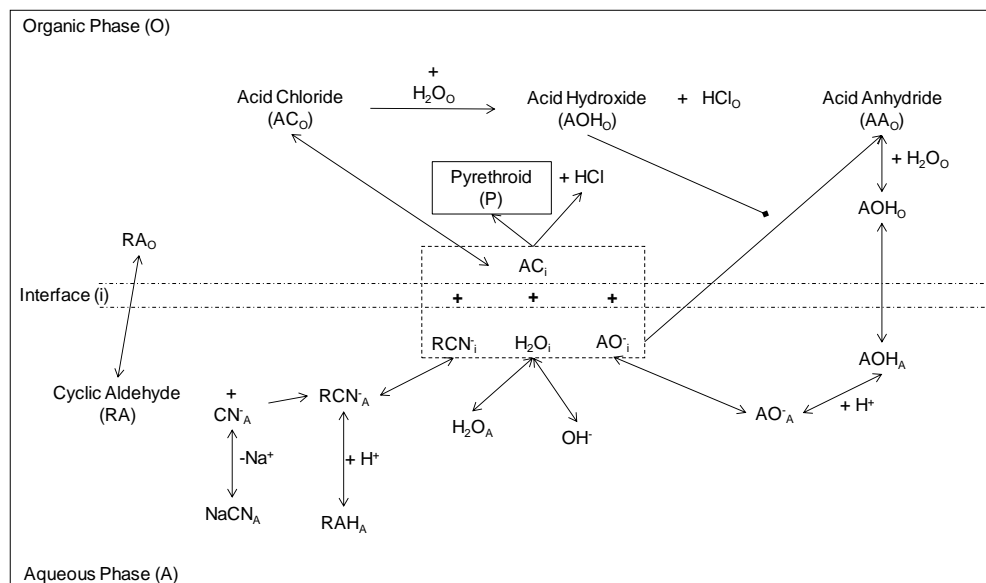$$P_i = \frac{\gamma_i^\alpha}{\gamma_i^\beta} \tag{6}$$

Figure 2: Pyrethroid-class compound production in multiphase reactor

In module 2, there are five kinetically-driven reactions, nine mass transfers to or across the interface of heterogeneous species, and three instantaneous equilibrium-controlled reactions. Only the five kinetically-driven rate equations are presented here in Eq(7) - Eq(11).

$$R_1 = k_1 C_{AC} C_{H_2O} \tag{7}$$

$$R_2 = k_2 C_{AOH} C_{AO^-} \tag{8}$$

$$R_3 = k_3 C_{AA} C_{H_2O} \tag{9}$$

$$R_4 = k_4 C_{RA} C_{CN^-} \tag{10}$$

$$R_5 = k_5 C_{AC} C_{RCN^-} C_{AO^-} C_{H_2O} \tag{11}$$

Since there are twenty reactive species, in which 9 are dissociated species and 2 non-dissociated species, the balance equations will not be displayed here.

The kinetic parameter regression was done with a successive quadratic programming (SQP) method (Sales-Cruz and Gani, 2003), the equilibrium constants and partition coefficients are calculated from the group contribution method, where the activity coefficients in the aqueous phase are calculated from the model developed by Kim et al. (Kim et al., 2016) with the parameters presented in the earlier work (Anantpinijwatna et al., 2016) and the activity coefficients in the organic phase are calculated by UNIFAC model (Constantinescu and Gmehling, 2016).

4. Results

The experiments are conducted in an atmospheric lab-scale batch reactor at 18 difference initial amount of sodium cyanide, acid chloride, cyclic anhydride, and solvents. Five sets of experiments are used for parameter regression, the values of regressed kinetic parameters are shown in Table 1. The graphical comparison between measured data (dot) and model calculated value (line) of the five selected experimental sets are displayed in Figure 3.

The parameters are then used to calculate the production amount of pyrethroid-class compound with other operating condition, where the graphical comparison of every experimental set is displayed in Figure 4. Ultimately, the overall average absolute deviation of all sets is 2.43 %.

