CHAPTER IV

RESULTS AND DISCUSSION

According to the described computer-aided framework for synthesis and design of industrial WWTN problem, this section presented the definition of problem, generation of alternatives, development of model, collection of data, formulation and solution of the design problem through developed and modified model here for different scenarios of petroleum refinery effluent treatment plant (existing process, grassroots system and retrofit design case) with recycling option and distributed treatment system.

4.1 Statement of WWTN Problem

The optimization-based design and synthesis of WWTN problem in this work based on the framework of (Quaglia et al., 2013) could be stated as follows (Figure 4.1): given are a set of different multiple wastewater streams (sources) from an industrial process defined by their flow rate, contaminant types and level, a set of alternative wastewater treatment units (relative to refinery effluent treatment) defined by different functional model in each unit (i.e. removal ratio, reaction conversion etc.), and treatment objective (sinks) defined by both maximum specification of flow rate, contaminant types and level (for discharge and recycling). The problem was to determine the optimal water treatment network configuration in order to satisfy certain defined treatment objectives with respect to both economic and environmental perspectives.

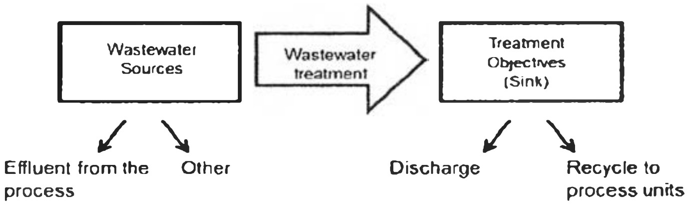

Figure 4.1 Detail of WWTN problem statement pattern.

4.2 Case Study: Petroleum Refinery Effluent Treatment Plant

A case study dealing with petroleum refinery wastewater treatment plant (Figure 4.2) in Thailand (PTT GC) was formulated and solved through the four main steps of the method described in chapter III. The case study was applied by considering both the design of base cases (PTT's existing process and grassroots system) and the retrofit design of the base cases, and emphasizing on the aspect of recycling opportunity, including with distributed treatment system.

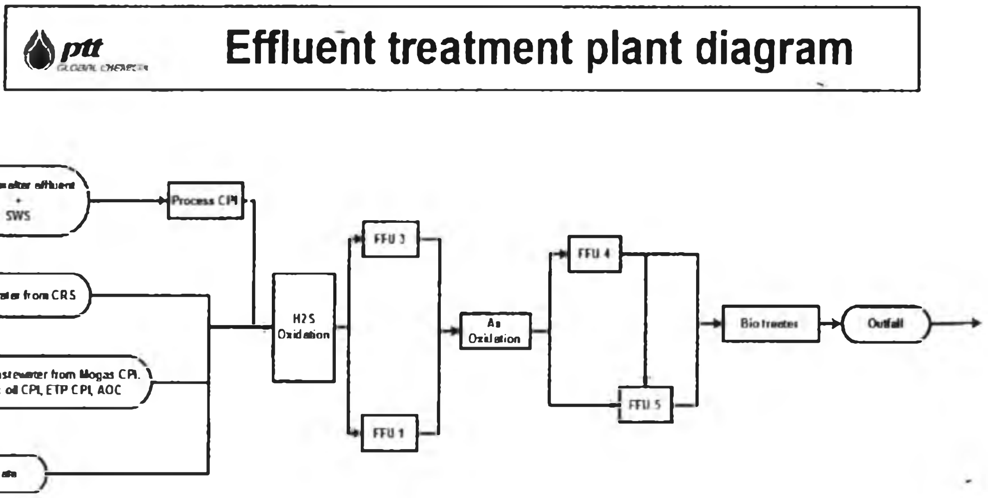

Figure 4.2 PTT's effluent treatment plant diagram (simplified diagram).

4.3 Problem Formulation (Step I)

4.3.1 Scope and Objective Function

The purpose of the study was to modify and develop a generic model-based synthesis for the optimization WWTN problem with respect to petroleum refinery effluent treatment plant for the benefit of the modern society and more specifically, for reducing the fresh water consumption together with re-using treated water in processes (Figure 4.3). The objective (Eq. (**4.1**) of the optimal wastewater treatment network design was to minimize the total annualized cost (TAC) through various design scenarios focusing on the recycling aspect

$$TAC = Cost_{capital} \cdot \left[\frac{i \cdot (1+i)^n}{(1+i)^n - 1} \right] + Cost_{operation} - Savings_{recycle} \qquad (4.1)$$

where TAC consisted of capital expenditure (CAPEX) and operational expenditure (OPEX). CAPEX was amortization based on a basis of a 15-year plant lifetime at an interest rate of 5% per annum while OPEX (utility consumption and waste disposal cost) was on a yearly basis. The Savings cost was an annual reduction cost of using recycled water.

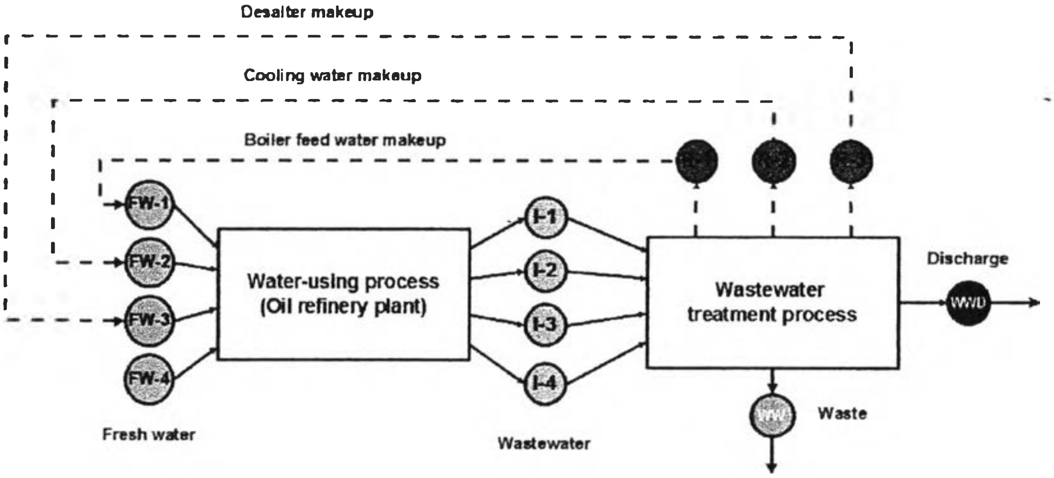

Figure 4.3 The overall mass flow balance between water-using process and wastewater treatment process.

4.3.2 Wastewater Sources Identification and Characterization

Major pollutants normally found and measured in PTT GC oil refinery wastewater consisted of carbonaceous organic species (represented by COD and BOD), oil and grease, suspended solid, gas (hydrogen sulfide), ion (ammonium ion) and heavy metal (i.e. arsenic). Therefore, the number of contaminant species, which were investigated and considered for this case study, were presented in terms of COD (Chemical oxygen demand), BOD (Biochemical oxygen demand), TSS (total suspended solid), FSS (Fixed suspended solid), O&G (Oil and Grease), NH_4^+ (ammonium ion), H_2S (hydrogen sulfide) and As (Arsenic). This characterization was needed in order to define a treatment process model with respect to a removal of those contaminants.

Wastewater sources in the case study came from several effluents in the process. However, four main sources were considered and identified as follows: Source 1 was the effluent of CDU desalter combining with sour water stripper, Source 2 was the effluent of condensate residual splitter, Source 3 was the effluent of various CPI (such as MOGAS CPI, Black oil CPI effluent) and source 4 was the effluent of decanter unit. All sources of wastewaters were characterized by the flow rate and the concentration of their contaminants as shown in Table 4.1.

4.3.3 Water Sinks and Users Identification and Characterization

A discharge of treated water to sea is the only one option included in the existing process of PTT GC that is abided by Thailand regulation. However, in order to reduce the discharge and fresh water consumption in the process, in this work, the recycling alternatives of treated water to process were considered. Typically, the main water consumption in a refinery was concerned with the cooling system, the boiler feed water systems and the process units, i.e. desalter makeup. Thus, these three water sinks as recycling options together with the discharge to sea were identified as the options of the treatment objective in the case study. These water sinks are designated as follows: Discharge to sea—WWD (sink 91), Recycle as boiler feed water makeup—BFW (sink 92), Recycle as cooling water makeup—CW (sink 93) and Recycle to desalter makeup—DS (sink 94).

The limit compositions and flow rates in each water sink were reported in Table 4.1. Moreover, the limit concentrations of each recycled water sink included not only the pollutants considered, but also all other species that might be also generated during treatment operation. In brief, the flow rate and the contamination level as well as type of the wastewater and their limitation were based on literature information as well as required specifications of the plant (Table 4.1).

Table 4.1 Wastewater influent (sources)—flow rate and composition; Treatment objectives (sinks)—limitations on the maximum flow rate and pollutant concentrations; Limitation of wastewater before entering to biotreater

Data	UOM	Wastewater influent specification				Water effluent specification			
		1	2	3	4	D	BFW*	CW*	DS
Flow rate	t/h	22	51	2	4	-	337	213	40
COD	mg/l	5014	4564	1750	9335	120	5	75	-
BOD	mg/l	1770	1611	618	3295	20	-	-	-
TSS	mg/l	561	3163	-	4681	50	5	50	-
O&G	mg/l	893	236	-	2380	5	25	25	10
FSS	mg/l	281	1581	-	2340	25	5	50	-
NH_4^+	mg/l	66	85	-	-	35	1.9	1.3	100
H_2S	mg/l	12	14	-	-	1	5	-	20
As	mg/l	-	-	18	-	0.25	0.25	0.25	-
SO_4^{2-}	mg/l	-	-	-	-	-	0.05	500	-
Cl^-	mg/l	-	-	-	-	-	3.2	302	10
Na^+	mg/l	-	-	-	-	-	6.8	-	-

*Some data taken from Otts (1963), Selby *et al.* (1996) , Alexander (2007), Asano *et al.* (2007), CSIRO (2008), IPIECA (2010)

4.3.4 Special Design Constraints Definition

Based on necessary constraints of treatment process, special design constraints were considered and defined as shown in the Table 4.2. In this case, bio-treaters cannot accept the high level of some pollutants (especially heavy metal) because heavy metals can inhibit or affect harmfully to the microorganism in the bio-treaters. Thus, the special constraints were specified to avoid such a problem.

