

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

Theoretical background

First of all, the fundamental concept with respect to process integration (Process synthesis, analysis, and optimization) was explained briefly. Then, the overview of the water network system and design would help point out the significance and principle in this area. This was followed by the basic concept associated with water and wastewater use and management (in petroleum refinery) so as to be able to apply in water/wastewater network and system design. Eventually, a summary of theoretical background involving with the integrated solutions framework in the synthesis and design of processing networks was introduced emphasizing on application and development.

2.1 Process Integration

A chemical process is an integrated system associated with interconnection of units and streams. The management of problem in process should not be specific for behaviour of problem but should identify the root causes of such problems through the implementation of the process as a whole. Effective modification and process synthesis have to be considered on for the integrated nature. Hence, the resource of process integration is a key element in designing as well as operating with cost-effective and sustainability in processes (El-Halwagi, 2012).

“ Process integration is a holistic approach to design, retrofitting, and operation for the unity of the process ” (El-Halwagi, 1997). For interactions among process units, resources, streams, and objectives, process integration provides an identical framework together with a proficient set of methodologies and enabling tools for sustainable design. The prominence of process integration stems from its ability to systematically provide as follows:

- Basic comprehension for the global insights of a process and the root that leads to the limitation of performance
- The ability to benchmark for the performance of various objectives for the process ahead of detailed design through targeting techniques
- Effective generation and screening of solution alternatives to accomplish the optimal design and operational strategies (El-Halwagi, 2012).

2.1.1 Process Synthesis

Synthesis involves interconnecting of separate elements or putting them together into a coherent whole. Westerberg (1987) defined a process synthesis as: “ *the discrete decision-making activities of conjecturing which of the many available component parts one should use, and how they should be interconnected to structure the optimal solution to a given design problem* ”.

Process synthesis is associated with the activities in which several process elements are incorporated and the system flow sheet is created in order to undergo certain objectives. Consequently, the goal of process synthesis (Johns, 2001) is “ *to optimize the logical structure of a chemical process, specifically the sequence of steps (reaction, distillation, extraction, etc.), the choice of chemical employed (including extraction agents), and the source and destination of recycle streams* ”. In process synthesis, inputs and outputs of-process are needed to improve the structure and parameters of the flowsheet (for retrofitting design of an existing plant) or even create a new flowsheet (for grassroots design of a new plant) as shown in Figure 2.1 (El-Halwagi, 2006).

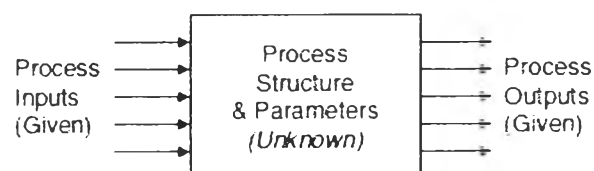


Figure 2.1 Process synthesis problems (El-Halwagi, 2006).

Generally, a few process alternatives based on experience and corporate preferences without a systematic approach are synthesized. The selection of the alternative and most promising economic potential and using it as the optimum solution may not guarantee the real optimal solution. However, there are two main approaches that can be employed to identify the optimal solution: the structure independent and structure based approaches (El-Halwagi, 1997). The structure independent (or targeting) approach is based on the synthesis through a sequence of stages. A design target can be identified within each stage and applied in subsequent stages. Whereas, the latter approach is the structure based which involves with a development of a framework by embedding all possible configurations of interest.

Two important process synthesis models are the hierarchical approach and the “onion model”. The hierarchical approach to process design is a generic methodology for outlining the conceptual flow sheet of a process that consists of: 1. Batch vs. continuous, 2. Input-output structure of the flow sheet, 3. Recycle structure of the flow sheet, 4. General structure of the separation system: Vapour and Liquid recovery system, 5. Heat exchanger network (Foo *et al.*, 2005). For the latter, Smith (2005) presented the onion model (Figure 2.2) as an alternative way to represent the hierarchical approach for process design. Process design begins at the centre of the onion, with the reactor and proceeds outward. The reactor designs influence the separation and recycle systems (the second layer of the onion) which are designed next. The reactor as well as separator and recycle system enforce the amount of overall heat recovery; therefore, the heat recovery network system is designed next. Then, the process utility system is designed to provide additional heating and cooling requirements that cannot be satisfied through heat recovery. Finally, the water and effluent treatment are designed to meet the environmental regulation (Smith, 2005). The model emphasizes on the sequential and hierarchical nature of process flow sheet synthesis (Hashim *et al.*, 2009).

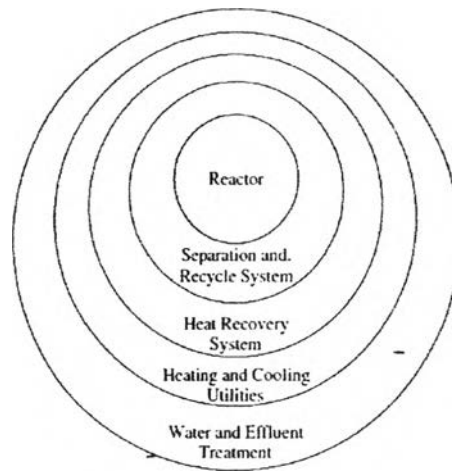


Figure 2.2 The onion model of process design (Smith, 2005).

2.1.2 Process Analysis

Whereas the process synthesis intended to combine the process elements into a coherent whole, process analysis relates to the decomposition of the whole process into its constituent elements for each individual study performance. Therefore, process analysis can be contrasted and complemented with process synthesis. Once an alternative is generated or a process is synthesized, its detailed characteristics (such as flow rate, compositions, temperature, and pressure) are predicted using analysis techniques.

The approaches include mathematical models, empirical correlations, and computer-aided simulation tools. Furthermore, process analysis may involve forecasting and validating performance through lab and pilot-plant scales, and even actual runs of existing facilities. Hence, the process inputs together with the process structure and parameters are known in process analysis problems while the process outputs are required to determine as shown in Figure 2.3 (El-Halwagi, 2006).

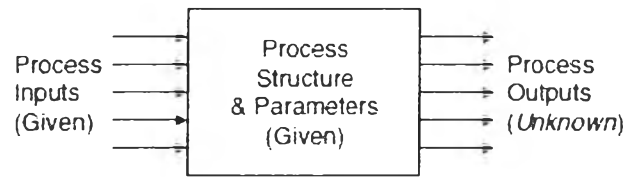


Figure 2.3 Process analysis problem (El-Halwagi, 2006).

2.1.3 Process Optimization

Process optimization involves specific techniques where the best solution from among a set of candidate solutions is selected. The level of a solution is quantified by an objective function (e.g. cost, profit etc.) which is to be minimized or even maximized. However, the search process is undertaken subject to the system model and limitations which are termed as constraints. These constraints may be in the forms of equality (material and energy balances, process modelling equations and thermodynamic requirements) or inequality (environmental policies and regulations, technical specifications and thermodynamic limitations) (El-Halwagi, 1997). The optimization component in process integration enforces the iteration procedure between synthesis and analysis towards optimum. In many cases, optimization is also used within the synthesis activities. For instance, the various objectives are reconciled using optimization in the targeting approach for synthesis (Hashim *et al.*, 2009).

General formulation of an optimization problem (Seider *et al.*, 2004)

The formulation of an optimization problem involves:

1. A set of $N_{\text{variables}}$ variable, \underline{x}
2. The selection of a set of suitable decision variables, \underline{d} from the set \underline{x}
3. A measure of goodness called an objective function, $f(\underline{x})$
4. A set of N_{equation} equality constraints, $\underline{c}(\underline{x}) = 0$
5. A set of N_{inequal} inequality constraints, $\underline{g}(\underline{x}) \leq 0$
6. Lower and upper bounds on some or all of the variables, $\underline{x}^L \leq \underline{x} \leq \underline{x}^U$

A general optimization problem is stated as follows:

Minimize (or maximize) with respect to \underline{d} , the design variables

$f(x)$, the objective function

subject to (s.t.):

$c(x)=0$, the equality constraints

$g(x)\leq 0$, the inequality constraints

$\underline{x}^L \leq x \leq \underline{x}^U$, the lower and upper bounds

2.2 Water Network and System Design

2.2.1 Introduction

Water is utilized in several processes from different industries, while the contaminants are transferred to water and wastewater must be eliminated in treatment processes prior to discharge to the environment. However, the awareness of the danger to the environment caused by wastewater is increasing. In some areas, water using is limited in the future. Meanwhile the imposition of rigorous discharge regulation drives up the cost of treatment, requiring capital expense with little or no productive return. Figure 2.4 illustrates a schematic of a typical water and effluent system for a processing site. Raw water enters the process and might need any pretreatment (such as sand filtration).

In many situations, the quality of the supplied raw water is good enough and can be fed to the processes directly. Water is utilized in several operations as an intermediate for reaction, for cleaning, and so on. Water turns into contaminated water and is discharged. In Figure 2.4, some raw water is required for the steam system. However, before entering the steam boiler, it is needed to be treated to dispose suspended solid, dissolved salts and gases to qualify the boiler feed water (BFW) specification. Additionally, deionized water might be required in some processes. The steam from the boilers is divided and some of the steam condensate lost to effluent. To remove solids, the boiler requires blowdown. Dissolved salts are removed by the ion exchange beds and soluble ions require to be regenerated by saline solutions or acids and alkalis and

the contaminants go to discharge. In the end, the evaporative losses and blowdown from the cooling water circuit are made up by evaporative cooling systems as shown in Figure 2.4. All of the effluents is combined, together with contaminated storm water, then is treated in a treatment system and discharged to the surroundings. Reuse/recycle of water is not only save the cost of supplied freshwater but also the cost of effluent treatment. Hence, it is motivated to reduce both freshwater requirement and wastewater generation by water reuse/recycle.

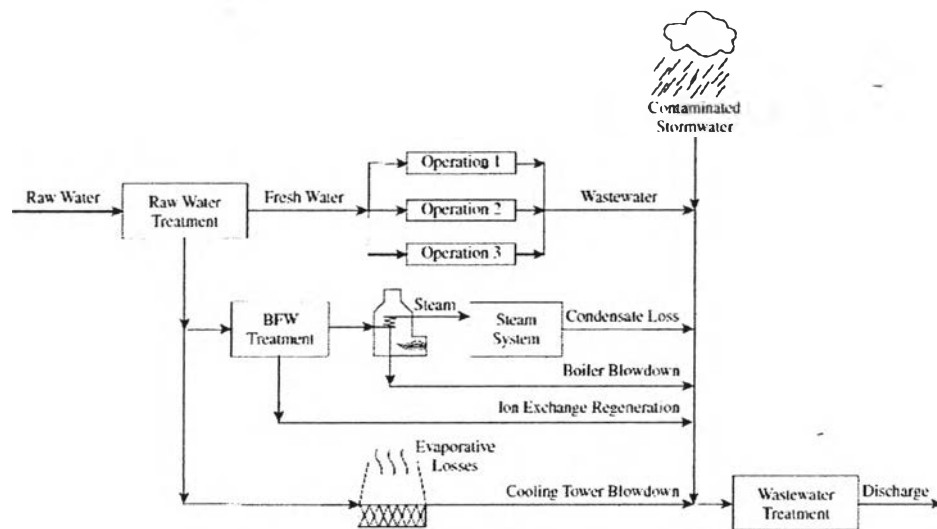


Figure 2.4 A typical water and effluent treatment system (Smith, 2005).

Figure 2.5a shows three operations that require freshwater and produce wastewater. In the contrary, Figure 2.5b shows an arrangement for a reuse of water from Operation 2 to Operation 1. Water reuse in this way decreases wastewater twice. However, any contamination degree at the outlet of operation 2 must be satisfied at the inlet of operation 1.

Figure 2.5c and Figure 2.5d both show the arrangements with respect to regeneration. Regeneration is any treatment process that regenerates the quality of the water so that it is acceptable for most use. Figure 2.5c shows the regeneration reuse where the contaminated outlet water from operation 2 is used directly in Operation 3. The regeneration reuse decreases both the freshwater consumption and the wastewater generation. The water reuse also removes some of

the effluent load (such as kilograms of contaminant) and otherwise removed in the effluent treatment before discharge.

The last option is shown in Figure 2.5d where a regeneration process is used on the outlet water from the operations and the water is recycled. The difference between the regeneration reuse shown in Figure 2.5c and the regeneration recycling shown in Figure 2.5d is the water in regeneration reuse only moves through any operation once. Figure 2.5c shows that the water goes from operation 2 to regeneration, then to operation 3 and finally discharge. Conversely, in Figure 2.5d, the water can go through the same operation. Regeneration recycling not only reduces the amount of freshwater and wastewater but also reduces the effluent load.

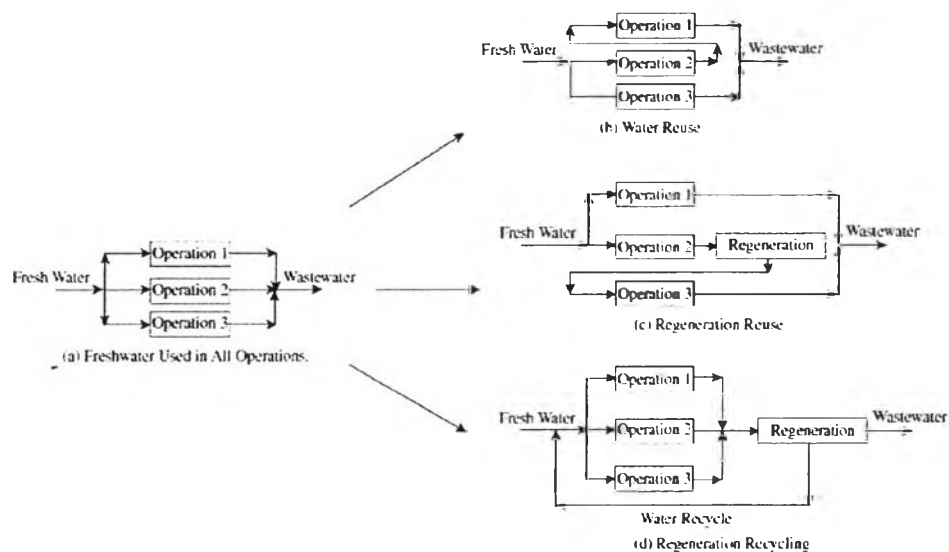


Figure 2.5 Water reuse and regeneration (Smith, 2005).

Although regeneration reuse and recycling are similar in terms of their results, regeneration recycling provides larger reductions in the volume of freshwater and wastewater usage. However, regeneration recycling is confronted with many problems because of the high regeneration costs. Moreover, the recycling may build up the undesired contaminants in the recycle, such as microorganisms or corrosion. These contaminants cannot be removed in the regeneration and cause problems in the process.

Apart from centralized effluent treatment as shown in Figure 2.4, another approach to tackle with the effluent treatment is the distributed effluent treatment or segregated effluent treatment as illustrated in Figure 2.6. In addition to water reuse between Operation 2 and Operation 1, distributed treatment is added to the outlet of Operation 1 and Operation 3. Then all of the outlets are combined and fed to the final wastewater treatment and discharge. The arrangement in Figure 2.6 features the combination of a number of the effluents before discharge. The more contaminated effluents from the Operations 1, 2 and 3 require to be diluted by the less contaminated streams before being treated and discharged in the arrangement in Figure 2.4. On the contrary, the pretreatment on the outlet of Operation 1 and Operation 3 is not required the dilution before final effluent treatment and discharge, as shown in Figure 2.6. Thus, the streams with only low contamination no longer need to be treated.

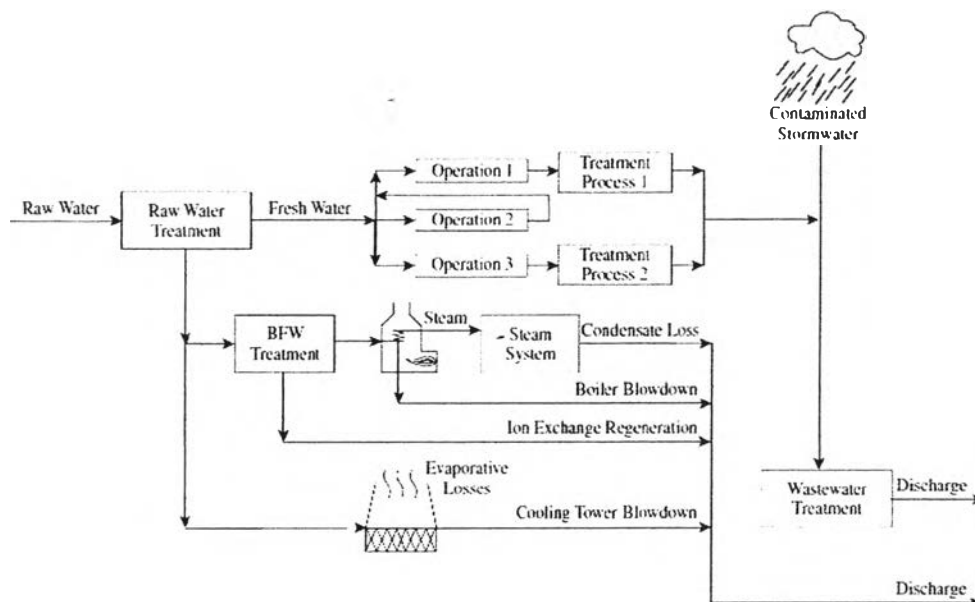


Figure 2.6 Distributed effluent treatment (Smith, 2005).