Table 1: Regressed kinetic parameter value

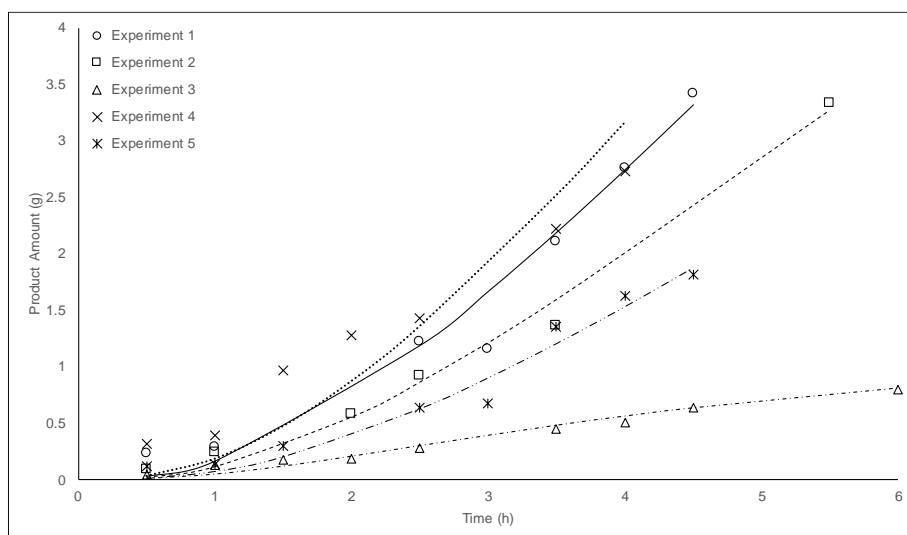| Parameter	Value
k_1	5.288
k_2	0.272
k_3	1.87×10^{-8}
k_4	6.12×10^{-3}
k_5	4.30×10^{-2}

Figure 3: Production amount of pyrethroid-class compound at various initial conditions comparing between model prediction and measured data of experimental sets 1, 3, 10, 15, and 18
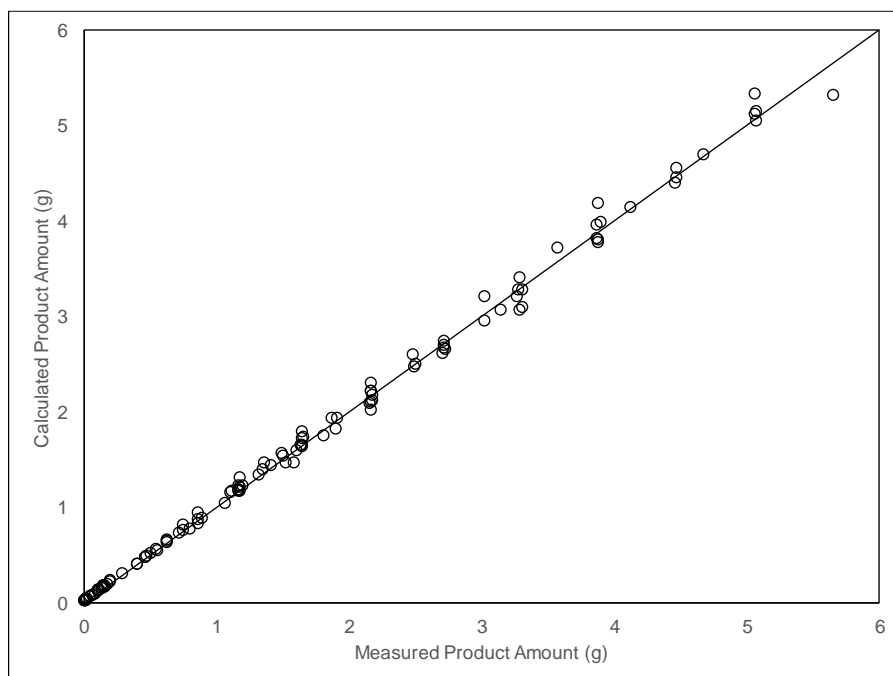