Table 4.2 Limitation of wastewater before entering to biotreater

Composition	Unit	Concentration
NH_4^+	mg/l	<60
COD	mg/l	<1500
As	mg/l	<0.25

4.4 Generation of Alternatives (Step II)

4.4.1 Treatment Process Tasks and Their Alternatives Identification

The possible treatment process for superstructure were considered on the basis of the pollutants (with respect to the case study) to be removed, or the principle (Tchobanoglous et al. (2003); IPIECA (2010)) on which the treatment was relied on. A list of the treatment units considered in this work is shown in Table 4.3

4.4.2 Superstructure Construction

The model database regarding treatment process interval of Quaglia *et al.* (2013) was referred to and modified in this case study to construct the WWTN superstructure for a specific problem. Based on the existing process and model database, the process CPI unit was represented as CPI/PPI unit interval. The H_2S oxidation unit and flocculation floatation unit (FFU1&3) that removed mainly H_2S, NH_3, COD O&G, TSS were considered and formulated as WAO unit—modified as a series of treatment with flocculation floatation in a process interval—combined with AirS unit. The role of arsenic oxidation unit followed by flocculation floatation unit (for precipitation) removed mainly arsenic, COD O&G and TSS. It was represented by AsOx unit generated as new sequential treatment within process interval. In addition, Biotreater involving a biological treatment was represented by TF and AS unit. Finally, all tertiary treatment units (GAC, IE, ED, MF/UF and NF/RO) were set up as alternative supporting treatment units for a higher specification of water effluent (that can remove various contaminants) in the future. In conclusion, total units in the modified superstructure were classified as equivalent units (for existing process) and alternative units (for potential expansion of existing process) as reported in Table 4.4.

Moreover, each treatment process task also included a bypass system (for split option) to design a distributed wastewater treatment system. Thus, the modified superstructure in the Figure 4.4 could represent more than 70,000 possible alternative treatment configurations.

Table 4.3 List of wastewater treatment process selected in the superstructure

Principle	Process interval (treatment process)	Abbreviation	Number ID
Gravity separation	American Petroleum Institute separator	API	101
	Corrugated and parallel plate separator	CPI/PPI	102
Floatation	Dissolved Air Floatation	DAF	111
	Induced Air Floatation	IAF	112
Oxidation and precipitation	Wet air oxidation	WAO	121
	Arsenic oxidation and precipitation	AsOx	151
Stripping	Sour Water Stripper	SWS	131
	H_2S Stripper	SS	132
	NH_3 Stripper	NS	141
	Air Stripper	AirS	142
Biological treatment	Trickling Filter	TF	161
	Rotating Biological Contactor	RBC	171
	Activated Sludge	AS	172
	Activated Carbon assisted activated	PACT	173
	sludge		174
	Membrane Biological Reactor	MBR	
Adsorption	Adsorption on Granular Activated Carbon	GAC	181
Electrostatic separation	Ion Exchange	IE	191
	Electrodialysis	ED	192
Tertiary filtration	Microfiltration/Ultrafiltration	MF/UF	201
	Nanofiltration/Reverse Osmosis	NF/RO	211
-	Bypass-No treatment (Empty interval)	BP1-BP11	103, 113, 122, 133, 143, 152, 162, 175, 182, 193, 202, 212

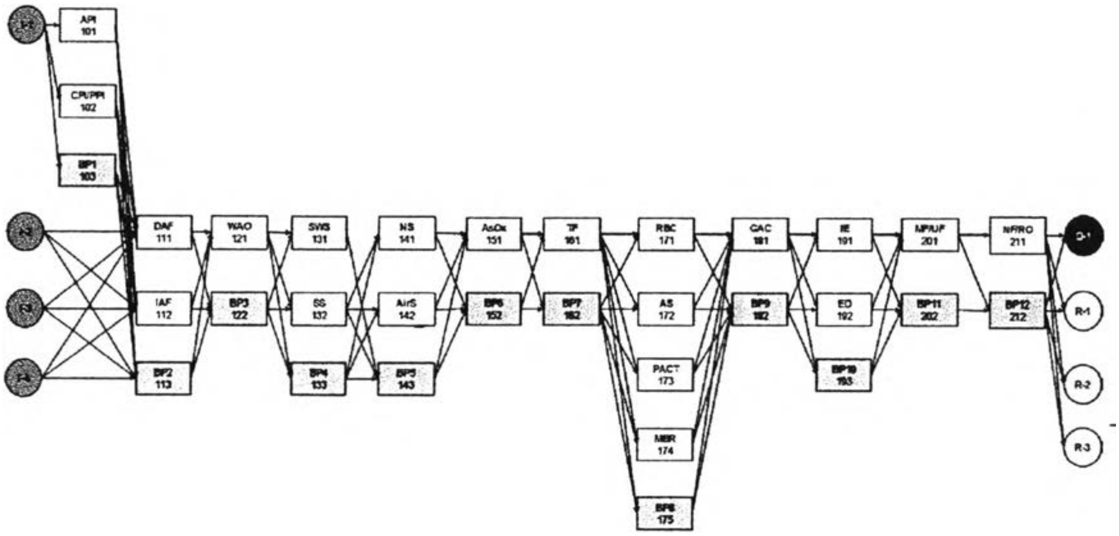

Figure 4.4 Schematic representation of superstructure for refinery effluent treatment network.

Table 4.4 Treatment process tasks and alternatives

Task	Existing process	Treatment Process interval		
		Equivalent unit	Alternative unit	
1	Process CPI	CPI/PPI	API	Bypass
2	-	-	DAF, IAF	Bypass
3	H2S oxidation	ModifiedWAO	-	Bypass
4	+	-	SWS,SS	Bypass
5	FFU 1&3	AirS	NS	Bypass
6	Arsenic oxidation + FFU 4&5	AsOx	-	Bypass
7	Bio-treaters	TF	-	Bypass
8		AS	RBC, PACT, MBR	Bypass
9	-	-	GAC	Bypass
10	-	-	IE, ED	Bypass
11	-	-	MF/UF	Bypass
12	-	-	NF/RO	Bypass

4.5 Model Development and Data Collection (Step III)

For model of wastewater characterization and wastewater treatment process (simple short-cut model), they were considered and based on the same method proposed by Quaglia *et al.* (2013) except those equations for reaction of aqueous dissolution and water pumping cost based the on pressure drop were not considered in this work for simplification. An additional data for new treatment process is reported in Table 4.4 while the complete list for all components (33 species) in the case study is shown in Table 4.5 .

For model of network, the network of treatment interval namely single stream problem was defined as the "non-split option" where a maximum of one interval per treatment task was allowed while the multi-stream problem was defined as the "split option" where a maximum of two intervals per treatment task and the selection of more than one effluent are allowed. Additionally, in this work the case study for existing process (base case) network problem was formulated as the non-split option while for the retrofit process, both non-split and split options were formulated. Also, the model database with respect to generic treatment model was implemented and modified on the specific problem.

Table 4.5 List for all component considered in the case study

Contaminants	Utilities	Species generated
H_2O	EL	SO_4^{2-}
COD	LPS	MO
H_2S	CW	OCl^-
FSS	H_3PO_4	Cl^-
NH_4^+	H_2SO_4	$H_2AsO_4^-$
O&G	NaOH	Na^+
H_3AsO_3	GAC	H^+
TSS	CO_2, N_2, O_2	
BOD	NG	
	Alum	
	NaOCl	
	$C_6H_8O_7$	
	$FeCl_3$	
	NH_3	
	Cl_2	

4.6 Optimization Problem Formulation and Solution (Step IV)

4.6.1 Optimization Problem Formulation

The different scenarios were considered with respect to effluent selection and required structure of the optimal solution by considering:

1. Number of water effluent: resulting in the definition of single-effluent (if only one effluent can be selected) and multi-effluent scenarios
2. Water recycle requirement: resulting in the definition of zero-liquid discharge (if complete recycle of the water stream is required) and non-zero liquid discharge scenarios.
3. Structure of the treatment process: resulting in the definition of split (distributed treatment/effluent system) and non-split (centralized treatment/effluent system) options, as described above.

The scenario list was defined through the combination of the abovementioned formulations resulting in the structure reported in Figure 4.5 for both new system (grassroots system) and the retrofit design in order to feature the advantages of the tool that could effectively synthesize and optimize the complex problem with a more detailed representation of water network design through the mathematical model in different scenarios.

However, zero liquid discharge case for a single effluent scenario could only be modelled by two possible alternatives, namely CW and BFW. Because the requirement for desalter makeup was less than the total flow of wastewater sources in the case study, thus, desalter makeup cannot be an option for zero liquid discharge case in single effluent scenario. In conclusion, all network scenarios that were considered in network set P (Existing process design and its retrofit design) and G (Grassroots system design and its retrofit design) are shown as Figure 4.5.

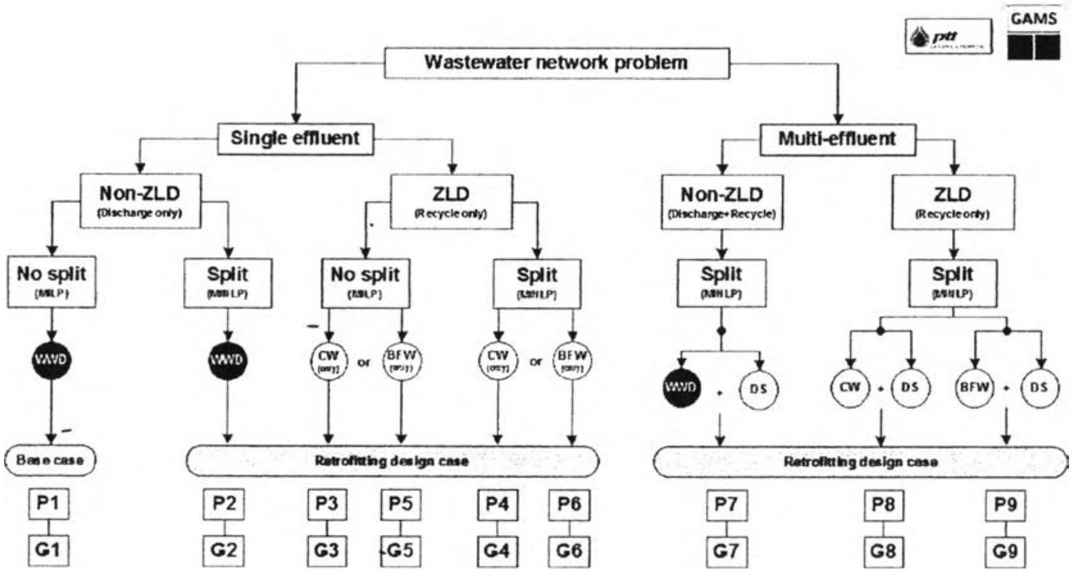

Figure 4.5 Classification of problem scheme for network problem P1-P9 and G1-G9.

