CHAPTER III
METHODOLOGY

3.1 Equipment and Software

3.1.1 Equipment

Desktop computer (Intel® Core™ 2 Duo CPU T5900 2.20 GHz, 2 GB of RAM, Windows 7 and Microsoft Office 2010)

3.1.2 Software

- ICAS version 15
- GAMS version 21.2
- PROII version 9.1
- ECON software

3.2 Task and Description of Work

3.2.1 Literature Review Study

- Find out related literatures and study the fundamental knowledge about separation processes of azeotropic mixtures with a focus on extractive distillation using heavy entrainer.
  - Study a general definition, a thermodynamic explanation, a physicochemical explanation and a category of azeotropes or azeotropic mixtures.
  - Study a separation process technology of azeotrope.
  - Study an extractive distillation technology.
  - Study a condition and technique of separation in an extractive distillation and selective solvents as entrainers.
  - Study a general definition, structure and property of ILs.
  - Study a use and application of ILs especially ILs as entrainers in an extractive distillation for both aqueous and non-aqueous systems.
  - Study a group contribution of Hildebrand solubility parameter model for ILs proposed by Roughton *et al.* (2012).

- Study a group contribution of critical property model for ILs proposed by Valderrama *et al.* (2009).
- Study a phase equilibrium and binary parameter model for ILs such as COSMO-RS, UNIFAC, NRTL models.

• Study the previous systematic screening methodology for screening of ILs and for design of the best IL-based separation processes proposed by Kulajanpeng (2014), which is shown in Figure 2.12.

- Review all steps of this proposed methodology.
- Study original concepts of this proposed methodology.
- Study details of screening criteria and conceptual simulation design of azeotropic separation processes with ILs.
- Study the importance of stability of ILs.
- Study the key target property of ILs with target solute in an azeotropic mixture i.e. miscibility or mole fraction of ILs in water for an aqueous system and in benzene for a non-aqueous system.
- Study the extended Hildebrand solubility parameter model for ILs from Group Contribution (GC) concepts.
- Study ICAS program to generate VLE graph.
- Study NRTL binary parameters to input in ICAS program.
- Study PROII program to simulate the separation processes of azeotropic mixtures with ILs as entrainers in an extractive distillation.
- Study how to optimize the separation processes and design the flexibility of azeotropic series.
- Summarize all data and parameters needed for the proposed methodology.

3.2.2 Investigation of the Viability in Other Systems of the Previous Systematic Methodology for Screening of ILs and Design of IL-Based Separation Processes

• Investigate pros and cons of this proposed methodology from demonstrating in the other systems especially in non-aqueous system.

- Examine a group contribution of the extended Hildebrand solubility parameter model to be suitable for further demonstrating in non-aqueous systems.

- Examine the key target property of ILs with target solute in an azeotropic mixture as the miscibility or mole fraction of ILs in other target solutes related to the screening criteria i.e. whether feasible IL candidates are completely miscible, the miscibility or mole fraction of ILs in that target solute should be over unity or not.

- Examine the viability of NRTL binary parameters model in other non-aqueous systems along with checking other alternative models such as COSMO-RS and UNIFAC (in a case of no enough NRTL binary parameters supported in non-aqueous systems).

- Examine the conceptual simulation design of the best IL-based separation process and recovery technology of ILs using a flash evaporation along with a stripper originally proposed by Roughton *et al.* (2012).

- List all weak points found from this proposed methodology.

3.2.3 <u>Improvement of the Previous Systematic Methodology for Screening of ILs and Design of IL-Based Separation Processes</u>

- Improve the screening criteria

- Use capacity and selectivity of ILs as initiated from Topphoff *et al.* (1999), Meindersma *et al.* (2010) and Meindersma *et al.* (2010) instead of the previous key target as the miscibility or mole fraction of ILs since there is no enough experimental miscibility of ILs in other systems and it is difficult to update data of ILs continuously.

- Keep using the Hildebrand solubility parameter revised by Kulajanpeng (2014) and the database to cover both conventional solvents and ILs for non-aqueous system.

- Make new screening criteria using new screening graph (i.e. Hildebrand solubility parameter of ILs in *x-axis* vs Capacity of ILs in *primary y-axis* and Selectivity of ILs in *secondary y-axis*) and target window (i.e. the minimum and maximum of Hildebrand solubility parameter, capacity and selectivity of ILs) for screening the feasible IL candidates.

- Improve the verification of ILs through VLE graph.

- Consider additional NRTL binary parameters calculated from LLE experimental extraction beyond VLE data.

- Consider additional hand calculations of critical property model proposed by Valderrama *et al.* (2009) for other ILs not included in the literature database.

- Observe the bell-shaped curve of ILs from a good performance of separation capability of ILs to break azeotrope or increase relative volatility through VLE graph and then compare each other to consider roughly the best IL.

- Improve the conceptual simulation design of the best IL-based separation processes for azeotropic mixtures.

- Use the Fenske calculation through the short-cut distillation in PROII for determining the first guess of the number of theoretical stage of EDC.

- Use only a simple flash evaporation as a recovery technology of ILs to be the fundamental process for comparison and the development in advance since the previous recovery technology of ILs (i.e. flash evaporation along with stripper) has been not accepted to employ in generic systems mentioned by (Hernández (2013)).