Generally, the capital cost of treatment operations is proportional to the total wastewater flow rate while the operating cost increases with the decrease of removing contaminant level. Consequently, if two streams need different treatment

technologies, it is not necessary to combine and treat the two streams in both treatment operations that will raise both capital and operating costs. The distributed effluent treatment is to treat the effluents that requires a specific treatment to particular contaminants. The advantage is to avoid combining and to increase the potential for material recovery, and, consequently, to generate less waste and lower cost of raw materials. Before developing water system design in a systematic way, one has to first take into account the general issues with respect to water contamination and treatment (Smith, 2005).

2.2.2 Analysis of Water Network Problems

Typically, Water is utilized in separation processes (i.e. extraction, absorption or distillation with steam) where water serves as a separating agent for mass exchange operations. In addition, water is necessary to wash various types of equipment as well as to consume in steam boilers and in cooling water cycles.

The minimization of fresh water use or the wastewater minimization has been the focus of many researchers. The decrease of the volume of fresh water and wastewater discharge has become one of the important design targets and optimization (Hashim *et al.*, 2009). As a result of the high cost of water treatment processes, the minimization of freshwater usage as well as wastewater generation in process systems is taken into account for environmental and economic significance. Both water-using processes and regeneration/treatment units are the important effects that lead to the optimization of water networks. Finally, zero discharge may be reached (Sieniutycz *et al.*, 2013).

The ways to reduce the amount of freshwater by water network optimization are water to reuse for water-using processes and water regeneration processes through redistributed water treatment. Usually, Fresh water is fed in a parallel arrangement to each water stream using process in existing industrial complexes. The outlet water streams are combined after each process and then moved to central treatment operation (no reuse or regeneration) as shown in Figure 2.7.

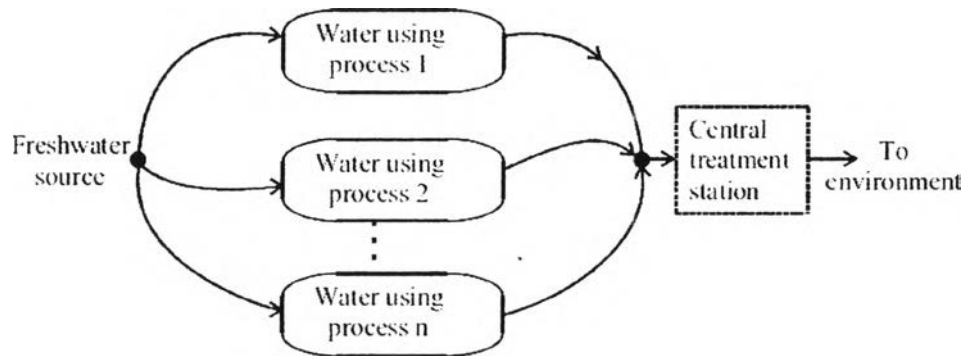


Figure 2.7 Traditional water network: freshwater supplied to processes in parallel with central water treatment station (Sieniutycz *et al.*, 2013).

The above network consumes a high volume of freshwater and also generates a high quantity of wastewater. Hence, Water reuse is applied in the existing process in order to reduce the freshwater requirement in other processes as illustrated in the water reuse network (WRN) in Figure 2.8.

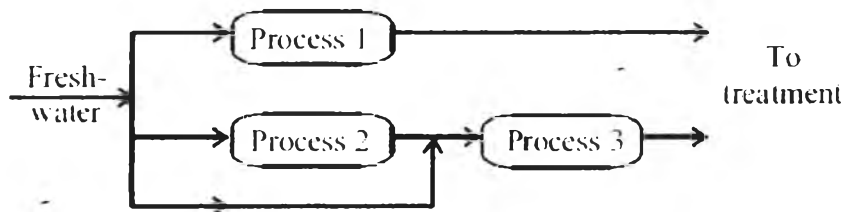


Figure 2.8 Example of water reuse network (WRN) (Sieniutycz *et al.*, 2013).

However, the design and optimization of the WRNs usually do not take into account the wastewater treatments or regeneration processes. Thus, another system namely the water treatment network (WTN) has been developed and the design the water treatment process is treated as a separate subsystem. The network is distributed with mixing and bypassing scheme as shown in Figure 2.9.

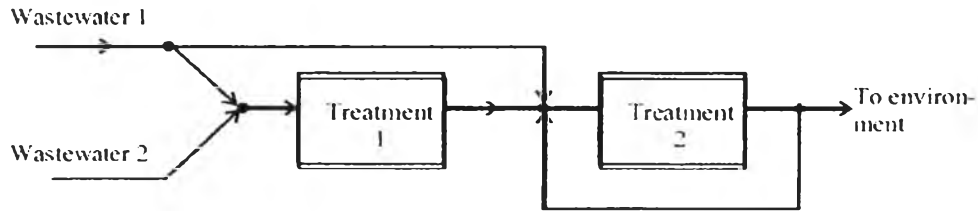


Figure 2.9 Example of distributed wastewater treatment network (WWTN) (Sieniutycz *et al.*, 2013).

The redistributed system has indicated the advantages because of the fact that the treatment cost is proportional to the flow rate of wastewater. Hence, the expense of centralized WWTN is high in most cases due to a total wastewater stream flowing through all treatment units. For a distributed treatment, the streams can be either treated separately or partially mixed, thus reducing the flow rate of the effluent to be processed. However, the segregation or combining the stream for treatment is dependent on an appropriate treatment system design. Therefore, the main objective of the treatment process is to minimize the wastewater flow rate. Figure 2.10 and Figure 2.11 show the application of wastewater regeneration processes within the water using process network that can reduce more both freshwater consumption and wastewater generation. The regeneration is divided into two cases: regeneration without recycles in Figure 2.10 and regeneration with recycles in Figure 2.11.

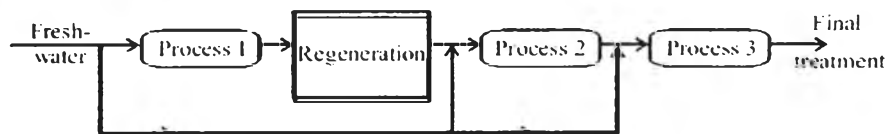


Figure 2.10 Regeneration without recycles (Sieniutycz *et al.*, 2013).

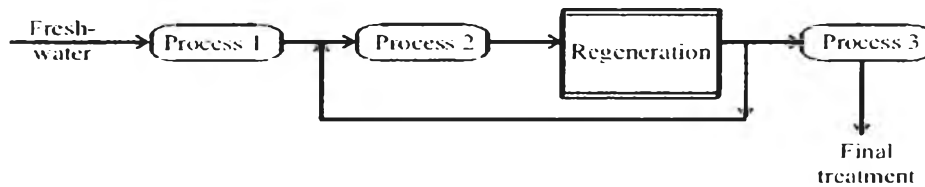


Figure 2.11 Regeneration with recycles (Sieniutycz *et al.*, 2013).

In the past, the regeneration operations in many works were implemented only to reduce freshwater intake. However, none of those works considered the limitation of the contaminant level in the effluents. Thus, it is necessary to cope with the stringent environmental regulation by adding a final treatment. That is contributed to the water network with reuse and regeneration (WNRR). Nevertheless, the difference between regeneration and the treatment processes will become irrelevant when the condition of the environment is limited on the final contaminant level of effluent streams.

As compared to the WUN and WWTN, the total (integrated) water network (TWN) combined both water usage and treatment network (WUTN) as shown in Figure 2.12. In TWN, water discharge to the environment may be possibly eliminated (zero liquid discharge) and it is the ideal solution for industrial sustainability.

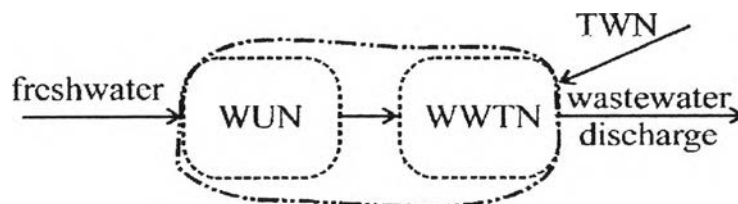


Figure 2.12 The division of a total water network (TWN) on water-using networks (WUNs) and wastewater treatment networks (WWTNs) (Jeżowski, 2010).

Whereas the objective may often focus on the minimization of fresh water consumed and wastewater treated, the total cost (capital and operation cost) should be considered as well. The cost of regeneration or treatment is regarded in WRN, WNRR and TWN design method. However, some methods still involve with the piping cost as well as the number of connections. Additionally, it is possible to apply an environmental impact into the design.

Typically, a total water network includes several water sources, water using operations, along with treatment/regeneration processes and waste disposal sites. The network consists of two important units that are mixers and splitters to redistribute among sources, process and sinks even reuse and regeneration process.

In some systems, batch-wise operation tanks are also taken into account for water using networks while some apply in continuous operation mode. Furthermore, the water network and heat integration can be simultaneously considered since some operations or sites may require a certain water temperature or even a certain phase of water (Sieniutycz *et al.*, 2013).

2.2.3 Approaches to Water Network Design (Overview)

Generally, the approaches to the water network problem can separate into two techniques: insight-based (heuristic or water pinch technique) and optimization-based (systematic- or mathematical-based). The former approach is a simple method but attractive solution. However, the major disadvantage of the water pinch technique occurs when applying to a system with a large number of contaminants. Meanwhile, the latter approach can better deal with a complex problem especially in the case of multiple contaminants, or a system with various constraints (Jezowski, 2010).

2.2.3.1 *Insight-based Method*

The limiting composite curve diagram is the first and may be the strongest insight-based method. This is called the water pinch method. The idea of water pinch targeting is rather associated with the composite curve (CC) plot in the heat pinch analysis, especially, the water composite curve which is targeting for a minimum flow rate of freshwater in the water using network (WUN). In addition, the same concept and technique can be applied to the wastewater treatment network (WWTN). The same concept employed in the existing targeting approaches for

identifying the minimum utilities in the heat pinch analysis is also implemented in the water network to compute the fresh water and wastewater targets (Jeżowski, 2010). In several researches, the mathematical optimization technique has been developed and applied in the water network design to deal with the difficulties and limitations of the water pinch approach.

2.2.3.2 *Optimization-based Method*

This method is usually employed for a superstructure optimization problem to perform simultaneous calculations in several steps to identify the (global) optimum solution. Additionally, some automated targeting methods combine both pinch insight and optimization. It is noted that solving the superstructure of water using network without regeneration processes is easier than solving the heat exchanger network problem because of the fixed number of water using processes. Other benefits of the optimization approach include the capability to carry nonlinearities and all topological issues. However, the superstructure formulation can be more complex depending on the number of treatment units as well as the number of apparatuses and their arrangement.

Even though, most superstructure are frequently proposed for mass-transfer water using processed, the non-mass transfer units are also included straightforwardly. This signifies the flexibility of the method which is a significant advantage. The specific conditions such as the sequential arrangement of treatment units can be embedded and simply modified by the superstructure as well.

Typically, the superstructure model may include binary variables to account for fixed cost of equipment investment charges as well as for topological constraints. It is difficult to solve for resulting complex MINLP formulation, especially when seeking a global optimum and has to address a large scale problem. However, there are several ways to cope with such difficulty and they are divided as follows:

- (1) Direct linearization
- (2) Generation of “good” starting point(s)
- (3) Sequential solution procedure
- (4) Meta-heuristic optimization approaches
- (5) Global (deterministic) optimization

- Direct linearization

For non-mass transfer processes, a fixed outlet concentration will be defined for a linearity of constraints in a water using network both with and without regeneration processes. For mass transfer processes, single contaminant problem can be easily linearized by assuming the optimal conditions that were proven by (Bagajewicz *et al.*, 2001). The conditions state that processes using freshwater must feature the maximum outlet concentration of at least one component (called the key component). Also, the condition of concentration monotonicity was derived and proven for the key component. These necessary conditions correspond to the optimal water allocation planning problem that considers wastewater reuse and where the objective is to minimize the fresh water consumption. In case of multiple contaminants, the model is linearized by using similar conditions for key contaminants (Savelski *et al.*, 2003) and also requires the application of “alternatives” by branching and generating special sequences of water-using processes (Bagajewicz *et al.*, 2000). In addition Wałczyk *et al.* (2008) could linearize the water using network model with logical conditions for choosing the parameter of water using process among heuristically selected conditions. This did not require a branching scheme; however, the solution does not yield or guarantee the global optimum but yields near the global optimum (at worst) over a short CPU time (reached a better solution than the result of the previous work). The solution can be more improved with NLP solver.

- Generation of “good” starting point(s)

For determining the global optimum, a deterministic optimization is started with a suitable initialization (most often using in WWTN for sequential arrangements of available treatment processes (Chew *et al.*, 2009). Commonly, the starting point can be found through problem linearization. For instance, the fixed outlet concentrations at the maximum values are used as the starting points for mass-transfer water-using operations in general practice.

- Sequential solution procedure

The NLP model was applied and the procedure was done by assuming maximum concentrations and relaxing equalities into inequalities (Doyle *et*

al., 1997). Some additional constraints including the maximum wastewater flow rates were specified to increase the convergence.

The procedure (Gunaratnam *et al.*, 2005) for solving the TWN problem is as follows:

(i) Relax the material balance with fixing the outlet concentration at the maximum and introduce slack variables to the balance equation for MILP formulation.

(ii) Use flow rates from the solution as a starting point for the LP model solution and solve for new concentration values, which are employed as data for MILP in the next step (The MILP-LP model solution).

(iii) After reaching the convergence (the sum of slacks is “small”), the solution of the full MINLP superstructure model is obtained.

For WWTN, the procedure is solved in cycles and it employs the pair LP-NLP with the solution from LP as the starting point for NLP. Also to generate the LP relaxation, it has to fix the spilt fractions with stepwise changes for a given parameter.

- Meta-heuristic optimization approaches

This approach can be called also the stochastic optimization. The genetic algorithms (GAs) (Tsai *et al.*, 2001) or Adaptive random search (ARS) (Poplewski *et al.*, 2007) are applied for both the WUN (Jeżowski *et al.*, 2007) and (Poplewski *et al.*, 2007) problems. The application of additional goal functions with suitable penalty term is necessary for this approach. The water network problem is nonlinearities because of the bilinear terms; therefore, the direct solution of equalities in the sequential procedure is the most effective manner.

- Global (deterministic) optimization

The approach is associated with a spatial branch and contract algorithms for NLP as well as piecewise under-and over-estimators (for estimation of nonconvex terms), and branch-and-bound schemes for binary variables. ((Zamora *et al.*, 1998, Grossmann *et al.*, 2004, Floudas *et al.*, 2005, Karuppiah *et al.*, 2008).

Thus, it can be seen that the methodologies used in the process integration can be divided into two sections: the method involving

mathematical programming techniques and another involving the pinch analysis techniques as shown in Figure 2.13. In the minimization of water problem, Figure 2.14 shows various solution techniques and the process integration tools for solving the problem (Hashim *et al.*, 2009).

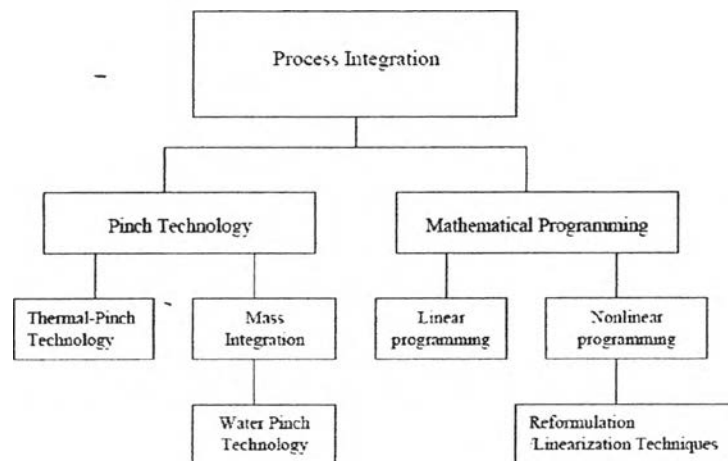


Figure 2.13 The tools of process integration (Hashim *et al.*, 2009).