4.6.2 Optimization Problem Solution

From this modification of general model formulation as well as specific problems in this work could be formulated by the specifications of different variables of a base case process and retrofit design scenarios—fixing all or part of the network topology and water effluent selection and flows. Moreover, two options (non-split and split) of the specific problem were employed based on the different solution strategies in the followings:

4.6.2.1 One-Stage Solution Strategies for LP/MILP Model (Direct Linearization)

Direct linearization was employed for non-split option of the problem and was solved through solver CPLEX (Rosenthal, 2012). Also, this MILP solution was loaded as initialization for MINLP model.

4.6.2.2 Two-Stage Solution Strategies for NLP/MINLP Model (Sequential Solution Procedure)

Because of the split option allowing for the selection of maximum two intervals per treatment task, the problem was formulated as MINLP model. For two stages, Loading initialization point from MILP solution and fixed binary variables (only one treatment interval as MILP solution) were a preliminary process to be set up (first stage). Then, the model was solved directly by solver DICOPT (Grossmann *et al.*, 2002) in second stage respectively for both base cases and their retrofit design cases (Figure 4.6).

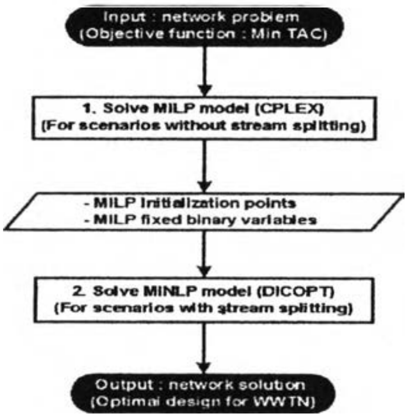

Figure 4.6 Two-stage solution strategy.

The statistics solution of both MILP and MINLP problem obtained in this model contained different number of variables, equations, binary variables together with an average CPU time as shown in Table 4.6.

Table 4.6 Optimization problem solution statistics

Model statistics	No split option		Split option	
Design problem (configuration)	PTT	GAMS	PTT	GAMS
Model	MILP	MILP	MINLP	MINLP
Number of variables	247022	247022	247088	247084
Number of binary variables	10	32	10	7
Number of equations	406351	406351	406511	406507
Number of non-linear equation	-	-	9216	9120
Relative optimality tolerance	0.00001	0.00001	0.00001	0.00001
Average CPU time(s)	~9	~11	~2640	~5710

4.6.3 Optimization Problem Results

In accordance with the case study, the model was highlighted by the application in the case study that was divided into two main parts: the first case was PTT's configuration case (Base case of existing process and its retrofit design cases) and the GAMS' configuration case (Base case of grassroots system and its retrofit design cases). In order to minimize the wastewater discharge generation and fresh water consumption, several options were included to study the recycling of treated wastewater at the effluent (sink) as alternative treatment objectives.

The results in each optimal network solution were considered in terms of process specification and economic benefit. Additionally, in order to feature the advantages of the tool that could effectively synthesize and optimize the complex problem with a more detailed representation of water network design through the mathematical model in different scenarios, different cases were compared to each other as follows:

4.6.3.1 Base Case and Retrofit Design of Existing Process (Network P's)

Network solution with process specification and cost breakdown analysis for base case (network P1) and its retrofit design (network P2-P9) were summarized as follows:

Their connection of treatment units and effluent streams in all network scenarios are shown in Table 4.7. It is of interest to note that some scenarios for some recycled effluent required more additional treatment processes (IE, ED, MF/UF and NF/RO) in order to polish the wastewater for recycling to CW or BFW makeup.

Table 4.7 Network connection of PTT's configuration case

Network	Connection of treatment units											
P1	CPI/PPI	BP2	WAO	BP4	AirS	AsOx	TF	AS	BP9	BP10	BP11	BP12	WWD
P2	CPI/PPI	BP2	WAO BP3	BP4	AirS	AsOx BP6	TF	AS	BP9	BP10	BP11	BP12	WWD
P3	CPI/PPI	BP2	WAO	BP4	AirS	AsOx	TF	AS	BP9	ED	MF/UF	NF/RO	CW
P4	CPI/PPI	BP2	WAO BP3	BP4	AirS BP5	AsOx BP6	TF	AS BP8	BP9	ED	MF/UF	NF/RO	CW
P5	CPI/PPI	BP2	WAO	BP4	AirS	AsOx	TF	AS	BP9	IE	MF/UF	NF/RO	BFW
P6	CPI/PPI	BP2	WAO BP3	BP4	AirS BP5	AsOx BP6	TF	AS	BP9	IE BP10	MF/UF	NF/RO	BFW
P7	CPI/PPI	BP2	WAO BP3	BP4	AirS BP5	AsOx BP6	TF	AS	BP9	BP10	BP11	BP12	WWD DS
P8	CPI/PPI	BP2	WAO BP3	BP4	AirS	AsOx BP6	TF BP7	AS	BP9	ED	MF/UF BP11	NF/RO BP12	CW DS
P9	CPI/PPI	BP2	WAO BP3	BP4	AirS BP5	AsOx BP6	TF	AS	BP9	IE BP10	MF/UF BP11	NF/RO BP12	BFW DS

Although some network scenarios could produce various recycled effluent without wastewater discharge, retentated waste water could be generated in the filtration unit (MF/UF and NF/RO) as a result of retentated water during treatment operation and must be wasted for disposal as shown in the network scenarios P3-P6 and P8-P9. The network P7 generated part of recycled water to DS makeup without any additional filtration processed so it included only wastewater discharge and recycled water. The different water effluent fraction (WEF) of all network scenarios are presented in Figure 4.7

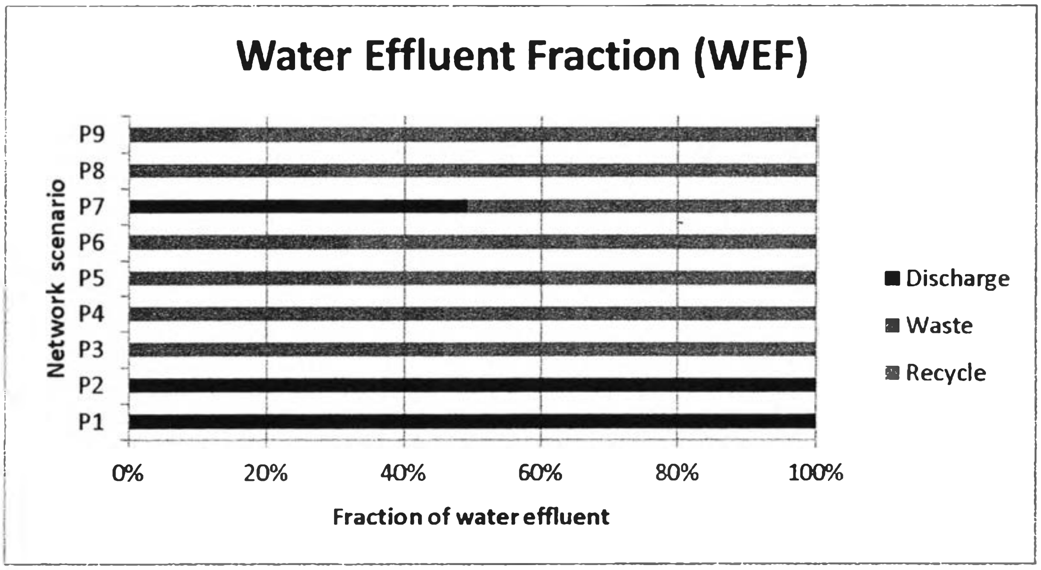

Figure 4.7 Water Effluent Fraction (WEF) of network P1-P9.

In term of cost analysis, TAC breakdown comparison is illustrated in Figure 4.8 while the detail of TAC is summarized in Table 4.8 that high proportion cost in TAC is an operational cost. As shown in Figure 4.8, cost of network P1 mainly results from both WAO and AsOx. Its TAC was 25.246 M$/y. Among all retrofit scenarios, there were two scenarios (networks P2 and P7) that reduced TAC while network P8 had similar TAC to the base case, but could produce recycled water to CW makeup more than 70 %. Other networks contributed to higher TAC due to the investment and operational cost of filtration unit for process of CW and BFW generation.

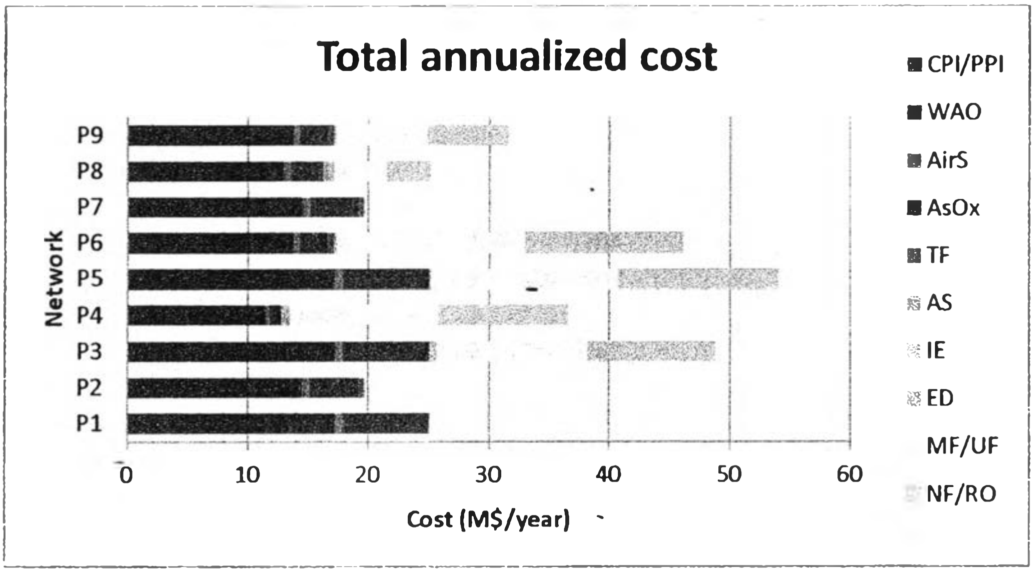

Figure 4.8 Cost breakdown (Total annualized cost) for network solution P1-P9.