- Simulate initially the conventional solvent process and then use the same condition of EDC to employ in IL process. In addition, to compare among different entrainers, some operating conditions and the purity of feed and products were fixed.

3.2.4 Improved Systematic Methodology of Selection and Design of the Best IL-Based Separation Process for Azeotropic Mixture in Generic Systems

The improved systematic methodology has been divided into three main stages; selection, verification and comparison, which is shown in Figure 3.1.

- Selection
  - Add the mixture selection step.
    - Classify the problem mixture and select the case studies.
  - Add the separation process selection step.

o Use extractive distillation technology for ILs.

- Use the developed screening criteria of IL pre-selection step.

o Make screening graph and target window for selecting the feasible IL candidates.

- Verification

- Add the verification of mixture step.

o Investigate the behavior of mixture and confirm the target solute using ProPred and ICAS program.

- Use the developed verification of IL step.

o Investigate the capability separation of ILs for breaking azeotropes and increasing relative volatility of mixture through VLE graph.

- Comparison

- Add VLE comparison step.

o Observe the best IL from a good performance of separation capability through VLE graph.

- Use the developed simulation step.

o Observe the best IL from the simulation process based on the most minimum energy requirement and solvent usage compared to other ILs and conventional solvents.

- Add economic comparison step.

o Evaluate the best ILs from the capital costs (CAPEX) and operating costs (OPEX) using ECON software.

o Calculate the economic cost ratio of IL by CS, $(X_{IL}/X_{CS})_{econ}$, that gave $NPV_{IL}=NPV_{CS}$ using ECON software.

3.2.5 Validation

- Apply the improved methodology to demonstrate through five case studies; ethanol + water, ethanol + hexane, benzene + hexane, toluene + methylcyclohexane (MCH), and ethylbenzene (EB) + P-xylene (PX) mixtures.
- Summarize and list out all exceptions and recommendations which might be found during the demonstration.

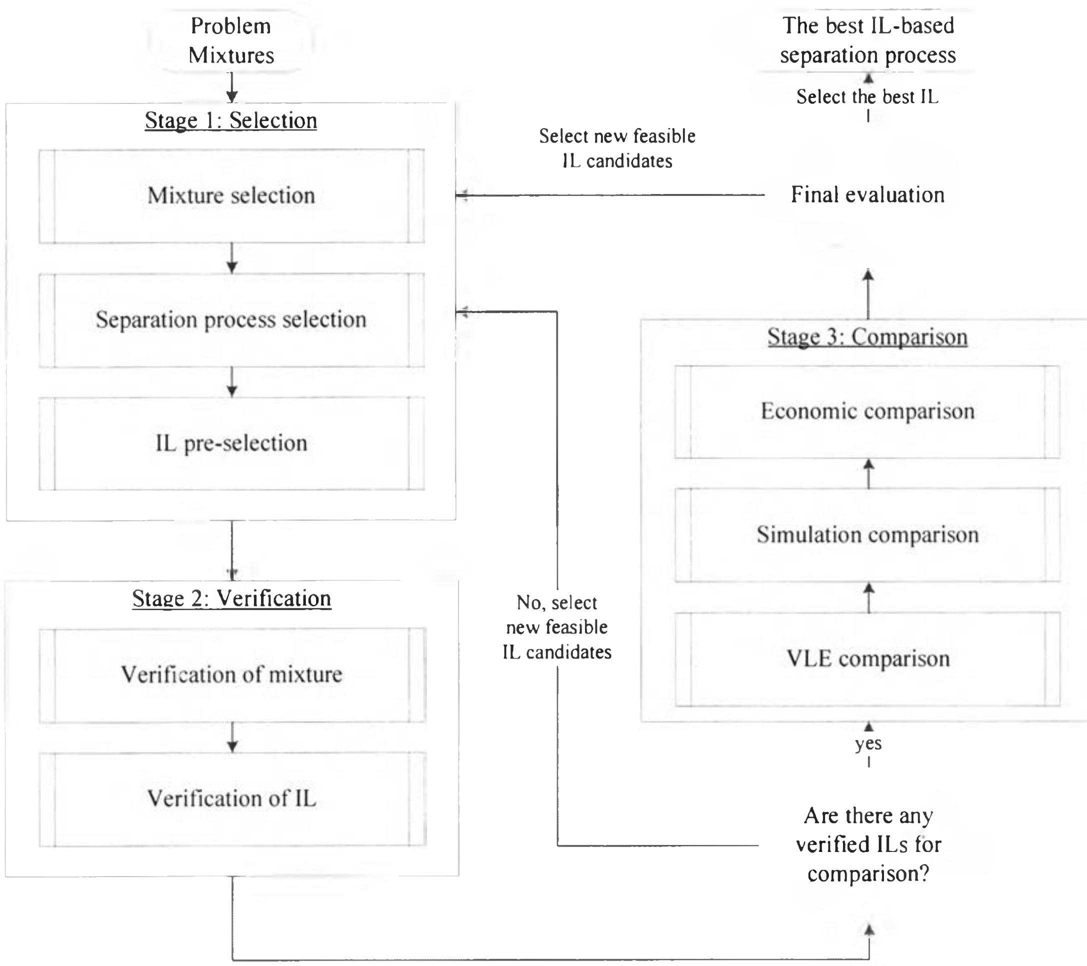

Figure 3.1 Improved systematic methodology of selection and design of the best IL-based separation process for azeotropic mixture in generic systems.