Figure 4: Production amount of pyrethroid-class compound at various initial conditions comparing between model prediction and measured data

5. Conclusions

A modelling framework for multiphase reacting systems has been implemented for the complex pyrethroid-class compound production process. The framework allows the construction of problem-specific models for different reaction conditions. With the implementation of group-contribution based thermodynamic model, number of unknown parameters is reduced to only kinetically-related parameters. The model is successfully matched with the measured data at different condition and requires only minimum amount of measured data to make a wide range of predictions. The optimization of this process by changing the organic solvent and feed scheme can be performed with the current stage of the study.

Nomenclature

Subscripts/ Superscripts

0	Initial condition
α, β	Phases (α is normally aqueous phase and β is normally organic phase)
i	Chemical species
j	Reaction

Variables

C_i	Concentration of species i
F_i	Flows of species i
G_j	Standard Gibbs free energy change for the reaction j
k_j	Rate coefficient of reaction j
$K_{Eq,j}$	Equilibrium constant of reaction j
N_i	Molar amounts of species i
R	Universal gas constant
R_j	Rate of reaction j
S	Effective area per volume
T	Temperature
V_j	Volume of the phase where the reaction j occurs
ε_{ij}	Orders of reaction for species i in reaction j
ξ_j	Extent of reaction j
γ_i^α	Activity coefficient of species i in phase α
ν_{ij}	Stoichiometric number of species i in reaction j

References

Aljbour S., Tagawa T., Matouq M., Yamada H., 2009, Multiphase surfactant-assisted reaction-separation system in a microchannel reactor, Frontiers of Chemical Engineering in China, 3, 33–38.

Anantpinijwatna A., Sales-Cruz M., Kim, S.H., O'Connell J.P., Gani R., 2016, A systematic modelling framework for phase transfer catalyst systems, Chemical Engineering Research and Design, 115, 407–422.

Borges M.E., Ruiz-Morales J.C., Martín-Zarza P., Esparza P., 2017, Biodiesel Production from Waste Oil in Multiphase Reactors with Bifunctional Catalyst for Sustainable Energy, Springer, Singapore.

Coelho P., Meinhold P., Chen M.M.Y., 2015, Synthesis of pyrethroids and pyrethroid-containing compositions, US Patent 9487471B1.

Constantinescu D., Gmehling J., 2016, Further Development of Modified UNIFAC (Dortmund): Revision and Extension 6, Journal of Chemical & Engineering Data, 61, 2738–2748.

Kim S.H., Anantpinijwatna A., Kang J.W., Gani R., 2016, Analysis and modeling of alkali halide aqueous solutions, Fluid Phase Equilibria, 412, 177–198.

Long Z., Chen G., Liu S., Huang F., Sun L., Qin Z., Wang Q., Zhou Y., Wang J., 2018, Synergistic combination of graphitic C 3 N 4 and polyoxometalate-based phase-transfer catalyst for highly efficient reductant-free aerobic hydroxylation of benzene, Chemical Engineering Journal, 334, 873–881.

Qiao C., Cai Y., Guo Q., 2008, Benzene alkylation with long chain olefins catalyzed by ionic liquids: a review, Frontiers of Chemical Engineering in China, 2, 346–352.

Sales-Cruz M., Gani R., 2003, A modelling tool for different stages of the process life, Computer Aided Chemical Engineering, 16, 209–249.

Thatheyus A.J., Gnana Selvam A.D., 2013, Synthetic Pyrethroids: Toxicity and Biodegradation, Applied Ecology and Environmental Sciences, 1, 33–36.

Umemura T., Hirohara H., 1989, Preparation of Optically Active Pyrethroids via Enzymatic Resolution, ACS Symposium Series, 389, 371–384.