Table 4.8 Summation of cost for each network solution P1-P9

		Opex (M$)				
Network		Waste disposal	Utility	Capex (M$)	Saving(M$)	TAC (M$)
P1	MILP	1.256	18.553	5.437	0.000	25.246
P2	MINLP	1.454	12.916	5.437	0.000	19.807
P3	MILP	1.324	41.806	5.675	0.008	48.796
P4	MINLP	0.838	30.025	5.675	0.008	36.529
P5	MILP	1.304	47.200	5.603	0.220	53.886
P6	MINLP	1.574	39.050	5.602	0.220	46.005
P7	MINLP	1.454	12.884	5.437	0.008	19.767
P8	MINLP	1.548	18.111	5.618	0.011	25.266
P9	MINLP	1.550	24.438	5.535	0.116	31.407

When compared to network P1 (Figure 4.9), the fraction of split stream in the network P2, P7 and P8 could be bypassed so as to help decrease the operating cost of such treatment unit tasks. Moreover, network P7 and P8 could produce the recycled water (DS or CW makeup) to the process that not only led to savings cost through reduction in fresh water, but also reduced the wastewater discharge simultaneously.

In network P2 (Figure 4.11), despite no any recycled water generation, TAC was lower than base case (-21.54%) because of this network involved the stream splitting, resulting in partially bypass the treatment units with high OPEX (WAO and AsOx). This was a retrofit design with distributed treatment system.

Meanwhile, network P7 (Figure 4.13) could generate recycled water to DS makeup (51.20% of total water effluents) requiring no additional treatment as well as the bypass stream before entering WAO, Airs and AsOx units. Thus, TAC was reduced (-21.70%) due to savings cost of DS makeup effluent and part of stream to bypass. This also helped decrease wastewater discharge.

Network P8 (Figure 4.15) had similar TAC to base case; however, this retrofit design presented zero liquid discharge option that all wastewater stream was treated as recycled water to CW and DS makeup. This indicated the improvement on the environmental impact. Even though, the network P8 required additional treatment units (ED, MF/UF and NF/RO) to further polish the water to meet with high specification of CW makeup, TAC is not high as compared to networks P3 and P4 since part of the stream could be split as bypass (before the inlet of WAO, AsOx, TF and MF/UF) and as recycled water to DS makeup.

With reference to these result of network solutions, they could be simplified as a treatment process scheme as shown in Figure 4.10, Figure 4.12, Figure 4.14 and Figure 4.16.

Note: the configuration of other network solutions was reported in Appendix C.

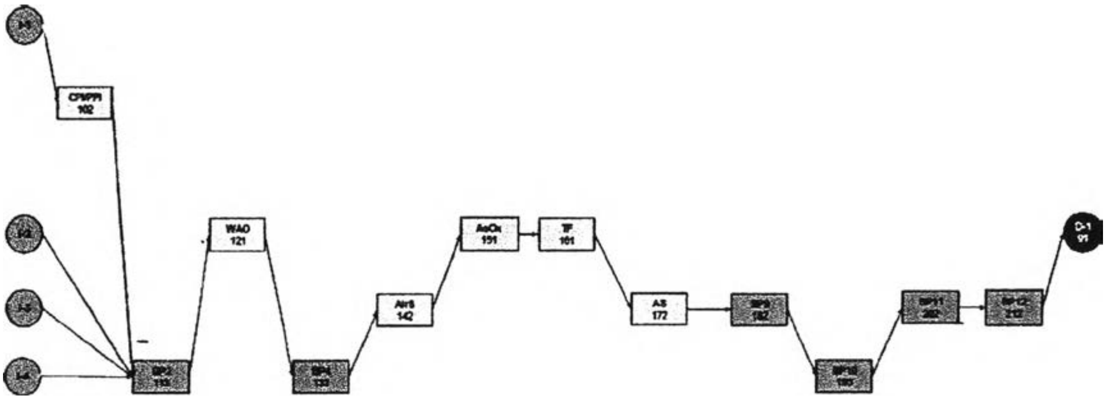

Figure 4.9 Network solution (P1) of PTT's configuration with only discharge (sink 91)-MILP model.

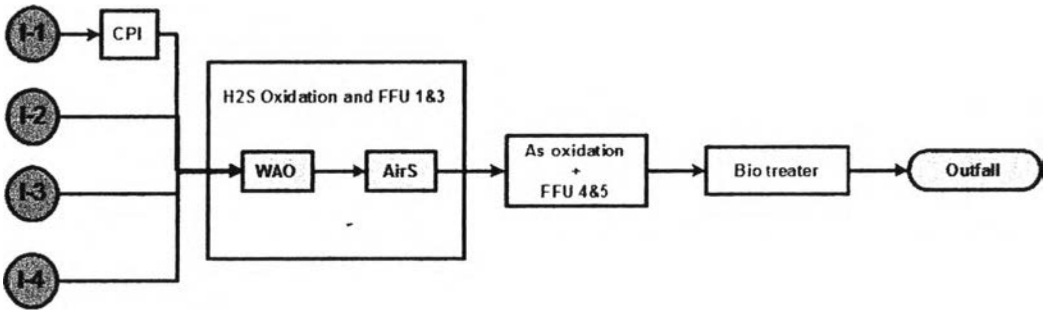

Figure 4.10 Simplified network of network solution (P1).

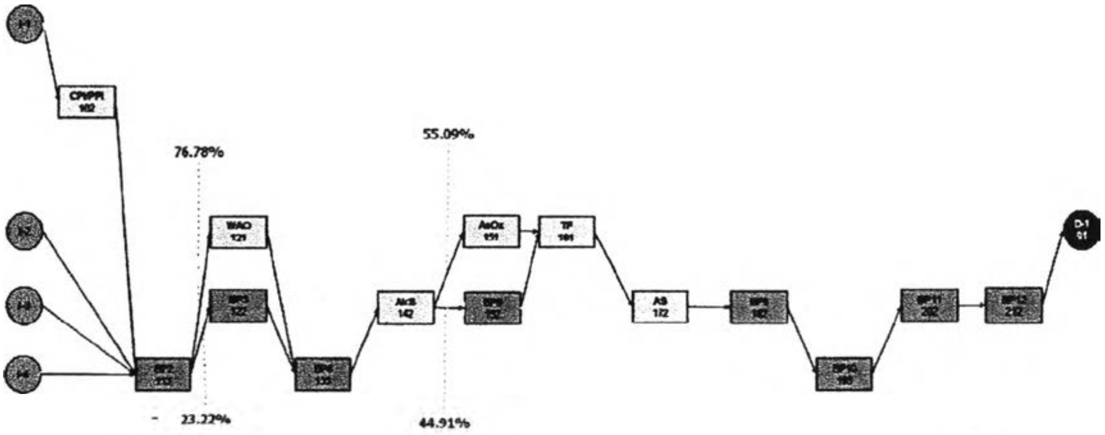

Figure 4.11 Network solution (P2) of PTT's configuration with only discharge (sink 91)-MINLP model.

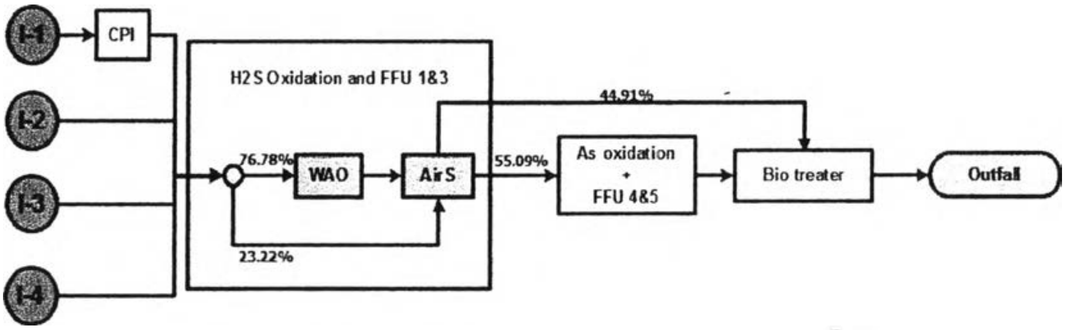

Figure 4.12 Simplified network of network solution (P2).

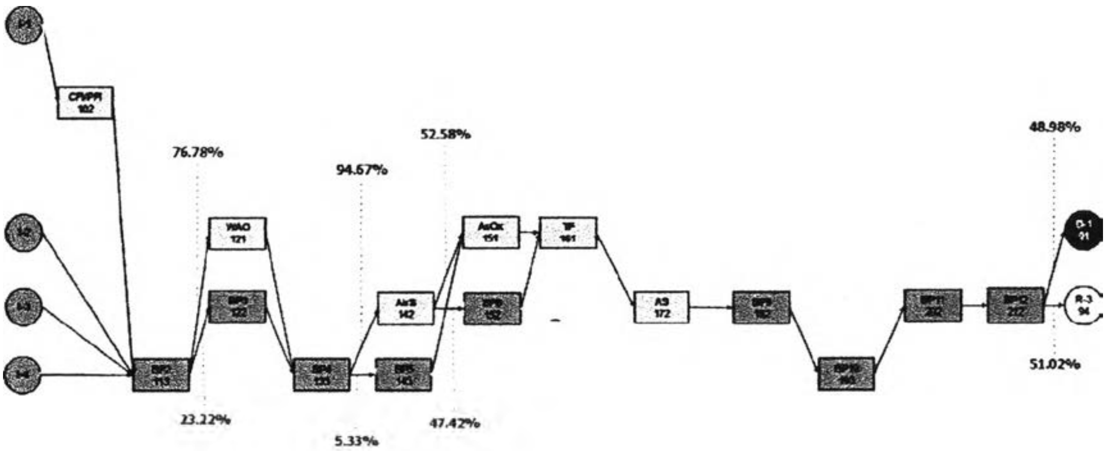

Figure 4.13 Network solution (P7) of PTT's configuration with non-zero liquid discharge for discharge (sink 91) and desalter makeup (sink 94)-MINLP model.