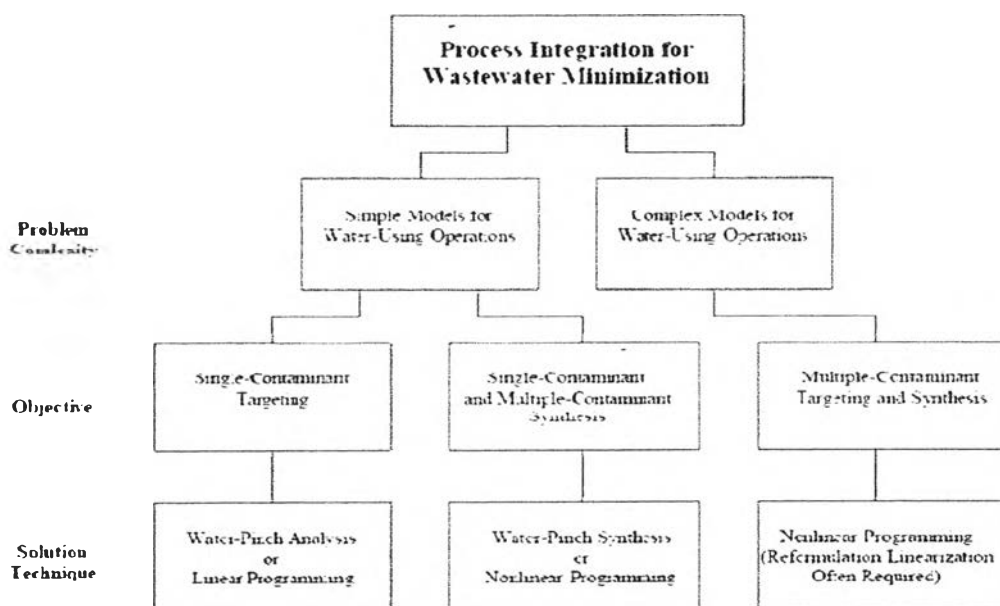


Figure 2.14 Solution techniques for water and wastewater minimization (Hashim *et al.*, 2009).

2.3 Water and Wastewater Use and Management (in Petroleum Refinery)

2.3.1 Overview of Water/Wastewater in Petroleum Refinery

Petroleum refineries are complex systems that consist of different and various unit operation and depend on the specific refinery considered such as size, crude, products and their operations, which demand a large water consumption with respect to other industries (IPIECA, 2010). An interesting case study in water management for refineries are characterized due to an intensive use of water, and also often locating in countries which are scarce in fresh water (Pennati, 2012). A typical refinery flow diagram is shown in Figure 2.15.

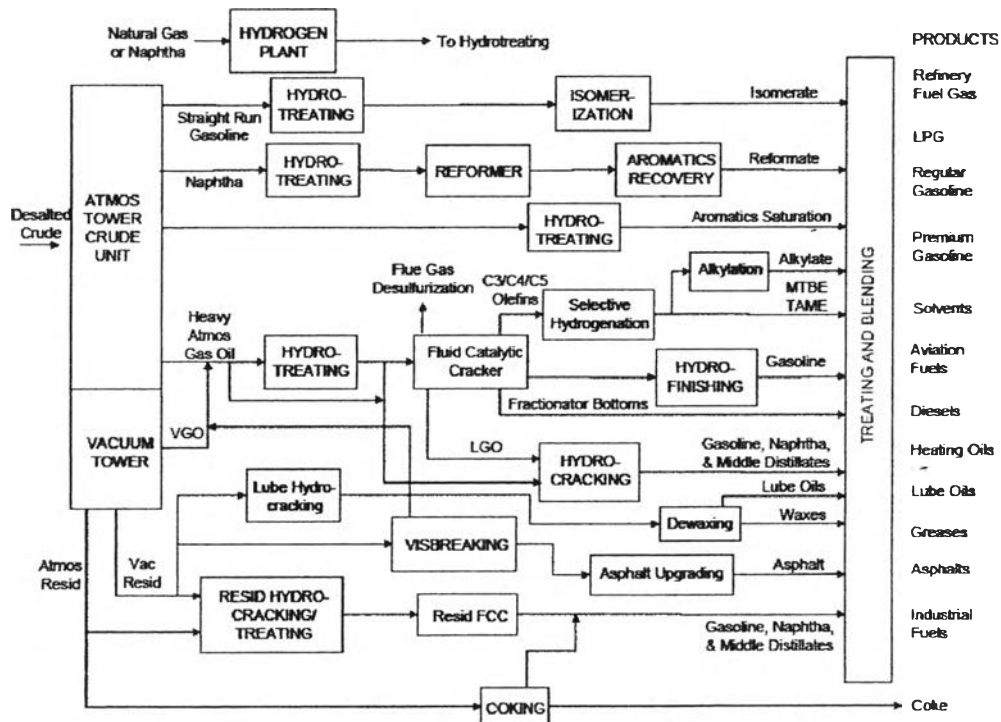


Figure 2.15 Typical Refinery Flow Diagram (Pellegrino *et al.*, 2007).

First, the crude is sent to the distillation unit to separate different hydrocarbon groups or light and heavy fractions. Then, heavy hydrocarbon molecules are cracked into smaller hydrocarbon molecules with heat or catalyst using (through Visbreaking, Catalytic cracking, Coking etc.). Next, two or more

hydrocarbon molecules will form a larger molecule in alkylation and polymerization (combination) to produce high octane gasoline blending stock while hydrocarbon arrangement for producing a new molecule with different characteristics are generally occurred in catalytic reforming and isomerization. Moreover, sulfur, nitrogen as well as heavy metals and other impurities in petroleum products need to be removed by treating with sweetening/sulfur removal unit, gas treatment unit and catalytic hydrotreating. Also, blending is used to obtain the final products and eventually, special products such as lubricating oil, grease, wax and asphalt are produced in various processes.

Generally, water is utilized in refineries as cooling tower makeup, fire water/construction water, boiler feed water, desalter and for various washing operations together with other chemical processing in refinery. Mostly, water is used in form of steam in many units; for example, steam stripping, sweetening, alkylation, etc. The general water consumption in a refinery is shown in Figure 2.16 (Pennati, 2012).

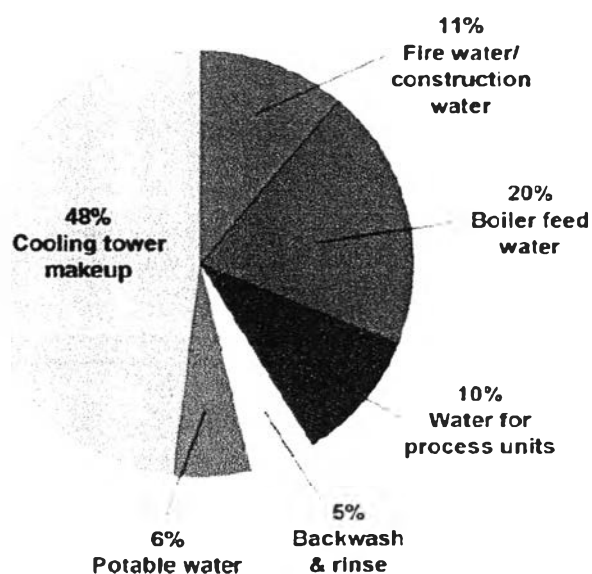


Figure 2.16 Water consumption in refinery (Hwang *et al.*, 2011).

In the refinery, water can be cascaded or reused in many sites. Most of water utilized in refinery can be consistently recycled within the process.

However, there are some losses to the environment such as steam losses, cooling tower evaporation and drifting or even water leaving with the products. Some processes need a certain continuous water intake to the operation such as steam generating or cooling water systems. Water balance for a refinery shown in Figure 2.17 is an overall schematic for a step toward optimization of water usage, recycle and reuse as well as the optimization of the performance of water and wastewater treatment systems (IPIECA, 2010). Figure 2.18 illustrates the typical water flow in the refinery.

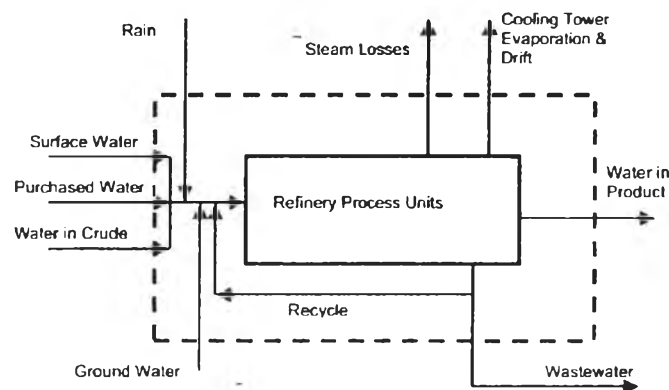


Figure 2.17 A schematic example of the typical water balance in a refinery (IPIECA, 2010).

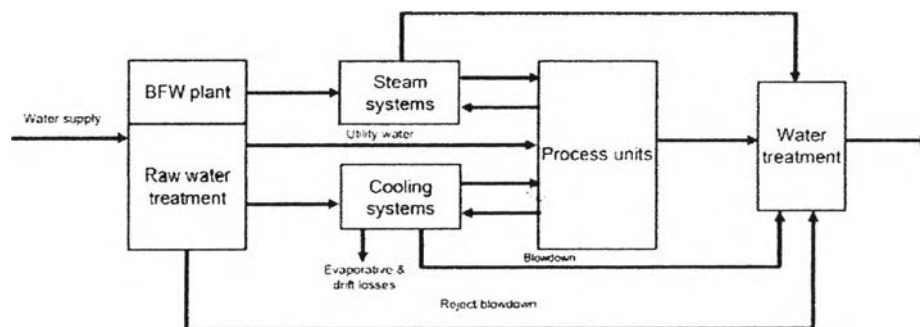


Figure 2.18 Typical water flow in refinery (Hwang *et al.*, 2011).

The wastewater generated in petroleum refinery is high variability in flow rate and composition. Typically, wastewater consists of suspended solids, ammonia, hydrocarbons, phenols and other compounds (Table 2.1). Cooling tower, boiler blowdown, stripping water, wash water and other related process water are the source of wastewater. However, the amount of wastewater discharged and its composition is dependent on the characteristic of each refinery, the crude oil properties, the type of process as well as the final mixed product and the treatment/disposal process.

Sour wastewaters containing ammonia, phenols, sulfide and other organic chemical compound can be produced in refinery process. They are generated from water that contacts directly with a hydrocarbon stream. Additionally, spent caustic is another kind of wastewater produced. The use of caustics to neutralize an acid solution and to separate acidic materials of crude oil is the cause of spent caustic formation. Acidic reaction products may be generated by a chemical treating process, and acidic materials produced during thermal and catalytic cracking. Furthermore, caustics are added to a desalter to neutralize acids and reduce corrosion and implemented for washing the isomerization, alkylation, drying and sweetening units.

Table 2.1 List of typical water contaminants in refinery (Hwang *et al.*, 2011)

TDS (total dissolved solids)	Alkalinity
H ₂ S	Dissolved oxygen
NH ₃	Sulfur
pH	Phosphate (PO ₄ ³⁻)
Aromatics	Chloride (Cl)
COD	SS (suspended solids)
Oil	Butane
Ca ²⁺	P (total phosphorus)
Fe ³⁺	Boiler additives
Hardness	Cooling tower additives

2.3.2 Overview of Wastewater Treatment (Petroleum Refinery)

The treatment process for wastewater in a refinery can be classified into both primary and secondary processes, or even a tertiary process. Some refineries have to also polish the discharge stream to meet environmental regulation. The distillation units and fractionators generate sour wastewater containing high concentration of ammonia and sulfides, thus it needs to be treated before mixing with the main wastewater stream. Generally, this is employed by air or steam stripping in a tower to remove hydrogen sulfide, ammonia and other organic sulfur compounds. Then, the wastewater is moved to the primary treatment or to the secondary treatment. Also, the stripped water can be reused in the desalter because a high grade water is not needed in such a unit (Pennati, 2012).

Various types of wastewater treatment processes that are usually practiced by refineries are different depending on the technology used for each refinery wastewater treatment system as well as the influent conditions and the level of treatment required. Figure 2.19 and Figure 2.20 show examples of the system for refinery water use and treatment.

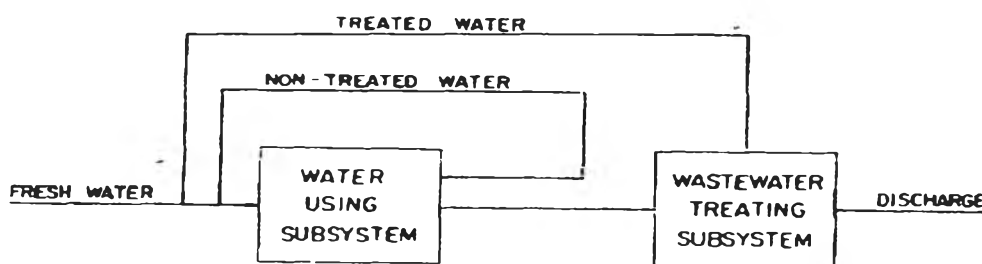


Figure 2.19 System for refinery water use and treatment (Takama *et al.*, 1980).

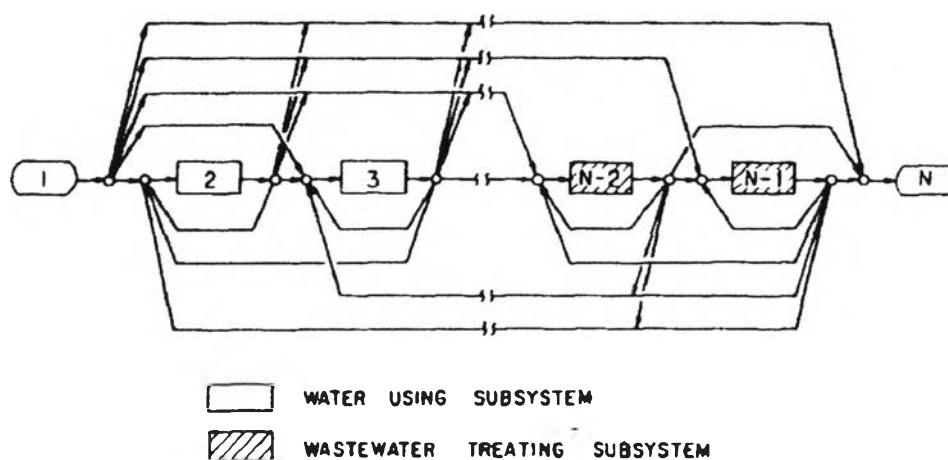


Figure 2.20 General system structure for refinery water use and treatment (Takama *et al.*, 1980).

The standard limitation of a refinery to discharge wastewater to open surfaces as shown in Table 2.2 (i.e. sea, river etc.) or to a municipal drain are greatly dependent on the refinery layout. Additionally, the maximum allowable level for each contaminant in water in a recycle stream is specific to the industrial site. Usually, the regulation for contaminants in refineries is focused on oil and grease, BOD₅, COD, total suspended solids, total and hexavalent chromium, phenolic compounds, ammonia, sulfides, pH and temperature (Pennati, 2012).

Table 2.2 General system structure for refinery water use and treatment (Hwang *et al.*, 2011)

Parameter	Unit	Refinery average
Temperature	C	45
pH	S.U.	5.5-9.0
Chemical oxygen demand (COD)	mg/l	200
Biological oxygen demand (BOD)	mg/l	30
Total suspended solids (TSS)	mg/l	45
Oil/grease	mg/l	10
Phenols	mg/l	1
Sulfides	mg/l	0.5
Nitrogen (i.e. Ammonia)	mg/l	10
Phosphates (inorganic)	mg/l	0.5
Cynides	mg/l	1
Iron	mg/l	2
Free chlorine	mg/l	0.6
Chromium as CrO ₄	mg/l	0.3
Zinc	mg/l	0.001-0.05

The wastewater treatment process is intended to purify the natural water process and to eliminate wastewater contaminants that might interrupt with natural process. A traditional system for wastewater treatment consists of physical, biological or even chemical processes. The alternative methods for wastewater treatment are divided into three main stages: (1) primary (physical process) treatment, (2) secondary (biological process) treatment, and (3) tertiary (combination of physical, chemical, and biological process) or advanced treatment as shown in Figure 2.21. However, it should include a preliminary treatment, disinfection and sludge management (treatment and disposal) depending on the necessary regulation requirement of wastewater characteristics (Lin *et al.*, 2007).