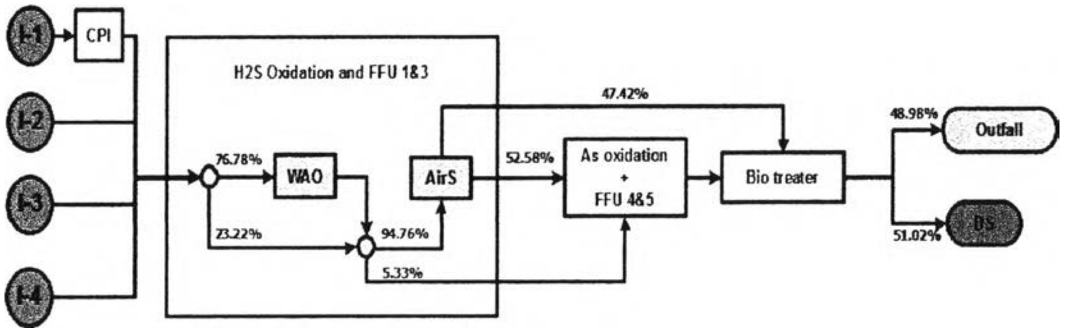

Figure 4.14 Simplified network of network solution (P7).

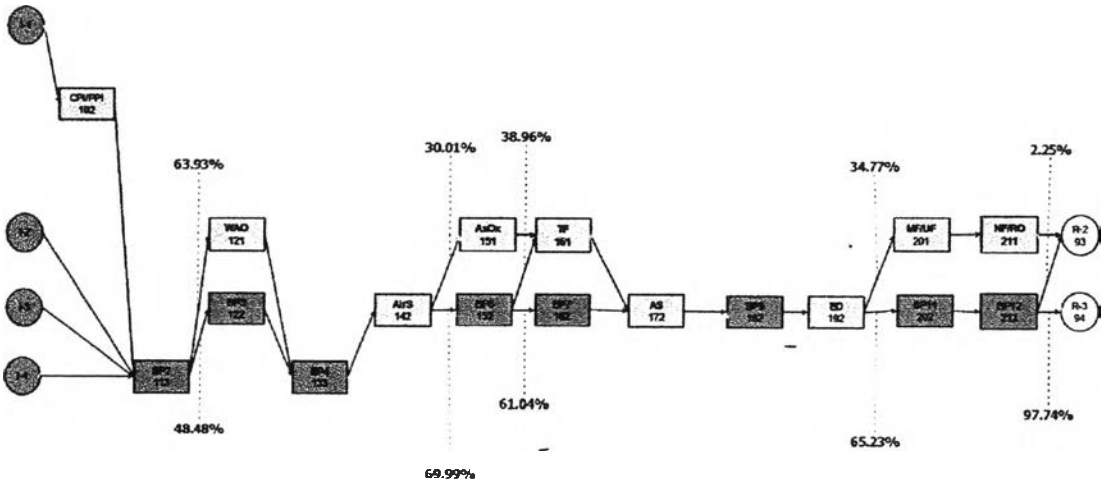

Figure 4.15 Network solution (P8) of PTT's configuration with zero liquid discharge for cooling water makeup (sink 93) and desalter makeup (sink 94)-MINLP model.

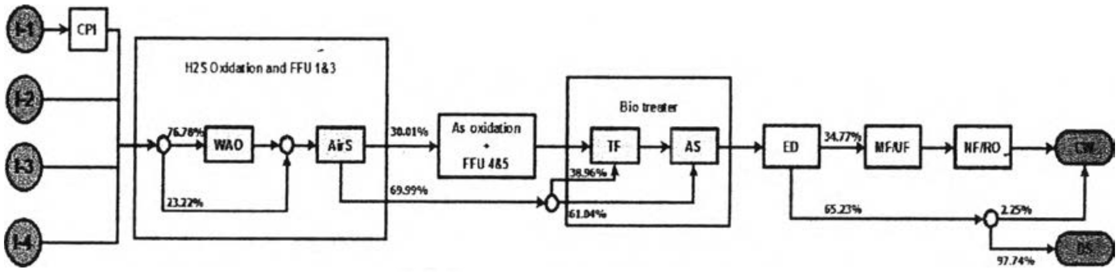

Figure 4.16 Simplified network of network solution (P8).

Furthermore, the results of the effluent composition for networks with TAC reduction are shown in Table 4.9. Other networks are reported in Appendix C. Also, it indicated that the effluent compositions of all retrofit design are optimized and are approaching the limitation or specification of the treatment objectives.

Table 4.9 Comparison of wastewater effluent composition for network solution P1, P2, P7 and P8

Component		Network solution						Limitation		
		P1	P2	P7		P8				
		WWD	WWD	WWD	DS	CW	DS	WWD	CW	DS
COD	mg/l	33.678	120.000	120.000	120.000	34.554	388.246	120	75	-
BOD	mg/l	12.290	20.000	20.000	20.000	5.997	73.068	20	-	-
TSS	mg/l	5.236	34.191	34.182	34.182	11.435	192.635	50	50	-
O&G	mg/l	0.514	2.358	2.357	2.357	0.585	10.000	5	25	10
FSS	mg/l	2.618	17.095	17.091	17.091	5.717	96.317	25	50	-
NH_4^+	mg/l	33.472	27.955	35.000	35.000	1.300	15.576	35	1.3	100
H_2S	mg/l	0.043	0.093	0.335	0.335	0.216	0.150	1	-	20
As	mg/l	0.020	0.011	0.011	0.011	0.001	0.007	0.25	0.25	-

In conclusion, Networks P8, P2 and P7 are better to the best promising system of the retrofit design, respectively and they contribute to better economic and environmental perspectives compared to network P1.

4.6.3.2 Base Case and Retrofit Design of Grassroots Process

Network· solution with process specification and cost breakdown analysis for base case of grassroots process (network G1) and its retrofit design (networks G2-G9) were summarized as follows:

In grassroots system design, network configurations (treatment processes) for the base case were selected independently (20 treatment processes and 12 bypasses). It could be noted that the grassroots design chose 6 out of 7 treatment processes the same as the existing process. Details of the design are as follows:

The connection of treatment units and effluent streams in all network scenarios are shown in Table 4.10. For grassroots system design, IAF was selected in the treatment task 1 while other treatment units were still the same as the base case of the existing process. Moreover, its retrofit design for recycled water to CW makeup (Network G3, G4 and G8) required additional two treatment processes (tertiary stage) namely GAC and IE; however, the retrofit design for recycled water to BFW makeup (Network G5, G6 and G9) selected different additional treatment processes including IE, MF/UF and NF/RO.

Table 4.10 Network connection of GAMS' configuration case

Network	Connection of treatment units												
G1	CPI/PPI	IAF	WAO	BP4	AirS	AsOx	TF	AS	BP9	BP10	BP11	BP12	WWD
G2	CPI/PPI	IAF	WAO BP3	BP4	AirS	AsOx BP6	TF	AS	BP9	BP10	BP11	BP12	WWD
G3	CPI/PPI	IAF	WAO	BP4	AirS	AsOx	TF	AS	GAC	IE	BP11	BP12	CW
G4	CPI/PPI	IAF	WAO BP3	BP4	AirS BP5	AsOx BP6	TF BP7	AS	GAC	IE	BP11	BP12	CW
G5	CPI/PPI	IAF	WAO	BP4	AirS	AsOx	TF	AS	BP9	IE	MF/UF	NF/RO	BFW
G6	CPI/PPI	IAF	WAO BP3	BP4	AirS BP5	AsOx BP6	TF	AS	BP9	IE BP10	MF/UF	NF/RO	BFW
G7	CPI/PPI	IAF	WAO BP3	BP4	AirS BP5	AsOx BP6	TF	AS	BP9	BP10	BP11	BP12	WWD DS
G8	CPI/PPI	IAF	WAO BP3	BP4	AirS BP5	AsOx BP6	TF BP7	AS	GAC	IE	BP11	BP12	CW DS
G9	CPI/PPI	IAF	WAO BP3	BP4	AirS BP5	AsOx BP6	TF	AS	BP9	IE BP10	MF/UF BP11	NF/RO BP12	BFW DS

It is of interest to note that the scenarios with recycle stream to CW makeup (networks G3, G4 and G8) did not produce any wastewater discharge or any retentated wastewater for disposal. Hence, these scenarios indicated the potential of retrofit design as zero liquid discharge aspect. For targeting effluent of BFW make up, these scenarios did not produce any wastewater discharge stream (ZLD aspect); however, the retentated wastewater was present due to the waste from MF/UF and NF/RO units. The network G7 generated part of recycled water to DS makeup without any additional filtration process so it included only wastewater discharge and recycled water. The different water effluent fractions (WEF) of all network scenarios are presented in Figure 4.17.

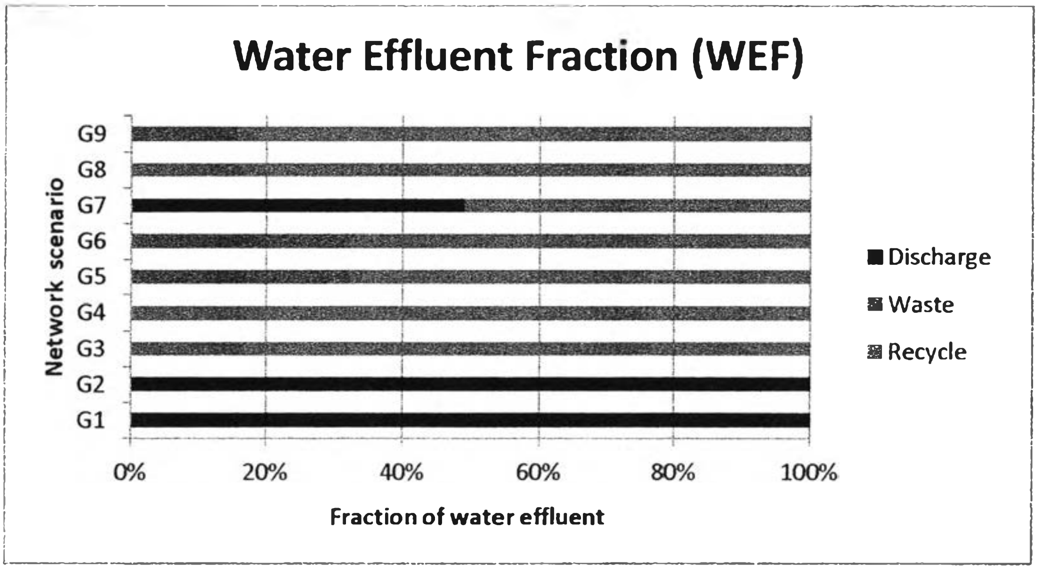

Figure 4.17 Water Effluent Fraction (WEF) of network G1-G9.

When considering the cost, TAC breakdown comparison is illustrated in Figure 4.18 while the details of TAC are summarized in Table 4.11. OPEX is the highest contribution in TAC, which is in agreement with the case of existing process. As shown in Figure 4.18, TAC (21.463 M$/y) of network P1 mostly resulted from both WAO and AsOx unit. However, the grassroots design (network G1) could present the network configuration and its process specification with lower

TAC than the existing process (-14.984 %) due to the addition of IAF unit that helped pretreat the wastewater before treating in WAO and AsOx units.

In the case of retrofit scenarios for grassroots process, there were another five scenarios (networks G2-G4 and G7-G8) that gave a lower TAC than the base case of the existing process (network P1) while other networks gave higher TAC because of the addition in CAPEX and OPEX of the filtration unit to produce high water quality for BFW makeup. However, it could notice that although the network G9 led to a higher TAC (+7.09 %) than network P1, it is of interest to design the ZLD option to produce high amount of BFW makeup.

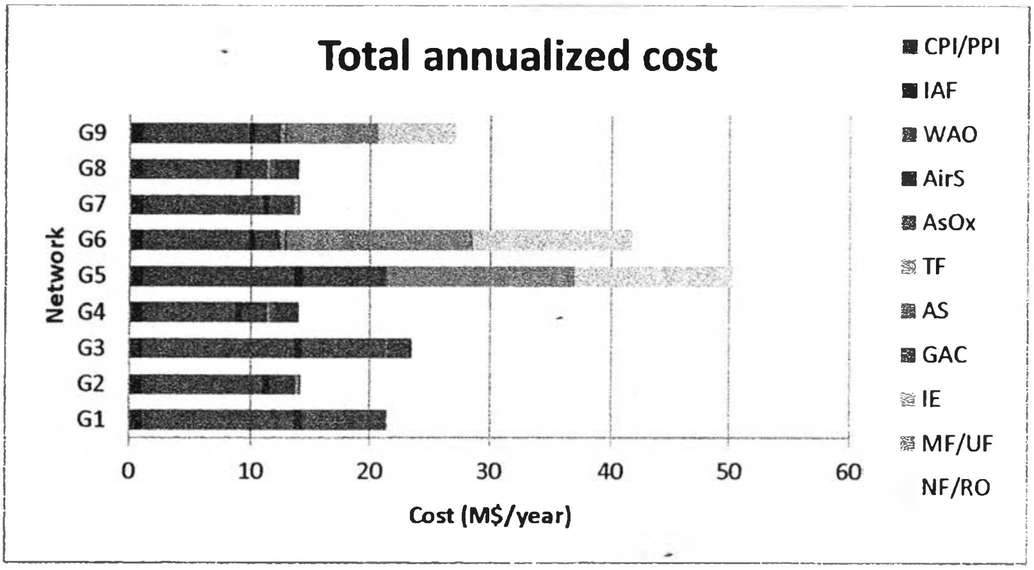

Figure 4.18 Cost breakdown (Total annualized cost) for network solution G1-G9.

Table 4.11 Summation of cost for each network solution G1-G9

		Opex (M$)				
Network		Waste disposal	Utility	Capex (M$)	Saving(M$)	TAC (M$)
G1	MILP	1.230	14.793	5.440	0.000	21.463
G2	MINLP	1.474	7.314	5.440	0.000	14.228
G3	MILP	1.230	16.590	5.732	0.015	23.537
G4	MINLP	1.587	6.767	5.733	0.015	14.071
G5	MILP	1.277	43.430	5.607	0.220	50.094
G6	MINLP	1.608	34.640	5.605	0.220	41.632
G7	MINLP	1.474	7.223	5.440	0.008	14.130
G8	MINLP	1.587	6.767	5.733	0.015	14.071
G9	MINLP	1.584	20.030	5.538	0.116	27.036

Comparing to the base case of network P1 (Figure 4.9), Network G1 (Figure 4.19) could improve the TAC as mentioned before. For network G2 (Figure 4.21), its configuration was similar to network G1, but there were some split stream at the inlet of WAO and AsOX units. As a consequence, retrofit design of network G2 gave lower TAC (-43.642%) compared to network P1.

In networks G3 (Figure 4.23) and G4 (Figure 4.25), GAC and IE units were selected in order to meet the specification of CW makeup, providing a lower CAPEX and OPEX than those filtration processes (i.e. MF/UF and NF/RO) without generation of any retentated wastewater. It could be noted that IAF unit was selected to help pretreat in the primary treatment stage in all network G's for wastewater pretreatment; therefore, instead of the requirement for high capable treatment process (such as MF/UF, NF/RO units), GAC and IE units were selected to treat water to an appropriate level to meet the CW makeup specification. Also, the bypass streams of network G4 were implemented for WAO, AirS, AsOx and TF units. The benefits of these bypass designs not only give the lower in TAC (-6.769% and -44.264%, respectively), but also obtain a design of zero liquid discharge. Additionally, the configuration and process specification regarding treatment process of network G8 (Figure 4.29) was the same as network G4, but network G4 only recycle water to CW makeup whereas network G8 recycle water to CW and DS makeup (48.96% and 51.04%, respectively). Moreover, the savings cost considered for recycled water price of DS makeup was approximately equal to CW makeup. In this work, the CAPEX with respect to the additional cost of splitter, mixer and piping before splitting and sending to recycled water in the water-using process (makeup units) was also neglected for simplification. Thus, percentage TAC reduction of both scenarios was still the same. However, network G4 is a better promising retrofit design because water consumption of the refinery process for CW is required significantly more than DS.

In addition, Network G7 (Figure 4.27) included many bypass streams (at WAO,-AirS, AsOx and TF) and could produce part of recycled water for DS makeup (51.04%), hence, it required no additional treatment units. Thus, the reduction of TAC compared to network P1 was 44.031%.

According to these results of network solutions, networks G1-G4 and G7-G8 could be simplified as a treatment process scheme as shown in Figure 4.20, Figure 4.22, Figure 4.24, Figure 4.26, Figure 4.28 and Figure 4.30, respectively.

Note: the configuration of other network solutions was reported in Appendix C.

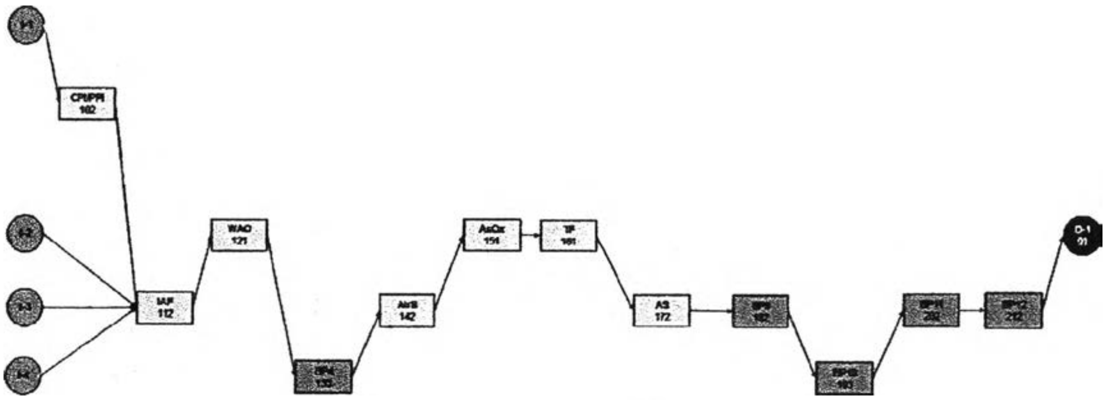

Figure 4.19 Network solution (G1) of GAMS' configuration with only discharge (sink 91)-MILP model.

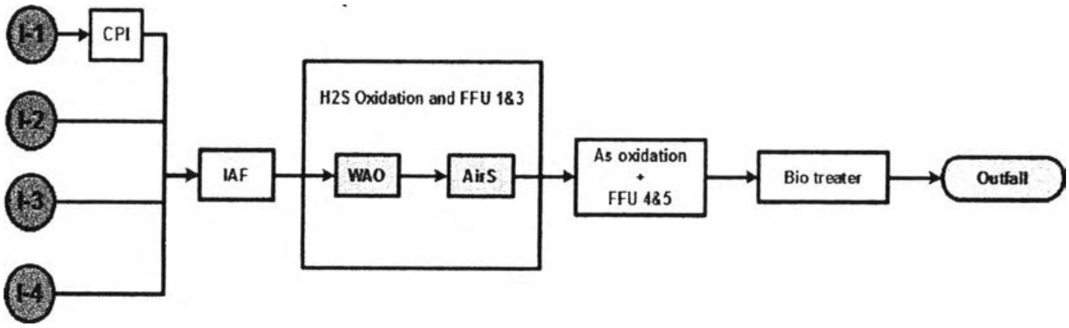

Figure 4.20 Simplified network of network solution (G1).

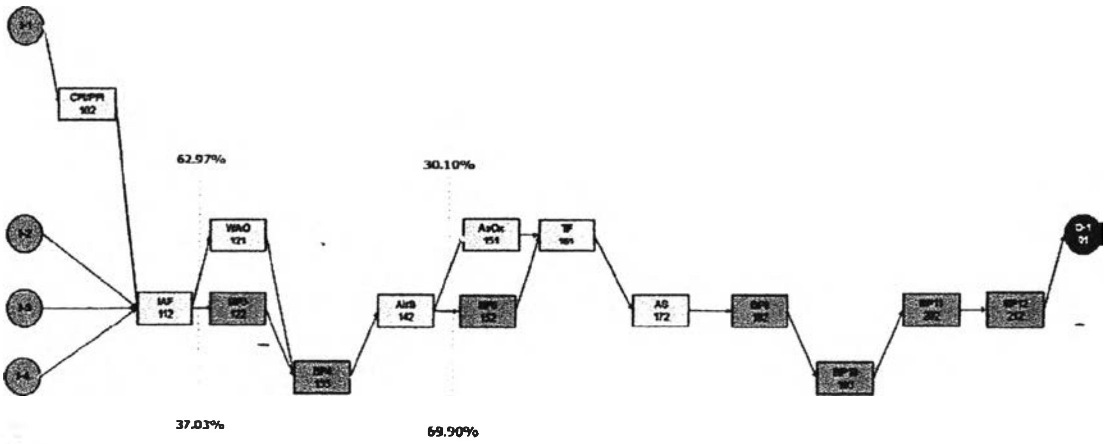

Figure 4.21 Network solution (G2) of GAMS' configuration with only discharge (sink 91)-MINLP model.