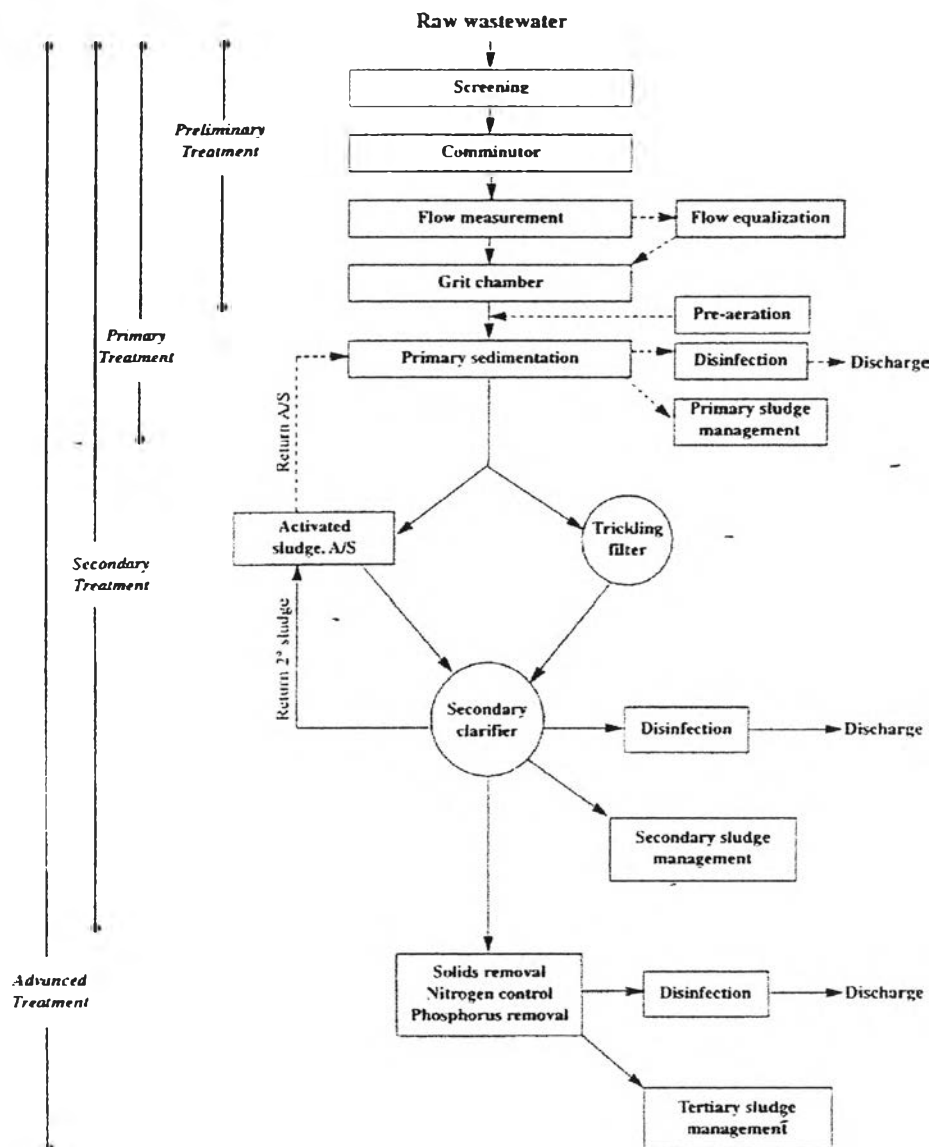


Figure 2.21 Flow chart for wastewater treatment processes (Lin *et al.*, 2007).

In industrial wastewater, contaminants can be appeared in various types of free oil, suspended solids, hydrocarbons, heavy metals, salts, to pathogens. The degree of contamination such as pH, color, odor and so on is also an important wastewater characteristic and needed to be identified. Both type and amount of pollutant in wastewater is significantly dependent on each industrial process. Although, at present, it can quantify the contamination of a water stream, the presence of some species in wastewater cannot be traced if their quantity is very small. Since a very wide range of different organic compounds contain in the

wastewater, the amount of each individual compound is quite difficult or even impossible to quantify completely. Hence, the most collective analyses for the organics are often performed by the biochemical oxygen demand over 5 days (BOD_5), the chemical oxygen demand (COD) and the total organic carbon (TOC). For the nutrients such as nitrogen and phosphorous, they can be proposed in several forms in wastewater and have to be observed to avoid eutrophication. Heavy metals causing toxic and sulfurous compounds causing unpleasant odors must be also handled. Moreover, the temperature and the alkalinity in wastewater discharge can vary the conditions of the receiving water surface. Meanwhile, suspended solids together with oil and grease may be dangerous for the environment. Other toxic compounds (such as phenols, benzene) are also worth paying attention. Especially, to recycle the treated water to process units, the contaminant level must be controlled stringently to satisfy all the constraints of the receiving process (Pennati, 2012).

- Biochemical oxygen demand (BOD).

This standardized test measures the oxygen utilized by microorganisms in contact with the wastewater over a five-day period at 20°C (BOD_5). The test can be continued until more than 20 days for measuring the ultimate demand. However, the BOD_5 test provides a good indication for the effluent affecting on the environment.

- Chemical oxygen demand (COD)

In this test, acidic potassium dichromate is employed in the oxidation process whereas a silver sulfate is needed to support the oxidation of organic compounds. Typically, COD value is higher than BOD_5 value because the COD test oxidizes only slow biodegradable matters. Even though the COD test can oxidize strongly in the environment, certain organic compounds may be oxidized slowly, or not at all.

- Total organic carbon (TOC)

This test measures the carbon dioxide generated when a wastewater sample is under a strong oxidizing environment. The sample is oxidized with a high temperature (800 to 900°C) stream (air) in a furnace and then the CO_2 evolution is measured. Other strong oxidizing environments can also be employed,

e.g. chemical oxidation. The inorganic carbon compounds need to be eliminated before testing with additional acid for converting to carbon dioxide in order to obtain the TOC requirement. The carbon dioxide must be stripped by a sparge carrier gas (Smith, 2005).

Generally, the refinery wastewater treatment plants consist of primary and secondary oil/water separation, followed by biological treatment, and tertiary treatment (if necessary), as shown in Figure 2.22.

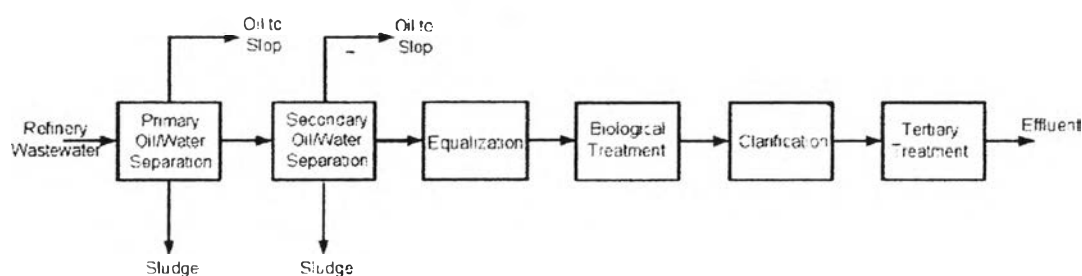


Figure 2.22 Typical refinery wastewater treatment (IPIECA, 2010).

For the treatment system of wastewater in a refinery, it requires two steps to remove free oil from the collected wastewater before entering into biological systems.

The oil removal is implemented by using an API separator followed by a dissolved air flotation (DAF) or induced air flotation (IAF) unit. Then, the fluctuations causing the sudden variation of flow and concentration are minimized or reduced by equalization system. Next, they are sent to the aeration tank/clarifier which performs the biological system. Finally, the outlet wastewater from clarifier is moved to the tertiary treatment (if necessary) prior to discharge (IPIECA, 2010).

- **Primary treatment**

This step involves a physical operation that is usually gravity separation in order to remove the floating and settleable matters. Typically, the primary treatment comprises of an oil/water separator and this is followed by a secondary oil/water/solids separation step (DAF or IAF) (IPIECA, 2010).

Sedimentation, filtration or grit removal is used to separate free oil and solids. Generally, free oil is separated by floating on the surface while solids settle to the bottom by (API and/or CPI/PPI), and then the oil is skimmed and scraped off, respectively. For the rest of emulsified oil with/without the addition of coagulants, they are separated by IAF/DAF/DNF systems. Solid and oily sludge generated from these treatments are harmful and need to be treated prior to disposal by dewatering and incineration (Pennati, 2012).

Note :

API = American Petroleum Institute separator

CPI/PPI = Corrugated or parallel plate interceptor

IAF/DAF/DNF=Induced air flotation or dissolved air/nitrogen flotation

- Secondary Treatment

This step associates with the biological treatment that is the most used treatment technology for the elimination of dissolved organic compounds. Generally, the biological treatment can be divided into two processes: suspended growth processes; and attached growth processes.

Suspended Growth Processes

The microorganisms are completely mixed with the organic in the liquid and kept as suspended liquid in this process. Organic constituents are used as food of microorganism to grow and clump until becoming the active biomass. The most common process used in practice is activated sludge process.

Attached Growth Processes

The microorganisms are attached to an inert packing stuff that can be rocks, gravel, plastic material and several synthetic materials. The wastewater will contact with the microorganisms on media and transform to biomass and CO₂. The biomass film on the media will be maintained until growing and reaching a certain thickness and finally be removed as slough (IPIECA, 2010).

Examples for biological treatment in brief:

The activated sludge systems

The bacterial mass is suspended in the basin and then separated through a clarifier and finally recycled back. Additionally, the system can be improved with an addition of powdered activated carbon (PACT process) for better efficiency.

The trickling filter or the rotating biological contactor

A biofilm grows on a fixed bed or on a rotating shaft with disks.

Aerated lagoons or stabilization ponds

These contain a basin for providing wastewater to rest under the biomass action. (This is not commonly used because of the requirements of huge ground surface.

Membrane bioreactor

The system combines an activated sludge with a microfiltration membrane. The membrane bioreactor acts towards the nitrogenous species in the wastewater. However, both nitrification (conversion of ammonium to nitrite and then to nitrate) and denitrification (conversion of nitrate to nitrogen gas) can be achieved depending on the operating conditions and the existing oxygen.

These biological treatment processes generate biomass sludge that has to be dewatered and treated before disposal (Pennati, 2012).

- Tertiary Treatment

The tertiary treatment is required when it is needed to meet the stringent discharge limitation such as TSS; COD, dissolved and suspended metals, and trace organics (i.e. polyaromatic hydrocarbons (PAHs)) or to be recycled to processes that required a certain level of contaminants (IPIECA, 2010).

This treatment step contains a various alternatives based on a wide range of techniques such as air/stream stripping, adsorption with activated carbon or sand, oxidation with chlorine, hydrogen peroxide, or other oxidants, precipitation of metals or phosphorous, filtration with a fine membrane (microfiltration, nanofiltration, ultrafiltration or reverse osmosis).

However, disinfection is necessary if pathogens present in the wastewater stream. Thus, levels of wastewater treatment can be summarized in

the Table 2.3. In addition, Table 2.4 and Table 2.5 illustrate unit operations and treatment processes to remove some common contaminants (Pennati, 2012).

Table 2.3 Levels of wastewater treatment (Tchobanoglous *et al.*, 2003)

Treatment level	Description
Preliminary	Removal of wastewater constituent such as rags, sticks, floatables, grit and grease that may cause maintenance or operational problems with the treatment operations, processes, and ancillary systems
Primary	Removal of a portion of the suspended solids and organic matter from the wastewater
Advanced primary	Enhanced removal of suspended solids and organic matter from the wastewater. Typically accomplished by chemical addition or filtration
Secondary	Removal of biodegradable organic matter (in solution or suspended) and suspended solids. Disinfection is also typically included in the definition of conventional secondary treatment.
Secondary with nutrient removal	Removal of biodegradable organics, suspended solid, and nutrients (nitrogen, phosphorus, or both nitrogen and phosphorus)
Tertiary	Removal of residual suspended solids (after secondary treatment), usually by granular medium filtration or microscreens. Disinfection is also typically a part of tertiary treatment. Nutrient removal is often included in this definition.
Advanced	Removal of dissolved and suspended materials remaining after normal biological treatment when required for various water reuse applications

Table 2.4 Unit operations and processes used to remove constituents found in wastewater (Tchobanoglous *et al.*, 2003)

Constituent	Unit operation or process
Suspended solid	Screening
	Grit removal
	Sedimentation
	High-rate clarification
	Flotation
	Chemical precipitation
	Depth filtration
	Surface filtration
	Biodegradable organics
Aerobic attached growth variations	
Anaerobic suspended growth variations	
Anaerobic attached growth variations	
Lagoon variations	
Physical-chemical systems	
Chemical oxidation	
Advanced oxidation	
Membrane filtration	
Nutrients	
	Nitrogen
Nitrogen	Chemical oxidation (breakpoint chlorination)
	Suspended-growth nitrification and denitrification variations
	Fixed-film nitrification and denitrification variations
	Air stripping
	Ion exchange
Phosphorus	Chemical treatment
	Biological phosphorus removal
Nitrogen and phosphorus	Biological nutrient removal variations
Pathogens	Chlorine compounds
	Chlorine dioxide
	Ozone
	Ultraviolet (UV) radiation

Table 2.5 Summary of treatment processes for some common contaminants (Smith, 2005)

Suspended solids	Dispersed oil	Dissolved organic
Gravity separation	Coalescence	Biological oxidation (aerobic, anaerobic, reed beds)
Centrifugal separation	Centrifugal separation	Chemical oxidation
Filtration	Flotation	Activated carbon
Membrane filtration	Wet oxidation	Wet oxidation
	Thermal oxidation	Thermal oxidation
Ammonia	Phenol	Heavy metals
Steam stripping	Solvent extraction	Chemical precipitation
Air stripping	Biological oxidation (aerobic)	Ion exchange
Biological nitrification	Wet oxidation	Adsorption
Chemical oxidation	Activated carbon	Nanofiltration
Ion exchange	Chemical oxidation	Reverse osmosis
		Electrodialysis
Dissolved solids	Neutralization	Sterilization
Ion exchange	Acid	Heat treatment
Reverse osmosis	Base	UV light
Nano-filtration		Chemical oxidation
Electrodialysis		
Crystallization		
Evaporation		

2.3.2.1 Recycle and Reuse Issues

By lacking of fresh water in many areas and the requirements of high amount of raw water in the refinery, recycle and reuse of water are attractive issues. To recycle/reuse water in a refinery, the performance and the possibility of water recycle/reuse should be evaluated together with the refinery wastewater.

Typical use of water in refineries can be distributed as follows:

- process water:
 - desalter makeup
 - coker quench water

- coker cutting water
- flare seal drum
- FCC scrubbers
- hydrotreaters
- boiler feedwater makeup
- cooling water makeup
- potable water
- fire water
- utility water

From water uses in refinery as shown above, the process water, boiler feedwater and cooling tower makeup are the biggest consumption (as shown in Figure 2.16) and are ideal candidates for water recycle. Table 2.6 and Table 2.7 illustrate the general specification of contaminant levels needed for these waters and the summary of refinery wastewater reuse, respectively. These values should be only employed for general purpose information; however, the detailed evaluation of the refinery specific application is required before initiating any water reuse and it is solely dependent on such processes (IPIECA, 2010).

Table 2.6 Contaminant specification for reuse water (IPIECA, 2010)

Water category	Contaminant specification	Potential source of re-use water
Desalter makeup	<ul style="list-style-type: none"> • Sulphide: < 10 mg/l • Ammonia: < 50 mg/l • Total dissolved solids (TDS): < 200 mg/l 	<ul style="list-style-type: none"> • Stripped sour water • Vacuum tower overhead • Crude tower overhead
Coker quench water	<ul style="list-style-type: none"> • Total suspended solids: < 100 mg/l • Biological solids: none • H₂S and other odorous compounds: none 	<ul style="list-style-type: none"> • Stripped sour water
Coke cutting water	<ul style="list-style-type: none"> • Total suspended solids: < 100 mg/l • Biological solids: none • H₂S and other odorous compounds: none 	<ul style="list-style-type: none"> • Stripped sour water
Boiler feedwater makeup (quality required is highly dependent on the pressure of steam being produced)	<ul style="list-style-type: none"> • Conductivity: < 1 μS/cm • Hardness: < 0.3 mg/l • Chlorides: < 0.05 mg/l • Sulphates: < 0.05 mg/l • Total silica: < 0.01 mg/l • Sodium: < 0.05 mg/l • Dissolved oxygen: < 0.007 mg/l 	<ul style="list-style-type: none"> • Treated and upgraded refinery wastewater
Cooling tower makeup	<ul style="list-style-type: none"> • Conductivity: < 6,000 μS/cm • Alkalinity: < 3,000 mg/l • Chlorides: < 1,500 mg/l • Suspended solids: < 150 mg/l 	<ul style="list-style-type: none"> • Treated and upgraded refinery wastewater

Table 2.7 Summary of refinery wastewater reuse (IPIECA, 2010)

Technology	Suitability
Media filtration	Removes suspended solids but not dissolved solids. Treated water not suitable for cooling water or boiler feedwater makeup but can be used for other uses such as utility water or fire water.
Ultrafiltration or microfiltration	Removes suspended solids (to a greater extent than media filtration) but not dissolved solids. Treated water not suitable for cooling water or boiler feedwater makeup but can be used for other uses such as utility water or fire water.
Ultrafiltration or microfiltration, with reverse osmosis	Removes both suspended and dissolved solids. Treated water suitable for all uses in the refinery including cooling tower and boiler feedwater makeup
Ultrafiltration or microfiltration, with nanofiltration	Removes both suspended and dissolved solids. Treated water suitable for all uses in the refinery including cooling tower and boiler feedwater makeup. Salt rejection is lower than reverse osmosis but this system can be operated at a lower pressure than RO systems
Ion exchange	Removes both suspended and dissolved solids. Treated water suitable for all uses in the refinery including cooling tower and boiler feedwater makeup. Usually applicable when the dissolved solids concentration is less than 400 mg/l.

Eventually, the treatment alternative, as well as their specific design is dependent on the type and the level of contaminants appearing in the wastewater. Most of aforementioned contaminants and the treatment options are general for any type of industrial wastewater treatment plant or petroleum refinery.

However, the structure and performance of the wastewater treatment along with the operating parameters and the specifications for each unit have to be adjusted for the specific case to accomplish the best performance. Typically, a certain treatment sequence is employed to treat a specific type of industrial wastewater and the alternatives are convinced mostly in common practice and previous experience as well as engineering insight (Pennati, 2012).

2.4 The Integrated Solutions Framework for Synthesis and Design of Processing Networks (Quaglia *et al.*, 2012)

The framework consists of 5 steps including the problem definition, data collection, model development, mathematical solving, and results analysis. A schematic representation of the workflow is illustrated in Figure 2.23.

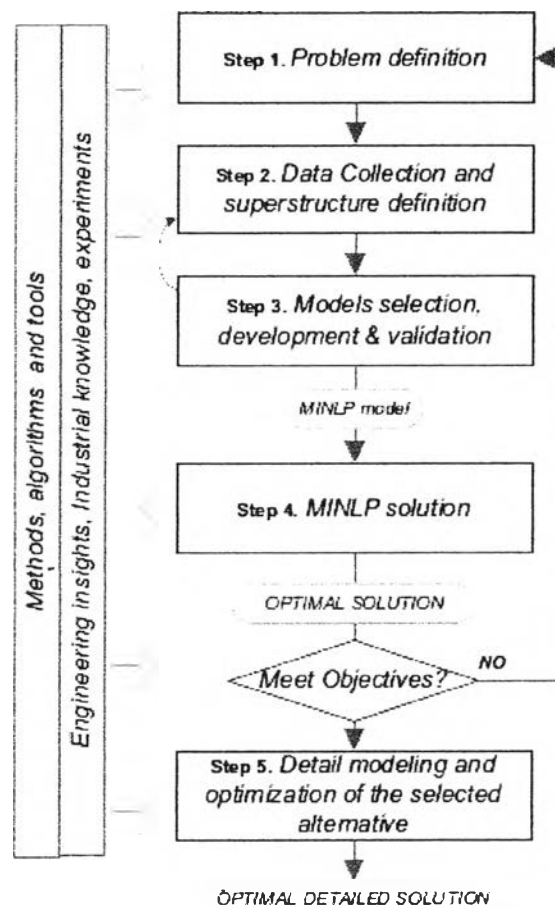


Figure 2.23 The integrated business and engineering framework (Quaglia *et al.*, 2012).

Step 1: Define the problem by identifying the scope, the scenario with respect to analysis and selecting the objective function together with all the

additional performance and sustainability indicators. Most data involves with business and strategic considerations.

Step 2: Collect the available industrial, commercial and regulatory data regarding the problem and manage with respect to a pre-defined knowledge structure. In addition, the potential raw materials and products are identified, and the different processing alternatives are defined in the form of a superstructure (Figure 2.24), composing of a network of process intervals (PI) and a list of logical constraints to eliminate infeasible and/or redundant alternatives (Figure 2.25).

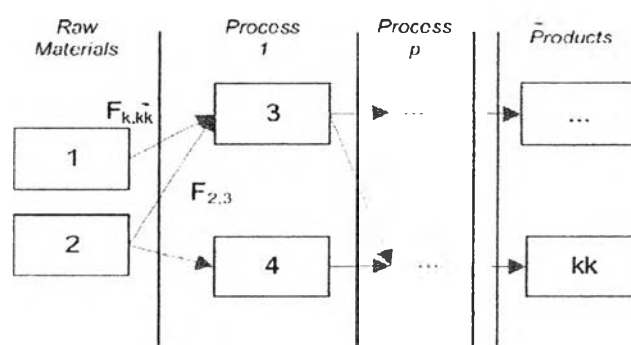


Figure 2.24 Schematic representation of the superstructure (Quaglia *et al.*, 2012).

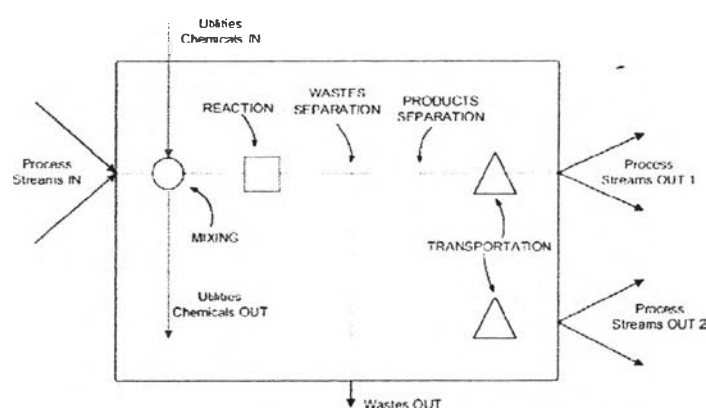


Figure 2.25 Generic process interval structure for a definition of process constraints (Quaglia *et al.*, 2012).

Step 3: Collect and generate all models needed to formulate a mathematical problem. The models associate with each of the process intervals of the superstructure, together with models for cost/value and sustainability metrics that are needed to compute the objective function and the performance metrics defined in step 1.

However, all models are validated against the experimental information or available industrial knowledge. The superstructure, the objective function, and all logical, operational and process constraints are compiled to formulate the MINLP problem:

$$\begin{aligned}
 & \text{Min } Z = f(x, y, p) \\
 & \text{s. t. } g(x, y, p) \geq 0 \\
 & \quad h(x, y, p) = 0 \\
 & \quad x \in X^n \\
 & \quad y \in (0, 1)^m \\
 & \quad p \in P^l
 \end{aligned}$$

where f is an objective function for the economic potential, x represents the vector of continuous variables, y is the vector of binary variables, X is a continuous feasible region of continuous variables defined by their lower and upper bounds, g and h are the vectors of inequality and equality constraints, respectively.

Step 4: Solve the MINLP problem formulated in step 3. The solution provides the optimal value of the optimization variables (where the binary represent the optimal strategic decisions and the continuous variables represent the optimal tactical decisions), along with the objective function and the performance metrics calculated at the optimal solution.

Step 5: Evaluate the identified solution based on the results in step 4 so as to decide whether to proceed to its implementation. If needed, the detailed modelling and optimization of the selected alternative are performed in this step by using a proper process simulator.

Literature review

In the literature review, it summarizes previous works regarding the design of water and wastewater network. Section 2.5 describes briefly the state of the art of the optimal design of the water network system (synthesis and design approach) and also refers to the literature review from various authors. For other sections, a total water network, water using network and wastewater treatment network are reviewed on sections 2.6 2.7 and 2.8 respectively. Additionally, sections 2.6 2.7 and 2.8 can be also classified by the characteristic of design, concept, objective, problem along with the solution, method and other factors. However, this review focuses mainly on the optimization-based method (and may include some previous works incorporating of both the insight-based method and the optimization-based method for addressing the problem).

2.5 The Review and State of The Art on Optimal Design of Water Network System

Water is one of the most important natural resources and used in the process industry. On the contrary, wastewater generated in the different processes and utility systems needs to be treated before discharge to the environment. However, the amount of fresh water usage and the increase of processing wastewater treatment cost have been the motivation to efficiently minimize the amount of water usage and wastewater generation for process industries in recent years (Yoo *et al.*, 2007).

Over the past decades, there has been a concern focused on the end-of-pipe wastewater treatment, and later shifted towards the maximizing of water reuse from conventional water treatment to more sustainable water minimization activities. Water reuse started as one of the active areas for water minimization activities so as to reduce the total water consumption and wastewater treatment costs in the early eighties. Moreover, a desired goal for grassroots and retrofit designs are taken into account for the zero water discharge cycles (Hashim *et al.*, 2009). However, many efforts have been increasingly created not only the end of pipe technologies but also

aiming toward the clean production technology by the fundamental structural changes to extend water reuse or decrease the wastewater generation.

There are two strategies implemented for reducing the water demand in a plant: the modification of individual process and utility units to reduce their inherent water demand (i.e. including replacing water-cooling with air cooling), and the engineering insight for seeking the opportunities to use the water effluent from one operation to satisfy the water requirement of another or the same operation. Four methods are used to minimize the water usage: process changes, water reuse, regeneration reuse and regeneration recycling. In many cases, the water may require some regeneration prior to reuse such as pH adjustment, filtration, membrane separation, etc. In particular, systematic strategies for such reuse maximization can reduce fresh water usage and wastewater discharges lower than 50% or more and can also significantly reduce the capital investment in treatment operation.

The two approaches (Yoo *et al.*, 2007) to obtaining fundamental designs of the water network systems are as follows:

2.5.1 Insight-based Method (Water Pinch)

This method is a stepwise approach in identifying the minimum freshwater flow rate as well as synthesizing a water using network, and is also effective for discovering the operational bottlenecks and revamping existing water using networks, that is used in the following sequence:

1. Identify the minimum freshwater flow rate
2. Construct a preliminary water reuse network
3. Simplify the network in step 2 through a heuristic approach by reducing the number of water reuse operation
4. Identify water reuse limited regions and suggest process changes to further reduce the minimum freshwater flow rate

2.5.2 Optimization-based Method (Mathematical Technique)

This method yields a minimum value for the freshwater flow rate subject to constraints in certain situations (i.e., large multiple contaminant problems). This method is appropriate when the alternative model in each water use operation is flexible. These may include connection, operating, and piping and pumping costs. In

addition, the optimization-based method may identify a local optimum rather than the global optimum because the mathematical optimization approach of NLP and MINLP is sensitive to the choice of initial values. However, the two approaches are complementary. The conceptual graphical design ability improves the engineering understanding while the mathematical model allows the complex problem management.

The water network system has been an active area of research for the past three decades that the seminal work was published since 1980, and is a major topic of process system engineering. However, the real development for water network system design and synthesis has started since 1994. This review will emphasize on the mathematical optimization approach and show the development as well as extension in this area from the past to present.

Huang *et al.* (1999) proposed a mathematical programming model for determining the optimal water usage and treatment network (WUTN) in any chemical plant. The aims of the model were to minimize the amount of fresh water consumption and/or wastewater treatment capacity. This model consisted of the design equations of all wastewater treatment processes and all units which utilized either process or utility water. The model can achieve more comprehensive integration on a plant wide scale as well as more reliable, more accurate, and more cost-efficient alternatives and much faster in synthesizing the network.

Then, Bagajewicz (2000) presented a first full review of the procedures to design and retrofit water networks as well as the methods proposed up to the year 2000 with the design of two interacting subsystems (the freshwater together with wastewater reuse allocation and wastewater treatment problem). This emphasized that the mathematical programming can produce globally optimal solutions and practically important sub-optimal solutions while conceptual insights were implemented to build the models.

Next, Yoo *et al.* (2007) considered new and existing technologies for the systematic design of water reuse networks for water and wastewater minimization in order to integrated the water resource management for clean production. This work also showed the alternative solutions, evolutionary solutions and stochastic design approaches to water system design along with some research

challenges encountered in this field such as simultaneous water and energy minimization, energy-pinch design, and eco-industrial parks (EIP).

The second review was done by Foo (2009). This work only presented a state-of-the-art overview of the insight-based techniques (Pinch analysis) developed in the 21st century, especially for a single impurity network of the fixed flow rate problems. His review compared these recent insight-based techniques and those developed for the fixed load problems in the past decade. The review included the detail of various flow rate targeting techniques developed for water reuse/recycle, regeneration, and wastewater treatment together with the network design techniques for implementing the targets. However, it was predicted that water pinch-analysis techniques would remain active, since there were still some research gaps to be filled.

In the same year, the definition and concept of the water/wastewater allocation problem for process plants and their appropriate architecture modified and simplified with the different assumption used in each of the subsystems as well as with the interaction among the subsystems were discussed by Bagajewicz *et al.* (2009). The result showed through examples that different structural choices can make significant changes. Additionally, they have suggested a complete water system comprising of one more subsystem and the water pretreatment subsystem. This work also investigated the predictions of freshwater consumption, total annual cost and zero discharge cycles and the impact of proper modelling on these parameters.

Next, a third and the latest review was stated by Jeżowski (2010). He described literature annotations on the WN problem from the year 1980. This review also provided an analysis of the WN problem formulation, together with an overview of solution techniques as well as statistics and classifications of the literature annotations. Finally, he presented thoughts on the direction of future research.

Those reviews indicated a noticeable accomplishment of publications in recent years. However, water network system and management problem are necessary to further develop for maximizing the benefits. Moreover, there is still a need for more flexible and effective approaches with extended

practical applications because of the increasing concern on scarce water resources, together with stringent regulations on wastewater discharge and sustainability.

Generally, the general diagram of water network design are comprised of freshwater streams, processing units, treatment units and disposal/waste streams as shown in Figure 2.26. Nevertheless, the major of water network architecture can be divided into three systems and each system can also have different characteristics depending on nature of the problem, method, design, concept and other factors (such as strategies for optimization, cost aspect etc.). The main problems are that the problems are single or multiple contaminants and the constraints base on components or properties. The insight-based or optimization-based method is implemented and finally, the design included recycle, reuse, bypass, or even regeneration as well as which superstructure concept they are constructed. Thus, the rest of this section reveals the development in this field from many researchers over the past two decades. Three water network systems will be covered as follows:

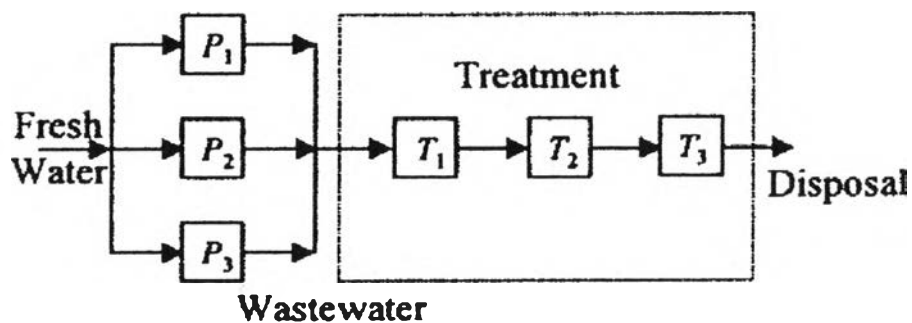


Figure 2.26 The general diagram of water network design (Bagajewicz, 2000).

2.6 Total Water Network (TWN)

This network is integrated between processing units and treatment units and each stream can be interconnected thoroughly among the units in the superstructure as shown in Figure 2.27.

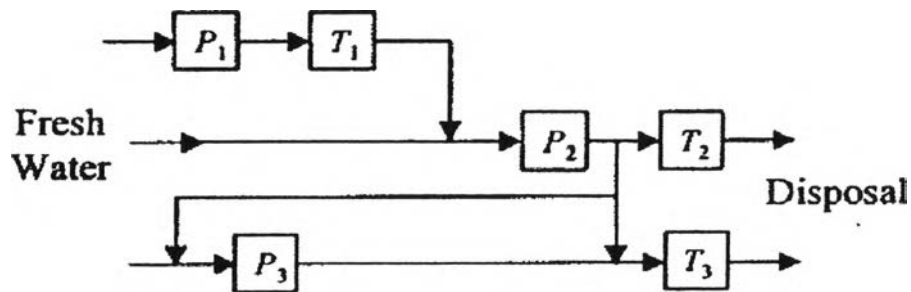


Figure 2.27 The diagram of water utilization systems for total water network (Bagajewicz, 2000).

2.6.1 Single Contaminant Problem

2.6.1.1 *Insight-based and Optimization-based Method*

With regeneration

The integrated process water management incorporating with regeneration and recycle through a single treatment unit by graphical technique and analytical algorithms was addressed by Bandyopadhyay *et al.* (2008). Their management of water in process units was to minimize the freshwater consumption and to optimize wastewater treatment in the process. A single treatment unit was applied for regenerated water production together with being accepted from the environmental regulations.

2.6.2 Multiple Contaminant Problem

2.6.2.1 *Insight-based Method*

With and without regeneration

Kuo *et al.* (1998) presented a new, systematic method of design option for the interactions between water-using operations and effluent treatment in the process industries. This introduced the minimization of effluent treatment cost and enables the trade-off between the water minimization and effluent treatment systems through re-use or recycling.