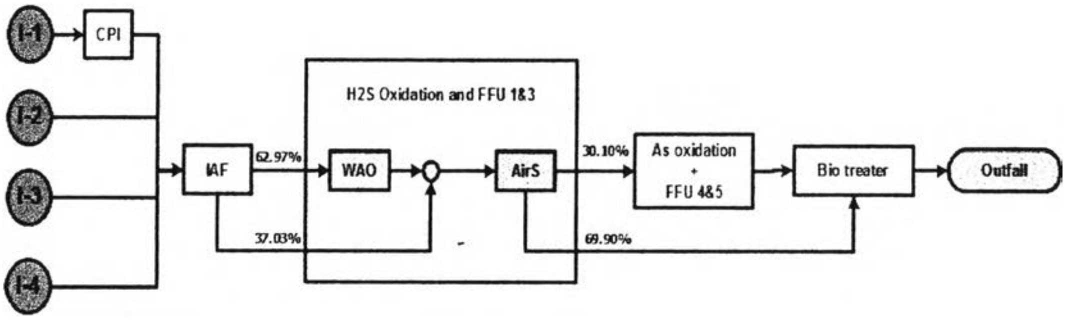

Figure 4.22 Simplified network of network solution (G2).

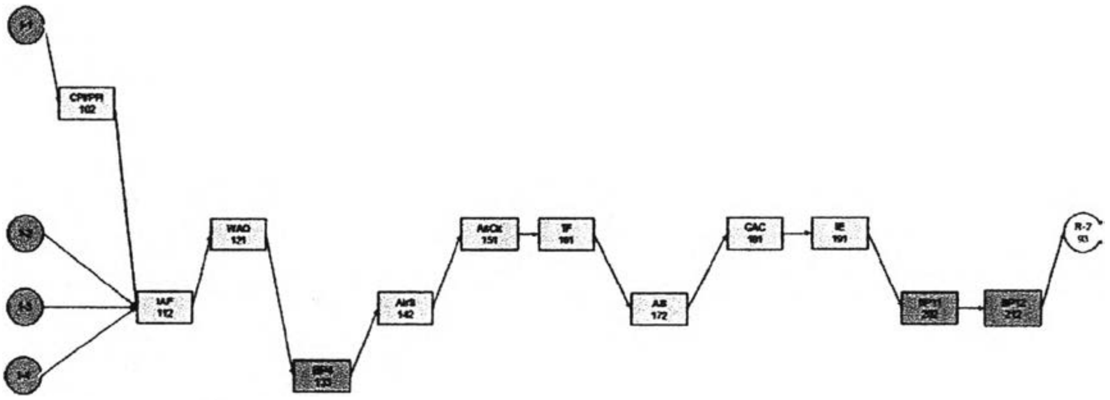

Figure 4.23 Network solution (G3) of GAMS' configuration with zero liquid discharge for cooling water makeup (sink 93)-MILP model.

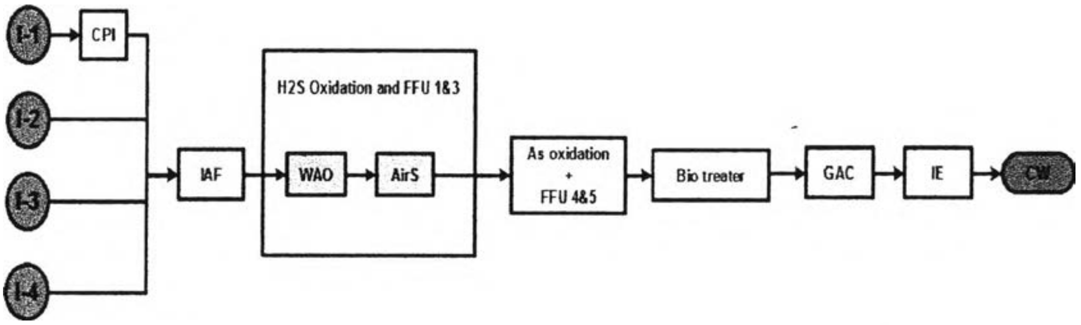

Figure 4.24 Simplified network of network solution (G3).

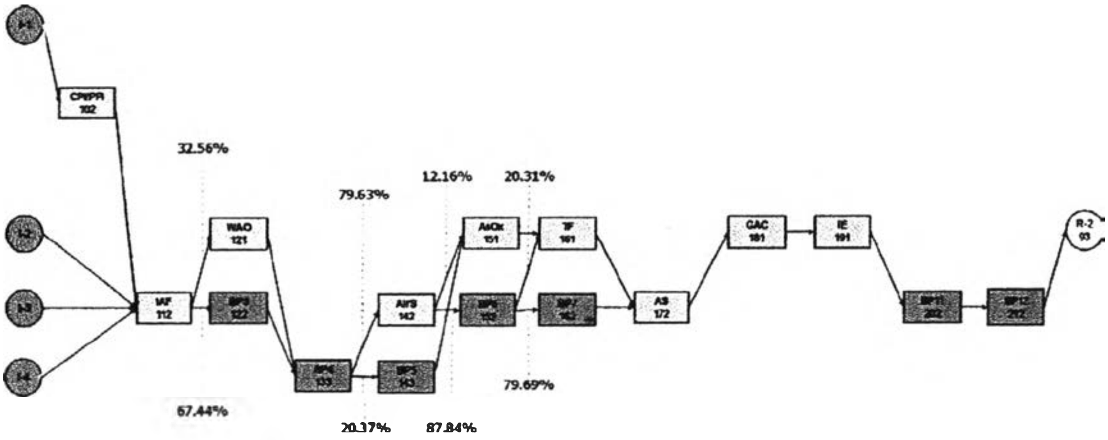

Figure 4.25 Network solution (G4) of GAMS' configuration with zero liquid discharge for cooling water makeup (sink 93)-MINLP model.

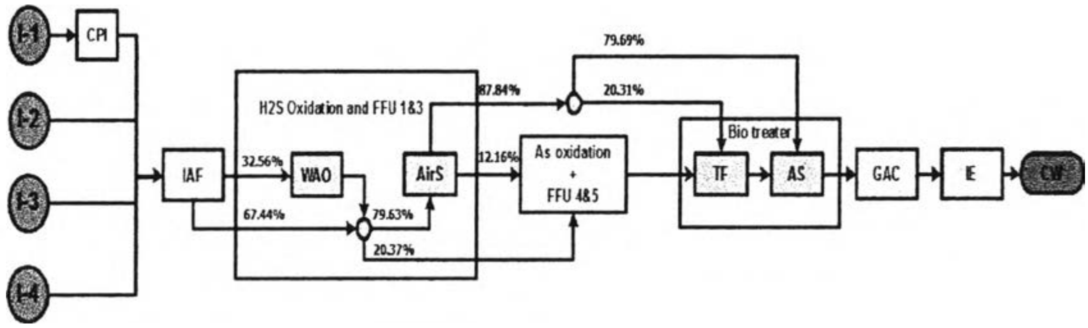

Figure 4.26 Simplified network of network solution (G4).

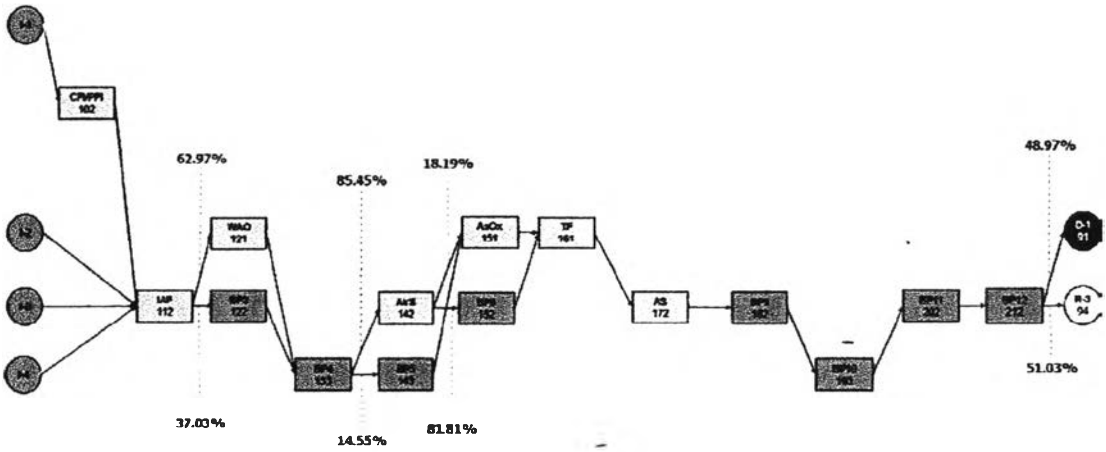

Figure 4.27 Network solution (G7) of GAMS' configuration with non-zero liquid discharge for discharge (sink 91) and desalter makeup (sink 94)-MINLP model.

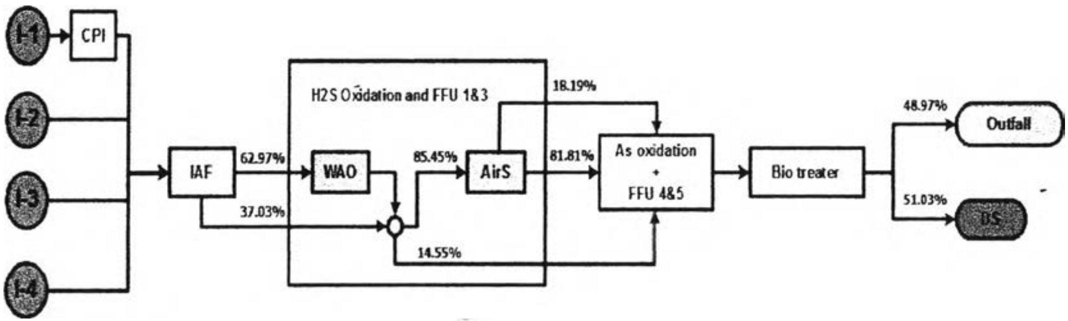

Figure 4.28 Simplified network of network solution (G7).