2.6.2.2 *Optimization-based Method*

Without regeneration (Figure 2.28)

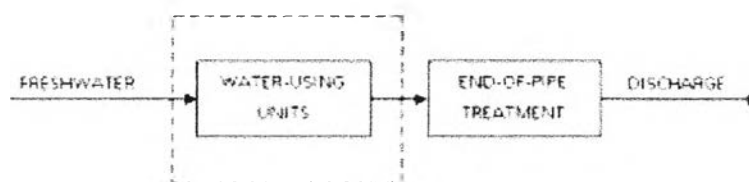


Figure 2.28 The conceptual diagram for water-using units with an implicit end-of-pipe (without regeneration) (Faria *et al.*, 2009).

The seminal work was published since 1980 by Takama *et al.* (1980) that applied the superstructure concept for water network problem in a systematic manner. The problem was implemented to minimize the total cost and subjected to constraints derived from material balances and interrelationships among water-using units and wastewater-treating units or split ratios (at the point where a water stream is split into more than two streams). The optimization problem was solved by using the Complex method illustrated by its application to a petroleum refinery.

Moreover, Alva-Argaez *et al.* (1998) proposed the synthesis and design of industrial water systems integrated between the water pinch analysis and mathematical programming tools. The optimization of a superstructure model included all the possible features of a design, the automated method is based on a decomposition scheme and on a recursive procedure (by using a branch and bound algorithm to find each optimal point). This new approach and the designs a network from the application in petroleum refinery featured minimum total annualized cost where the complexity of the network structure is dominated by the many designers and practical constraints. However, this work avoided these drawbacks by performing a simultaneous optimization of the overall system.

The improved optimization strategies for generating practical water usage and treatment network structures (WUTNs) were proposed by Chang *et al.* (2005). The modification of NLP model formulations was introduced into the design procedure, especially, an incorporation of additional design options as well as

a determination of the number of repeated treatment units in the superstructure. The method provided a good initial guess to enhance convergence efficiency.

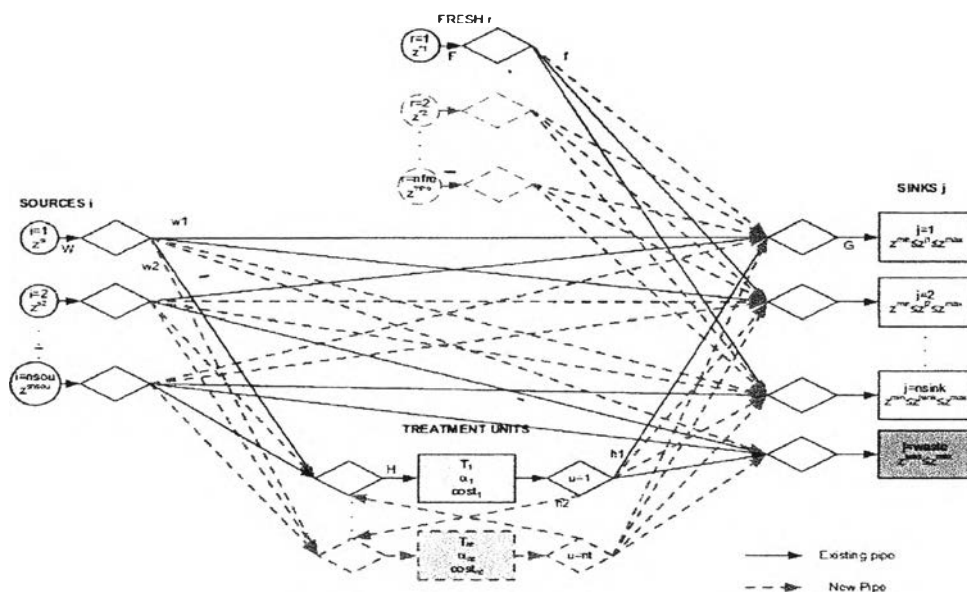


Figure 2.29 Proposed superstructure for the retrofit of recycle, reuse and regeneration networks (Sotelo-Pichardo *et al.*, 2011).

In addition, Sotelo-Pichardo *et al.* (2011) presented a new general mathematical programming model for the optimal retrofit of material conservation networks. The model was considered recycle, reuse and regeneration schemes (Figure 2.29) based on a disjunctive programming formulation that was reformulated as an MINLP problem. The reuse of the existing treatment units and their modification for the capacity and performance of the existing units as well as the installation of new treatment units and even the reconfiguration of the pipes or existing networks were considered as well. This was done to satisfy the more stringent process and environmental constraints at the minimum cost, and easy to modify to consider different objective functions, the plant layout, situation to identify the appropriate pipe and pumping costs.

With regeneration (Figure 2.30)

Ahmetović *et al.* (2004) proposed a general superstructure, which consisted of multiple sources of water, water-using processes, wastewater treatment and pre-treatment operations, together with a model for the global optimization to design the integrated process water networks as well as its separate subsystems. This superstructure included all feasible interconnections of water reuse, water regeneration reuse, water regeneration recycling, local recycling around process and treatment units in the network as well as multiple water sources used in various operations, and incorporated both mass transfer and non-mass transfer operations (Figure 2.31).

The proposed model by Ahmetović *et al.* (2004) was formulated as a Nonlinear Programming (NLP) and as a Mixed Integer Nonlinear Programming (MINLP) problem containing binary variables. For MINLP, the cost of piping and/or selection of technologies for treatment were modelled to find optimal network designs with different number of streams in the piping network. This work presented the bounds on the variables that are derived as general equations obtained by physical inspection of the superstructure. Furthermore, to expedite the global optimization search, logic specification needed to use for solving model. This work also proposed a two-stage procedure for solving large-scale models.

Afterward, Karuppiah *et al.* (2006), Ahmetović *et al.* (2010) and Ahmetović *et al.* (2011) employed such a general superstructure (Figure 2.31) to address the superstructure problem of optimal synthesis of an integrated water system into a single network. In the work of Karuppiah *et al.* (2006), The problem was taken the form of a non-convex Generalized Disjunctive Program (GDP) allowing an alternative of different treatment technologies for the removal of the various contaminants in the wastewater streams. For Ahmetović *et al.* (2010), they proposed strategies to readily obtain networks of varying degrees of complexity by limiting the number of piping. And a year after, Ahmetović *et al.* (2011) has applied the proposed model to solve industrial water network problems as well as to establish optimal trade-offs between the network cost and network complexity with reasonable computational time for solving to global optimality.

2.7 A Review on Water Using Network (WUN)

The attention in reducing water usage in process system (Figure 2.32) for sustainability has arisen in recent years because of the scarcity of water resources as well as the increase of fresh water and wastewater treatment cost. Process integration techniques for the water network synthesis have been adopted as a promising tool to reduce fresh water and wastewater flow rates through water reuse/recycle in the plant. In particular, a mathematical programming technique has become a useful tool for the design of optimal water networks because of the limitations of conceptual approaches in dealing with complex industrial water systems consisting multicontaminant.

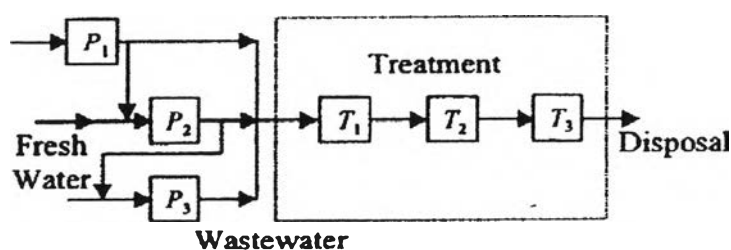


Figure 2.32 The general diagram of water using network system (Bagajewicz, 2000).

2.7.1 Single Contaminant Problem

2.7.1.1 *Insight-based Method*

Without regeneration-Reuse (Figure 2.33)

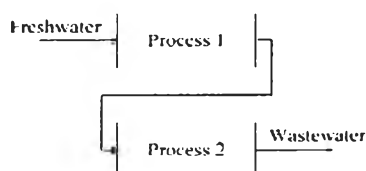


Figure 2.33 General diagram for water network system with reuse (Hashim *et al.*, 2009).

Dunn *et al.* (2001) presented the design techniques which consisted of a two-stage graphical approach in any wastewater streams. In the first stage, the water pinch diagram was used to identify the key design targets (i.e., the minimum freshwater requirement, the amount of water recycling and reuse etc.). In the second stage, the source-sink mapping diagrams were used to identify the water recycling and reuse network, and any alternative networks.

The targeting for threshold problems and plant-wide integration of water network through the numerical tool of water cascade analysis (WCA) were addressed by Foo, D.C. (2008). To reduce the overall fresh water and wastewater flow rates simultaneously, this work has sent water sources across different geographical zones in plant-wide integration that the main rule is to use excess water from the area below pinch in the other area above pinch (no regeneration process)

2.7.1.2 Optimization-based Method

With regeneration-reuse/recycling (Figure 2.34)

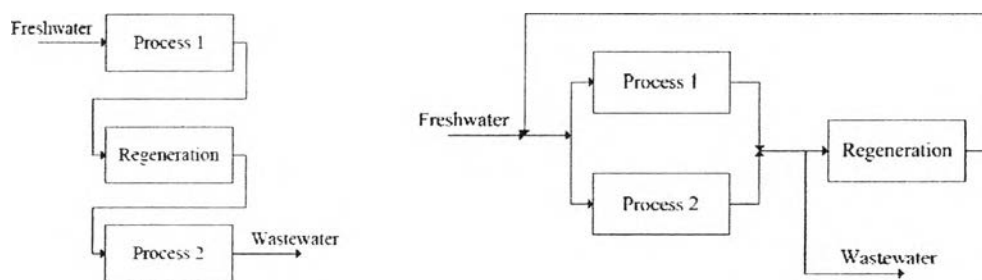


Figure 2.34 General diagram for water network system with regeneration-reuse (left) and regeneration-recycling (right) (Hashim *et al.*, 2009).

Meanwhile, Bagajewicz *et al.* (2001) addressed the optimum design of water using network systems with a regeneration and without regeneration through the application of the necessary conditions of optimality by allowing an LP or MILP formulation depending on the objective function of choice.

2.7.2 Multiple Contaminants Problem

2.7.2.1 Insight-based Method

With and without regeneration

Wang, Y. *et al.* (1994) addressed the minimization of the wastewater problem in various process industries. Two simple design methods allowed targets (for maximization water re-use) to be achieved in the design. The design was to maximize the use of the available concentration driving forces in individual processes and to minimize the number of water sources for individual processes via bypassing and mixing. The approach developed can identify possible alternative structures for the same problem, and those design features are essential to achieve the target and option. Furthermore, regenerator design can evaluate the effect of a regenerator on the overall system, and the approach could be used to help specify the most appropriate regenerator type and specification.

2.7.2.2 Optimization-based Method

Without regeneration

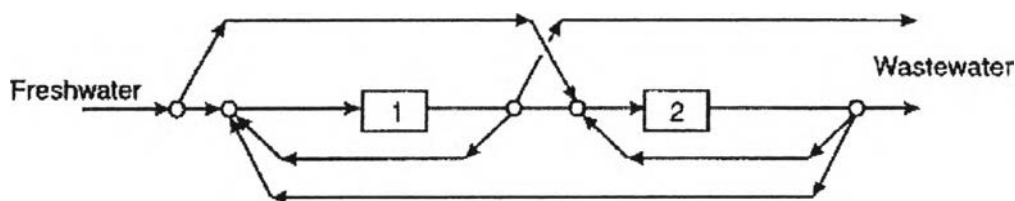


Figure 2.35 The schematic representation of the water-using networks with reuse/direct recycle (Doyle *et al.*, 1997).

To minimize the consumption of the water using process, Doyle *et al.* (1997) has developed a new method for targeting maximum water reuse (Figure 2.35). The objective was to minimize water use and wastewater generation through reuse in process systems. Two approaches were employed: a fixed mass load (solved as a nonlinear optimization problem) and fixed outlet concentration (solved as a linear optimization problem). Their work presented a combination of the linear model used as an initialization for nonlinear optimization. Also, it showed the

sequential linearization of the WUN nonlinear model applied to find a near-global optimum solution. Moreover, Yang *et al.* (2000) have minimized effectively wastewater with reusing for maximum extension in existing plant and introduced a mathematical approach to design an optimal wastewater reuse network (WWRN) as well.

For sustainability in environment, Lim *et al.* (2008) has developed a model to synthesize an environmentally friendly water network system (WNS). The approach minimized environmental impacts of a WNS and integrating life cycle assessment (LCA) into the objective function of the model to evaluate the environmental effect scores (EESs) together with optimizing tradeoffs among their EESs. This model can be used to effectively improve the environmental performance of a WNS on both implementing a new water system and in retrofitting an existing water system. The integration of LCA into the model enabled the minimization of the total environmental impacts and the optimization of the tradeoffs among the environmental impacts of principal contributors. In addition, the model can be also applied to other process integration technologies, such as heat or hydrogen network synthesis, in order to improve the environmental performance of various processes and systems.

Then, Poplewski *et al.* (2010) addressed the problem of designing water usage network consisting of fixed flow rate water using processes with a mixed-integer linear programming (MILP) optimization model of WUN superstructure. This approach was applied to several industrial scenarios, various performance indices and imposing conditions of continuous variables.

Apart from such a problem, the optimization problem can be also involved the multiobjective. Thus, Li *et al.* (2011) developed a systematic multiobjective optimization procedure to generate appropriate realistic in water using network designs. This work was solved by three water-using mathematical programming models (one nonlinear program and two mixed-integer nonlinear programs) sequentially to satisfy different criteria (minimum freshwater usage, minimum interconnection number and minimum total throughput).

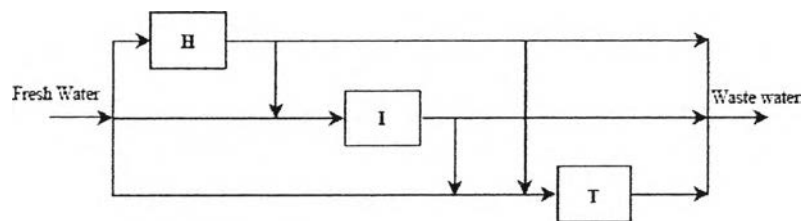


Figure 2.36 The schematic representation of a water-using network that H is head processes, I is intermediate wastewater user process and T is terminal wastewater user processes (Savelski *et al.*, 2003).

Furthermore, Savelski *et al.* (2003) presented necessary conditions of optimality for multiple contaminants in water allocation systems (Figure 2.36) in refineries and process plants. The freshwater minimization and the conditions must feature the maximum outlet concentration of at least one component (called the key component). Additionally, the condition of concentration monotonicity was derived and proven for the key component.

Additionally, Ponce-Ortega *et al.* (2009) presented an approach to optimize simultaneously direct recycle-reuse networks along with the wastewater treatment processes (Centralized system) as shown in Figure 2.37 through MINLP model to satisfy the environmental regulations. The model is applied with a disjunctive programming formulation and considered treatment technologies. The property-based and environmental constraints such as toxicity, theoretical oxygen demand, pH, color, and odor were taken into account. The MINLP model was formulated and used to minimize the total annual cost of the system.

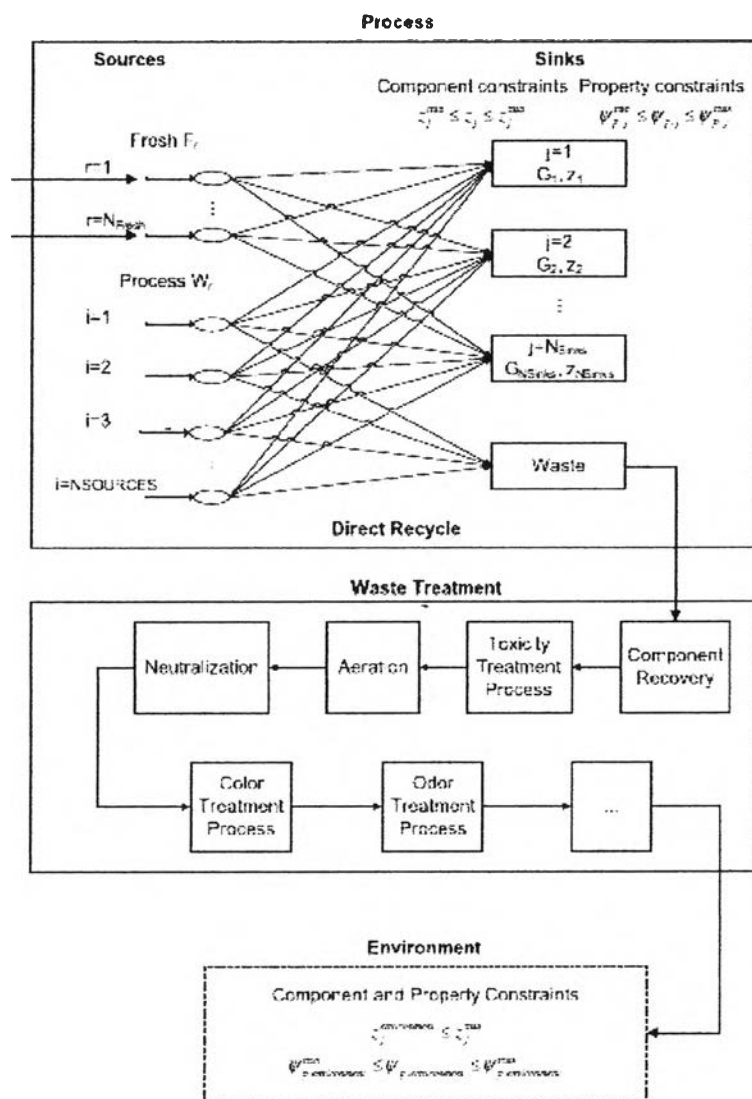


Figure 2.37 Source-sink representation for mass and property integration including waste treatment (Nápoles-Rivera *et al.*, 2010).

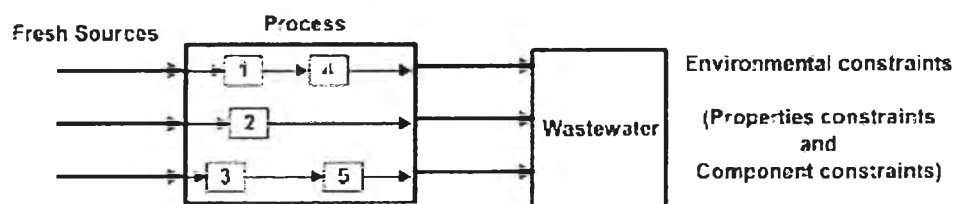


Figure 2.38 The conceptual diagram for water-using network system with properties constraints and component constraints (Ponce-Ortega *et al.*, 2009).

With regeneration and component constraints (Figure 2.38)

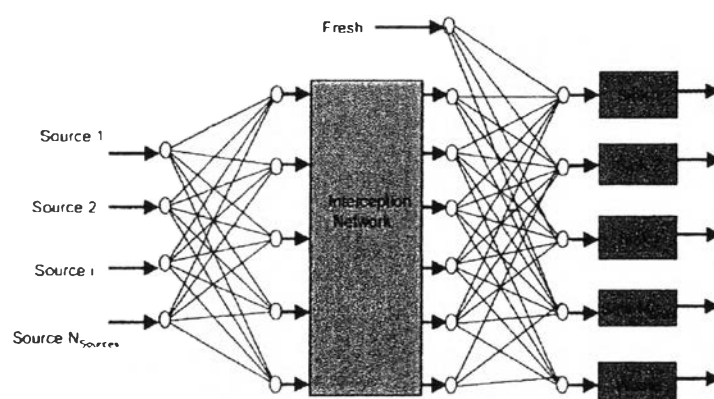


Figure 2.39 The structural representation of the problem for source and sink system with interception networks (Gabriel *et al.*, 2005).

Dunn *et al.* (2001) presented a design technique, which comprises of a single nonlinear optimization program based on general water allocation principles. The goal was to minimize the wastewater discharged (or maximize the amount of recycled wastewater) and to determine the treatment/regeneration operation position by system analysis (not optimized) using the transshipment model. For standard disposal site, the model of superstructure was formulated as an LP problem while the irrigation field (or spray field) as a disposal site for land application technology was formulated as an NLP problem. Their network could illustrate in Figure 2.39.

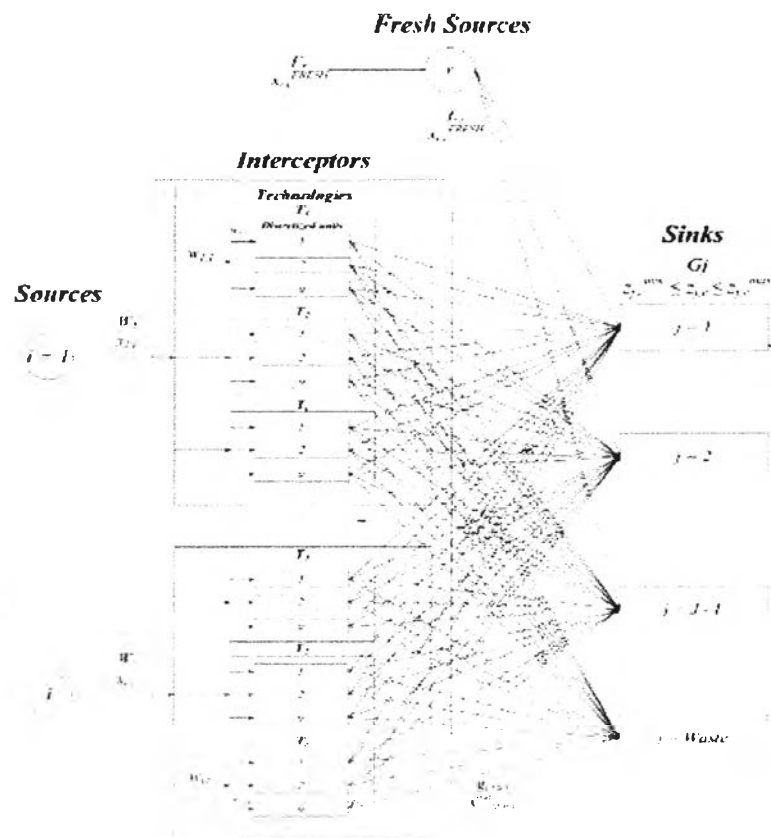


Figure 2.40 The structural representation for the recycle-reuse strategy for the multi component case with discretized units of treatment technologies (Nápoles-Rivera *et al.*, 2012).

One of significant strategies for pollution prevention is recycling and reuse material. However, in several cases, such strategies and waste streams may not be feasible due to the intolerable levels of contaminants that can be detrimental to the performance of process or can enlarge the unacceptable levels (it may not be able to manage effectively contaminant level in wastewater). Hence, selective pollutant removal by using separation devices or interceptors was represented as interception. Gabriel *et al.* (2005) developed a systematic method for the simultaneous synthesis of material recycle-reuse and waste interceptions networks as shown in Figure 2.40. The solution alternatives were a source-interception-sink structural representation. A general mathematical model was reformulated by reason of nonconvexities so that the problem yields a linear program

and effective global optimum of the solution. The problem reformulation was decomposed by source substreams and interceptors. Furthermore, the performance and cost of interceptor could be calculated for pre-synthesis that did not decline exactness of the model.

Subsequently, Nápoles-Rivera et al. (2012) presented the approach for that the separation of all the components presented in the mixture in only one unit, and that the removal efficiency was a function of the design and operation variables of the selected technology as well as the stream characteristics. The method comprised of a two-step and a simplifying superstructure as the result of the nonlinear and nonconvex nature of the optimization model. First, this was to solve a pre-synthesis problem to identify the performance and cost of interceptors with specific tasks. Second, this was to formulate a representation that avoids the mixing of different streams in the treatment system. Moreover, the model showed convenient robustness properties that could be used in extensions to include uncertainty considerations by reason of its linear formulation.

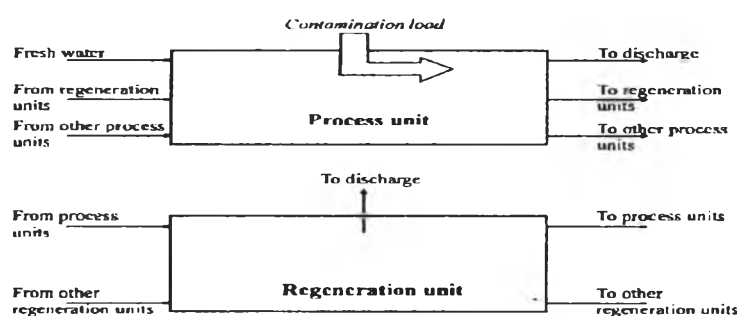


Figure 2.41 Generic elements of the superstructure of water-using unit with regeneration unit (Boix *et al.*, 2011).

However, regeneration recycling water networks were more interested so as to enhance the minimization of water use. Feng *et al.* (2008) used model coupling with superstructure to optimize regeneration recycling water networks (Figure 2.41) at the stage of grass-roots design; a fixed removal ratio and

fixed outlet concentrations (treatment technology is not a decision variable and the arrangement of treatment units is not variable).

Moreover, the number of interconnections among processes was also set as the objective function to simplify the network structure. In this work, the problem was solved step by step as virtually a multiobjective problem because of several important parameters on regeneration recycling involved for minimization of the freshwater consumption, regenerated water flow rate and contaminant regeneration load.

In the same year, Faria *et al.* (2008) proposed the approach to create MILP by discretization one of the variables (concentration interval) of the bilinear terms for addressing water allocation problems, which contained the nonlinearities and non-convexities (due to bilinear terms) and determining the global optimum. For an interval elimination procedure proposed, it could reduce the gap between this lower bound and the upper bound that identified the feasible space shrinks after each iteration and the global optimum. Also, this approach can be applied to maximize outlet concentration from regeneration processes under the minimum freshwater flow rate condition

To recover the maximum water, Hashim *et al.* (2009) showed the development of a Model for Optimal Design of Water Networks (MODWN) applicable for water operations involving contaminants and utilities. This work was analysed in two stages: fresh water savings mode (MILP) which is solved to provide some initial values for the second stage, and economic mode (MINLP) that is used to optimize an existing design of water systems by considering elimination, reduction, reuse, outsourcing as well as regeneration and cost constraints simultaneously to select the best water minimization schemes. In addition, the MODWN has effectively yielded more accurate results and would be very beneficial for the design and retrofit of municipal and industrial water networks.

Next, Boix *et al.* (2011) presented a multiobjective optimal design of multicontaminant industrial water networks under three antagonist objectives (the freshwater flow rate at the network entrance linked to environmental purposes, the water flow rate at the inlet of regeneration units related to economical insight, and the number of interconnections in the network associated

with the network complexity). The generic formulation of a wide variety of the water allocation problem (WAP) given as a set of nonlinear equations with binary variables represented the presence of interconnections in the network. The MINLP solution procedure was implemented with the set of efficient solutions in the form of Pareto fronts.

Recently, the water network synthesis in refinery has been considered again by Hwang *et al.* (2011) by using water pinch technology and a mathematical optimization programming individually for the latest technology of water network synthesis and its applications. This work referred to case study focusing on practical application to industry from refinery complex, and provided more reliable and achievable solutions for the minimization of fresh water consumption and wastewater effluents. Water pinch technology was employed at the first step for maximum water saving target and the second step employed the mathematical modelling for the improvement of water networks for raw water saving and cost reduction of waste water effluents.

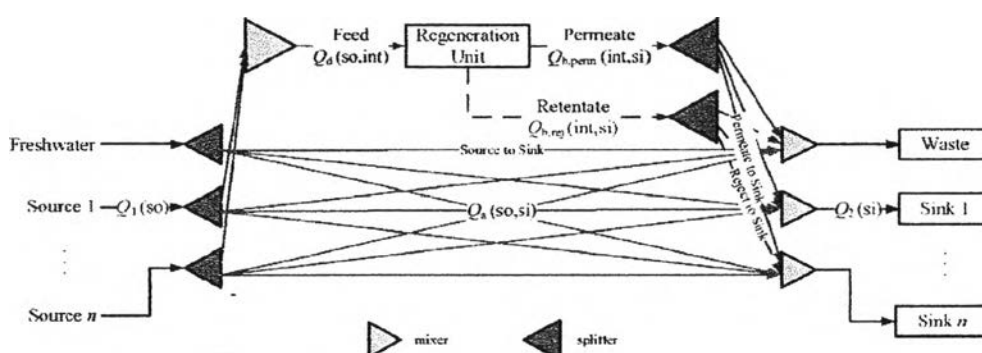


Figure 2.42 The general representation of the source-regeneration-sink superstructure with mixers and splitters (Khor *et al.*, 2011).

Besides, Khor *et al.* (2011) proposed the detailed nonlinear mechanistic model representation for water regeneration network synthesis (Figure 2.42). This incorporated within superstructure-based an overall MINLP optimization framework (both continuous variables for water flow rates and contaminant

concentrations and binary variables for selection of piping interconnections). The model produced a rigorous cost-based relation, and enabled a simultaneous evaluation of both direct water reuse/recycle and regeneration-reuse/recycle opportunities.

In addition, the approach was not limited to only demonstrate on membrane separation-based partitioning regeneration unit by investigating the interactions of a single stage reverse osmosis network, but also was certainly possible to apply with multiple treatment technologies in series or parallel (for example, a sequence of an ultrafiltration unit and an RO unit). However, the complexity occurred from the arrangement of these two technologies and the determination of intermediate composition.

With regeneration and property-based constraints (Figure 2.43 Figure 2.45)

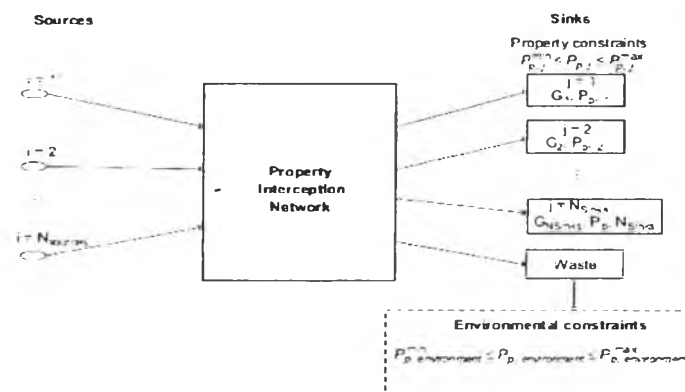


Figure 2.43 Recycle and reuse network scheme with property interception network (Nápoles-Rivera *et al.*, 2010).

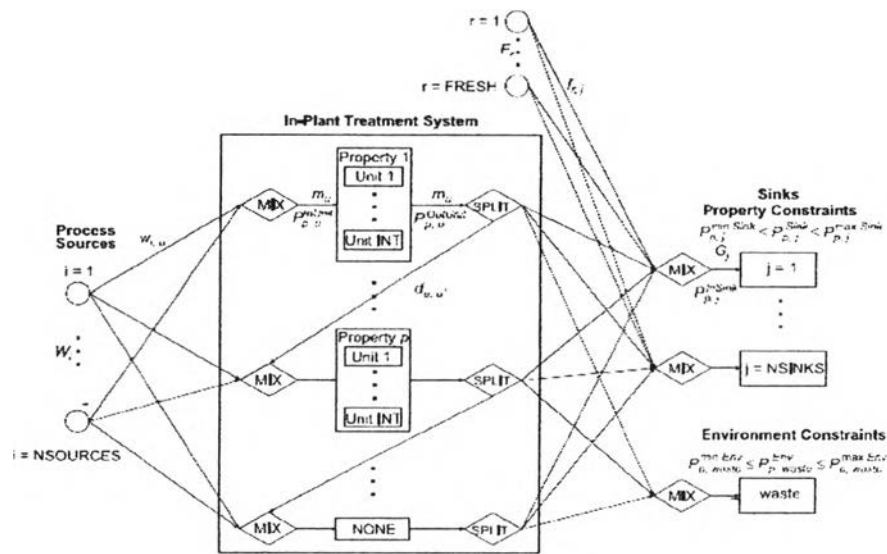


Figure 2.44 Recycle and reuse network scheme with property interception network in-plant treatment system (Nápoles-Rivera *et al.*, 2010).

To develop toward an environmental sustainability, Ponce-Ortega *et al.* (2010) showed a mathematical formulation for the direct recycle and reuse networks analysing process and environmental constraints simultaneously (Figure 2.43-Figure 2.45). The proposed model was implemented by mass and property integration strategy. In addition, the property constraints for the process sinks and the environmental constraints were considered such as pH, density, COD, color or even odor (those properties caused pollution to the environment and are difficult to quantify in terms of composition.). The model got rid of the nonlinearities of the system and managed the bilinear term in order that a global optimal solution can be identified for the minimization of TAC.