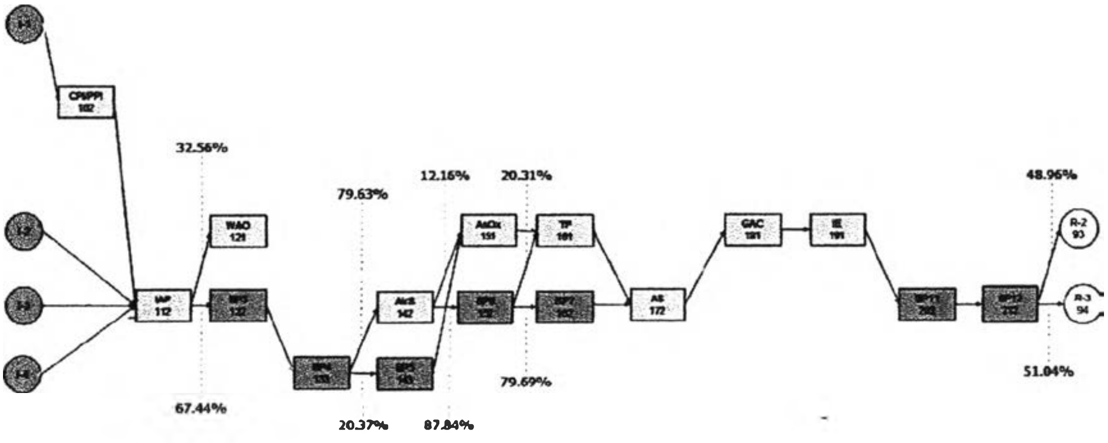

Figure 4.29 Network solution (G8) of GAMS' configuration with zero liquid discharge for cooling water makeup (sink 93) and desalter makeup (sink 94)-MINLP model.

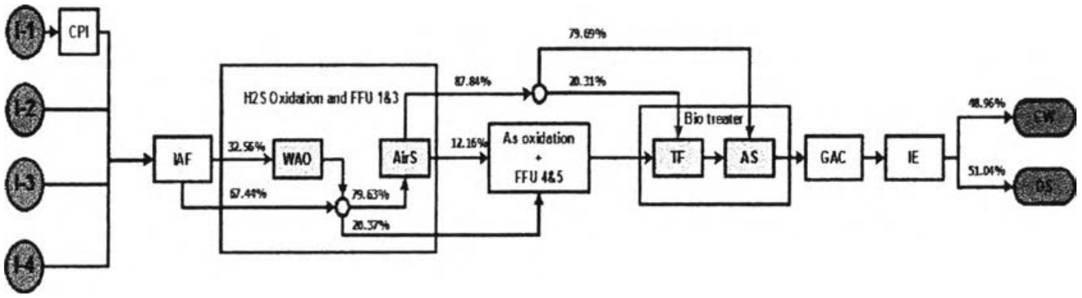

Figure 4.30 Simplified network of network solution (G8).

The process specification for effluent composition for the networks that gave a reduction in TAC is tabulated in Table 4.12. The specification of other networks was reported in Appendix C. Also, it indicated that the effluent composition of all base case and retrofit design of grassroots system is optimized to approach the limitation or specification of the treatment objectives as the retrofit design of exiting process.

Table 4.12 Comparison of wastewater effluent composition for network solution G1-G4 and G7-G8

Component		Network solution								Limitation		
		G1	G2	G3	G4	G7		G8				
		WWD	WWD	CW	CW	WWD	DS	CW	DS	WWD	CW	DS
COD	mg/l	21.899	120.000	4.380	75.000	120.000	120.000	75.000	75.000	120	75	-
BOD	mg/l	6.762	13.850	1.150	7.695	13.852	13.852	7.695	7.695	20	-	-
TSS	mg/l	0.890	10.503	0.223	12.014	10.503	10.503	12.014	12.014	50	50	-
O&G	mg/l	0.036	0.279	0.005	0.144	0.279	0.279	0.144	0.144	5	25	10
FSS	mg/l	0.445	5.251	0.111	6.007	5.251	5.251	6.007	6.007	25	50	-
NH_4^+	mg/l	26.421	20.624	1.057	1.300	35.000	35.000	1.300	1.300	35	1.3	100
H_2S	mg/l	0.043	0.122	0.043	2.047	0.992	0.992	2.047	2.047	1	-	20
As	mg/l	0.020	0.006	0.000	0.000	0.006	0.006	0.000	0.000	0.25	0.25	-

In summary, networks G4, G8, G7, G2, Gl and G3 are the most promising system as a preliminary guideline for the retrofit design based on the grassroots system that gave better economic and environmental perspectives compared to existing process, respectively.

4.7 The Analysis and Discussion of the Overall Results

The overall results of the optimization solution step were classified in two main design options: i). Base case of existing process and its retrofit design ii). Base case of grassroots process and its retrofit design.

Overally a number of aspects have been considered in the design of water network including the number of water effluent options, water recycle requirement and structure of the treatment process and these aspects have contributed to the reduction in TAC and the improvement in environmental impact. Some scenarios could produce various recycled water effluents, reducing the consumption of fresh water and re-using more processed water and at the same time, reducing the amount of water which indirectly led to the reduction in energy demand.

The comparison among 18 network scenarios for both base cases and their retrofit design are reported with different results in

Figure 4.31. This figure presents the two benefit indicators of trend for reduction of TAC (main indicator) at y-axis and WWDR (minor indicator) at x-axis-in each scenario. Therefore, the more network scenarios were plotted near the origin point, the more benefits in the economic and environmental impact aspects they attained. The best scenario obtained from retrofit design of the existing process (network P's) was network P7 that could be analyzed the benefits with respect to cost breakdown and enumerated environmental impact indicators compared to the existing process (network P1) as shown in Table 4.13.

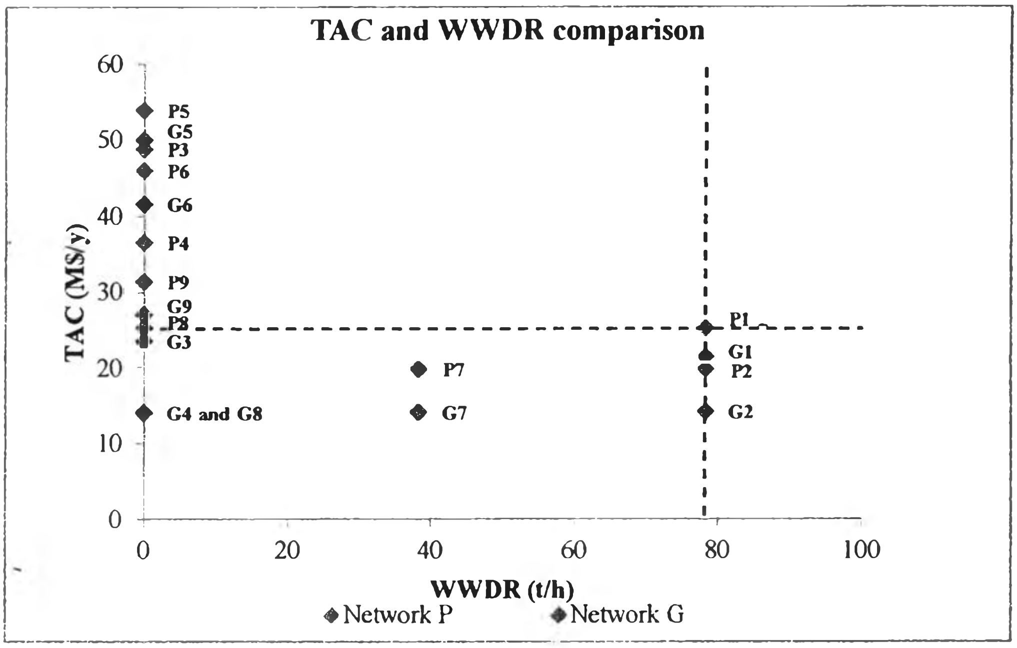

Figure 4.31 TAC and WWDR (Wastewater discharge rate) comparison of network P (existing process) and G (grassroots process).

Table 4.13 Network comparison between existing process (P1) and retrofit process (P7)

Index		Network P1 (Existing process)	Network P7 (Retrofit process)	% Relative variation
Economic aspect				
TAC	M$/y	25.246	19.767	-21.702
Capex	M$/y	5.437	5.437	0.000
Opex	M$/y	19.809	14.338	-27.619
Utility cost	M$/y	18.553	12.884	-30.556
Waste disposal cost	M$/y	1.256	1.454	15.764
Saving cost	M$/y	0.000	0.008	0.000
Environmental aspect				
Water discharged	t/h	78.402	38.400	-51.022
Water wasted	t/h	0.000	0.000	0.000
Water recycled	t/h	0.000	39.993	0.000
Total water	t/h	78.402	78.393	-0.011

Additionally, the best scenario obtained from the retrofit design of grassroots process (network G's) was network G4. This network provided high percentage of TAC reduction and water effluent with respect to ZLD aspect for CW. Thus, it is more interesting and promising retrofit design than network P7. The benefits with respect to cost breakdown and enumerated environmental impact indicators compared to the existing process (network P1) are reported in Table 4.14.

Table 4.14 Network comparison between existing process (P1) and retrofit process (G4 and G8)

Index		Network P1 (Existing process)	Network G4 and G8 (Retrofit process)	% Relative variation
Economic aspect				
TAC	M$/y	25.246	14.071	-44.264
Capex	M$/y	5.437	5.733	5.444
Opex	M$/y	19.809	8.354	-57.827
Utility cost	M$/y	18.553	6.767	-63.526
Waste disposal cost	M$/y	1.256	1.587	26.354
Saving cost	M$/y	0.000	0.015	0.000
Environmental aspect				
Water discharged	t/h	78.402	0.000	0.000
Water wasted	t/h	0.000	0.000	0.000
Water recycled	t/h	0.000	78.358	0.000
Total water	t/h	78.402	78.358	-0.056

In summary, the comparison among all scenarios (new system and retrofit design) of the case study emphasized on the improvement of process/plant scale for economical (TAC) and environmental impact (WEF/WWDR) perspectives in an effective time frame. The WWTN designs obtained from the developed model were expected to be able to be implemented as beneficial preliminary guideline for detailed design (involving with detailed engineering and dimensioning of unit operations) together with process simulation of a pilot plant scale and/or enterprise scale to acquire for complete detailed modelling of treatment process design.