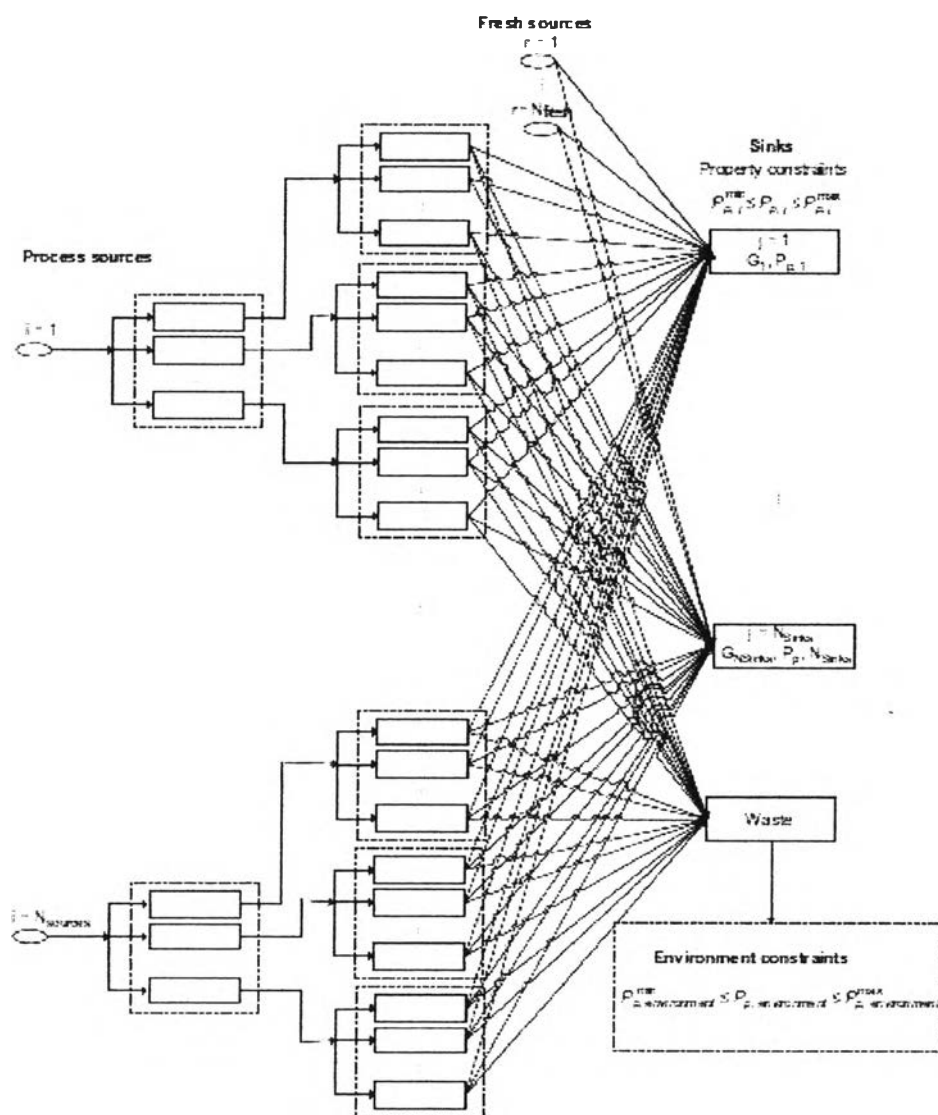


Figure 2.45 Simplified formulation for recycle and reuse mass and property integration (Nápoles-Rivera *et al.*, 2010).

Afterward, Nápoles-Rivera *et al.* (2010) presented the model comprised of process and environmental constraints likewise the above method proposed by Ponce-Ortega *et al.* (2010), while a global optimization technique was solved by the MINLP problem with bilinear terms in the property balances. Simultaneously, Nápoles-Rivera *et al.* (2010) proposed such a model that the property interceptors involved a set of disjunction formulation.

Later, Ponce-Ortega *et al.* (2011) the optimal design considered simultaneously to minimize the total annual cost and an overall Environmental Impact (EI). Additionally, the property operators and segregation of the process stream were employed for a global optimization and yielded a quasi-linear model.

Recently, Vázquez-Castillo *et al.* (2012) introduced a multiobjective systematic approach to the property-based synthesis of batch water networks. The approach considered the process intensification aspect by the simultaneously minimizing the economic objective and safety objective. The constraints of concentration-based, water characteristics and property-based on process sinks were taken into account. A multi-objective model was formulated as an MINLP problem which consisted of logical variables, mass and property sinks and environmental constraints as well as time restrictions. By the reason of quasi-linear model, the global optimal solutions could be identified.

2.8 A Review on Wastewater Treatment Network (WWTN)

The water network system for industrial process is a complex problem relating different trade-offs. Additionally, the consideration for problem about freshwater resources as well as rigorous environmental regulations on discharge has also driven to identify and develop water recovery together with disposal strategies. The water system is not only improved by such strategies but also modified by principle involving water re-use, regeneration and recycling or even process changes (i.e. wet cooling towers cannot be replaced by air-coolers, etc.). Hence, the development of a systematic method should be intended to deal with the large dimension of problem in term of various pollutants, several treatment processes or complexity of the process.

In 1994, Gupta *et al.* (1994) have improved the concept of “mass exchange network (MEN)” synthesis to address for multicomponent of waste reduction problems which frequently desire the removal of multiple toxic species from plant streams. To decompose the network synthesis problem and optimize the total network simultaneously, the State Space Approach was employed for the evaluation

of the actual unit operation, and the distribution network. In addition, the different sub-networks for the flows and unit operations provided absolute flexibility to select among all possible configurations.

2.8.1 Single Contaminant Problem

2.8.1.1 *Optimization-based Method*

Distributed wastewater treatment system

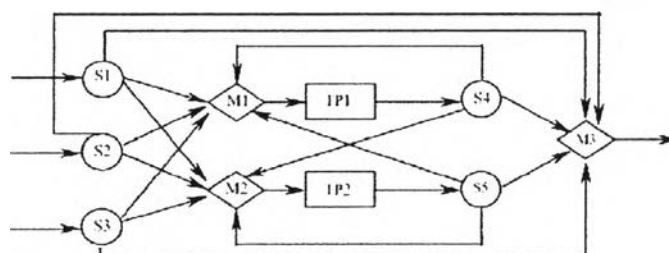


Figure 2.46 Superstructure model of wastewater treatment networks (Lili *et al.*, 2006).

Lili *et al.* (2006) presented a new water network design (Figure 2.46) based on the variable removal ratio of the treatment process. The plug-flow reactor model of Monod and Andrews was employed to calculate the removal ratio and solve the wastewater network incorporating with pinch method and mathematical programming. The method identified the general optimal solution of the minimum total annual cost.

2.8.2 Multiple Contaminant Problem

2.8.2.1 *Insight-based Method*

Distributed wastewater treatment system

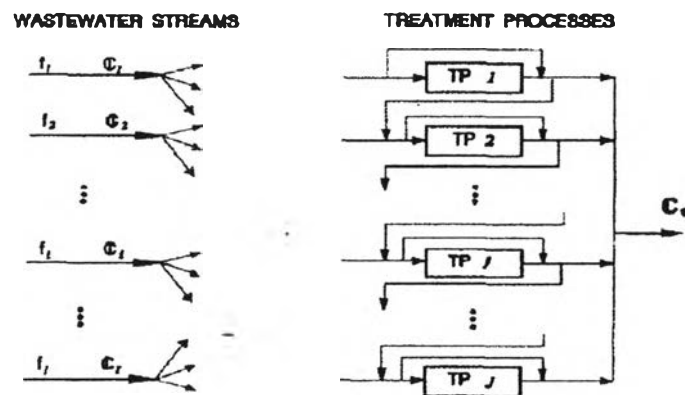


Figure 2.47 General design of wastewater treatment systems (Wang, Y.-P. *et al.*, 1994).

The distributed effluent treatment can reduce the capital and operating costs while centralized treatment will combine two waste streams needed different treatment technologies that cause treating expense for the combined streams more expensive than individual treatment of the separate streams. Wang, Y.-P. *et al.* (1994) presented and developed a design of distributed effluent treatment systems by setting targets for effluent flow rates through the treatment processes in order to minimize treatment cost. The design for distributed system should first segregate effluent stream and combine them when it is suitable (Figure 2.47).

However, previous methods were unsuccessful to address the problem of multiple treatment process, Kuo *et al.* (1997) presented the improvement in design of distributed effluent treatment systems and extended an existing system to retrofit cases. The treatment network for multiple contaminants is developed in a staged approach that targets and design was implemented repeatedly. The treatment flow rate was targeted and the distribution of the load between multiple treatment processes was addressed in this method. Although, it cannot guarantee the minimum flow rate for multiple contaminants, it could introduce towards the best solutions. The wastewater decomposition concept has been guided to consider for treatment process sequence.

2.8.2.2 Optimization-based Method

Distributed wastewater treatment system

Galan *et al.* (1998) presented the optimum design of a distributed wastewater network for reducing the concentration of several contaminants (Figure 2.53). A heuristic search procedure was proposed to find a good upper bound of the global optimum of different objective functions. Also, the method was based on the successive solution of a relaxed linear model and the original nonconvex nonlinear problem which often exhibits local minimum and causes convergence difficulties. The procedure was solved as a relaxed LP (MILP) of the original nonconvex model and to use this solution as a starting point of the NLP-problem. Additionally, the model was also included the selection of different treatment technologies (the arrangement of technology units was fixed: one unit for each technology) and for handling membrane separation modules.

Later, Hamad *et al.* (2003) applied a mass integration concept for reducing wastewater treatment and discharge in mini-industrial plants. The functional analysis, graphical analysis tools, and mathematical formulation were used as a solution procedure to reduce the size of the problem. Additionally, the comparison among all scenarios of interception/separation was implemented by sensitivity analysis to identify the optimal cost-effective solutions (minimization of wastewater discharge). The solution associated with an existing settling tank of the wastewater stream, reverse osmosis and evaporation to satisfy environmental target, while segregation, recycling, and mixing strategies were carried out to reduce the cost of treatment.

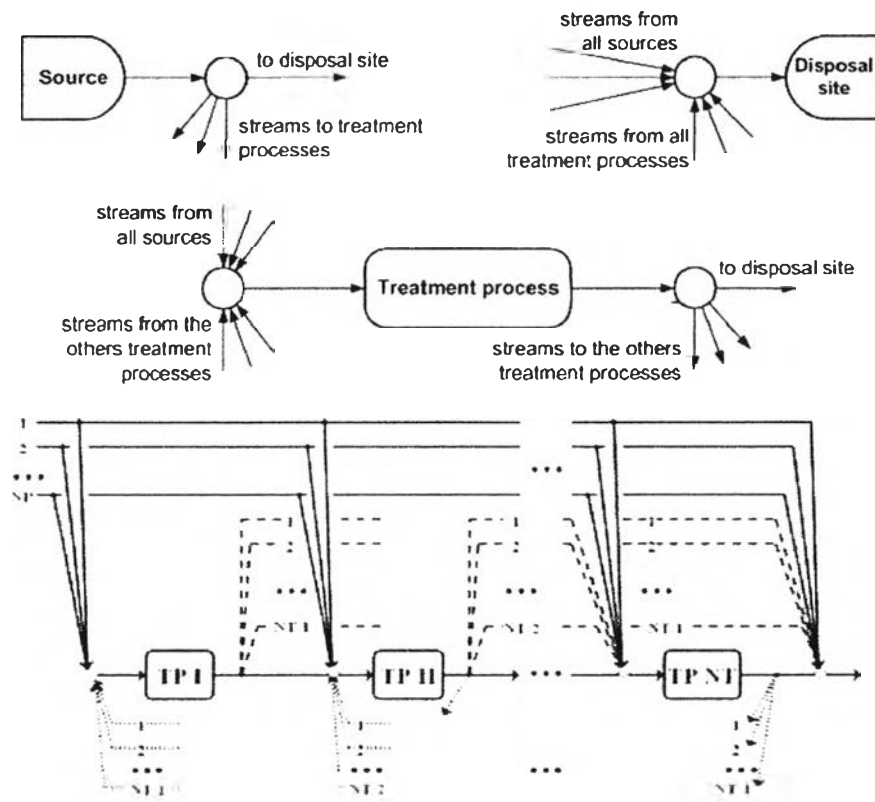


Figure 2.48 The superstructure of WWTN (Poplewski *et al.*, 2007, Statyukha *et al.*, 2007).

With more concern on economy and environment in optimizing wastewater treatment network, Poplewski *et al.* (2007) addressed a single-stage optimization based on simultaneous approach to design an optimal wastewater treatment network (WWTN) as shown in Figure 2.48. They used a direct stochastic random search technique to deal with complex nonlinear problem.

To show the application via a real case study from industrial process, Statyukha *et al.* (2007) developed a sequential method implemented pinch techniques followed by mathematical programming to minimize wastewater treatment and piping cost for wastewater treatment network design (WWTN). Additionally, this method applied models for treatment process and also retrofit the

system in industrial plants. The WWTN design procedure in treatment processes considered removal ratios and flow rates change.

Moreover, by reason of the uncertain data and specific conditions of realistic problems, Statyukha *et al.* (2008) presented WWTN through a simple sequential approach. This approach employed water pinch techniques for an initial structure and followed by mathematical techniques for minimization of treatment process cost. The superstructure consisting of splitters, mixers and piping sections used as starting point for nonlinear optimization.

And next year, Dzhygyrey *et al.* (2009) employed a sequential approach to consider the relation between removal ratio and treatment flow rate as well as concentration of certain contaminants for treatment processes. This provided the contaminant losses and gains in particular treatment process and could determine the total flow rate change within a design procedure of the wastewater treatment network. The approach was applied to solve various industrial plant problems to design and retrofit wastewater treatment systems.

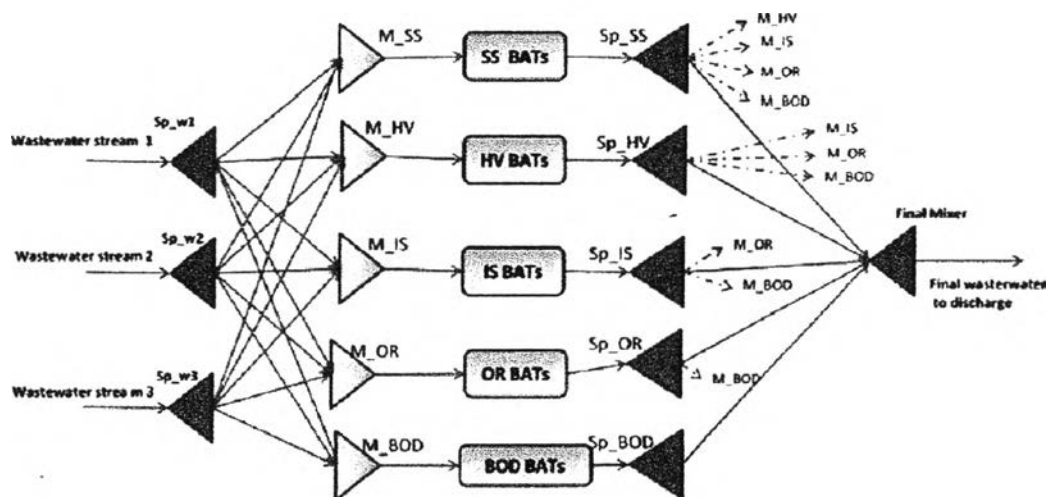


Figure 2.49 Superstructure of the end-of-pipe technologies wastewater network (Galán *et al.*, 2011).

However, The real industrial wastewater treatment networks has been designed by Galán *et al.* (2011). They have proposed a superstructure,

which was formulated as an MINLP for wastewater treatment network design. The important feature has been the incorporation of best available technologies for the removal of the contaminants (following a specified sequence to avoid reducing the efficiency in the downstream technologies). The real world process problems could be addressed, and the optimal solution involved filtration, microfiltration, reverse osmosis and aerobic biological treatment (Figure 2.49).

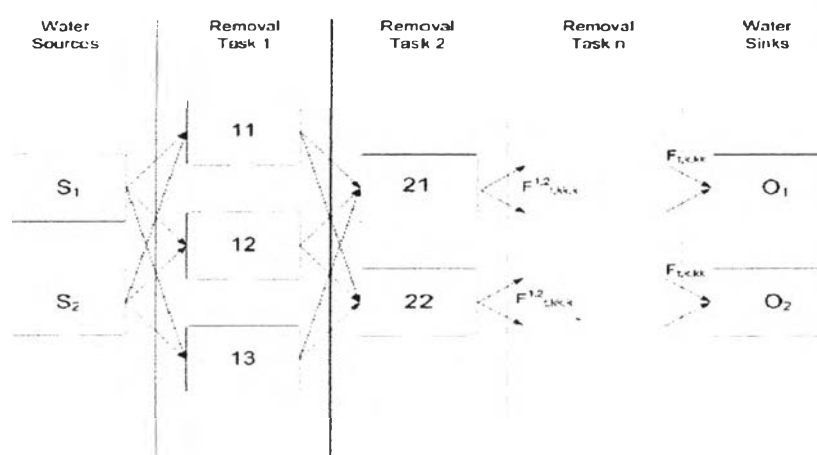


Figure 2.50 The schematic representation of the superstructure architecture (Pennati, 2012).

Recently, Pennati (2012) proposed a systematic method framework for the formulation and solution of water network problems. The optimization was formulated as a Mixed Integer Linear or Non-Linear Programming (MIP/MINLP), and solved to determine the best wastewater treatment process among a set of different predefined alternatives, according to selected optimum criteria. A superstructure of available technologies for water purification was used to identify different process paths dividing the treatment operation in tasks to remove the various pollutants. For each task, it was considered various alternatives among process units currently used in industry (Figure 2.50).

This systematic method offered a comprehensive characterization of the water stream and a functional model of the treatment units. Also the method showed its ability to handle the complexity and the dimension of an

industrial problem as well as flexibility for the evaluation of different scenarios. Hence, it made a useful tool for the design of wastewater treatment network systems for a new plant, retrofitting or expansion of existing plants that provide various contaminants and allows a more descriptive model of the treatment units.