CHAPTER II
LITERATURE REVIEW

Chemical process design is the scheme to be attained the desired physical and chemical transformation of materials in the facilities or the existing facilities which need further improvement. Process design concerns in several unit operations and starts at a conceptual level or preliminary level and finishes in the construction plans. A preliminary design is used as a basis for determine whether the process is feasible to be proceed with the proposed venture. The acceptable preliminary design should achieve economic goals, environmental aspects, as well as other problems regarding the process. In order to evaluate environmental performances, LCA and LCA software are mentioned together with property prediction method for prediction of environmental factors. Process sustainability and economic analysis and software for process evaluation are mentioned.

2.1 Life cycle assessment (LCA) for process evaluation

LCA is a method for assessing the environmental impacts of products and processes over the entire product life cycle. In various process and plant designs, the examination of life cycle analysis is vital to evaluation of the energy needs, material inputs and environmental releases of a manufacturing process. Life cycle assessment has enabled manufacturers to quantify how much energy and raw materials are consumed, as well as how much solid, liquid and gaseous waste are generated at each stage of the process.

2.1.1 Methodology of LCA

Methodology of LCA comprises a set of different methods for the impact assessment in a particular process. The LCA framework was standardized by the International Organization for Standardization (ISO), and it is constituted by four elements.

2.1.1.1 Goal definition and scoping

This element is where the purpose and method of the project are defined, also the product, process or activity in the life cycle are described. Establish the context of the assessment and identify system boundaries. The items that must be determined are the type of information needed, how accurate the results must be and how the results should be interpreted and displayed.

2.1.1.2 Life Cycle Inventory (LCI)

LCI is consisted of inputs or what should be added in order to produce the product of the system and outputs of the studied system which are product, by-product, and waste for all process stages in the system boundary. To conduct LCI, the flow diagram of the processes and process databases are needed for calculation. However, LCI data contains thousands of processes linked together. Therefore, radical analysis is required to understand.

LCI model composes of input/output (I/O) matrix to model inter-processes, interactions, or interactions between processes, and environment (Leontief, 1986). LCI database can contain thousands processes linked together and knowledge management of LCI data is not noticeable. Using ontology of the system information, keywords are store in the knowledge base where every keyword can be associated with another one.

2.1.1.3 Life Cycle Impact Assessment (LCIA)

LCIA is where LCI data on inputs (materials and resources) and outputs (waste and emissions) are translated into information regarding the environmental impacts the product system has on the environment, human health, and resources. LCI data that is used to asses environmental impacts compose of hundreds of released substances which many of them create environmental impacts such as global warming, ozone depletion, and human toxicity. Substance-specific characterization factors (CFs) which represent the substance's potency are necessary in order to assess environmental impacts. Although a number of different models have been developed for this purpose but they cover a limited number of substances. Therefore, for many substances, the characterization factor needed to assess impacts may not be available. Estimation of environmental factors using group contribution$^+$ method (GC)$^+$ is used.

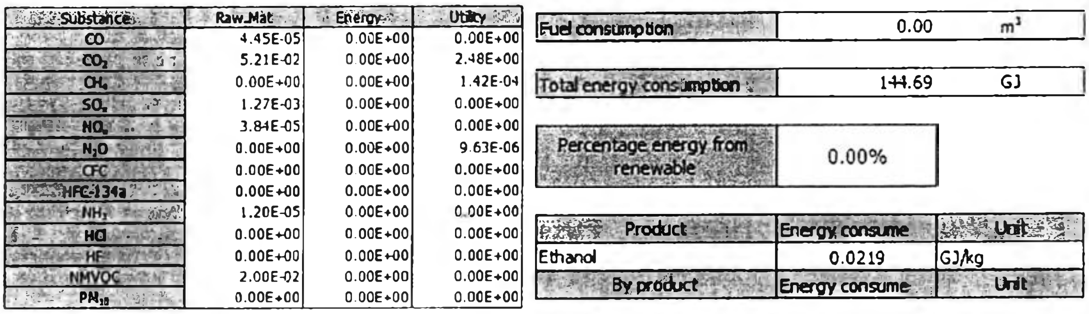
2.1.1.4 Interpretation

This step is where the results from the previous step will be related with the goal of the project. In this step, sensitivity and uncertainty of LCA results are also analyzed.

2.1.2 LCSoft-overview

LCA software is used as a tool to design alternatives and reduce environmental impacts by calculating resource and energy consumption and releases to the environment such as CO_2. Various software has been developed such as SimaPro, BOUSTED and GaBi. While most of the programs were expanded to include LCI and LCIA standards, they are being used for only limited parts of LCA analyses. Among the software above, LCSoft has been developed for chemical processes. The software is not complex to use and able to be integrated with other software. The first version of LCSoft is LCSoft version 1.0 (Piyarak, 2012) for analysis of environmental impacts, carbon footprint, and energy consumption of the process. Mass and energy balances obtained from simulation results can be easily linked to the software. Calculation models; environmental impact model, based on ISO method, and energy and fuel consumption models, calculated from the energy and fuel used in the process which are defined by user.

The output consists of inventory data covering thirteen emission substances, energy and fuel consumption, carbon footprint and eight environmental impacts, as shown in Figures 2.1 and 2.2 which are not difficult to communicate or understand and LCSoft version 1.0 is very useful for process evaluation. However, since there are several processes in the chemical industry, more LCI data need to be added into the software, and more characterization factors for each environmental impact are need to be added in order to analyzed the process more efficiently.



Substance	Raw_Mat	Energy	Utility
CO	4.45E-05	0.00E+00	0.00E+00
CO_2	5.21E-02	0.00E+00	2.48E+00
CH_4	0.00E+00	0.00E+00	1.42E-04
SO_x	1.27E-03	0.00E+00	0.00E+00
NO_x	3.84E-05	0.00E+00	0.00E+00
N_2O	0.00E+00	0.00E+00	9.63E-06
CFC	0.00E+00	0.00E+00	0.00E+00
HFC-134a	0.00E+00	0.00E+00	0.00E+00
NH_3	1.20E-05	0.00E+00	0.00E+00
HCl	0.00E+00	0.00E+00	0.00E+00
HF	0.00E+00	0.00E+00	0.00E+00
NMVOC	2.00E-02	0.00E+00	0.00E+00
PM_{10}	0.00E+00	0.00E+00	0.00E+00

Fuel consumption	0.00	m^3
Total energy consumption	144.69	GJ
Percentage energy from renewable	0.00%	
Product	Energy consume	Unit
Ethanol	0.0219	GJ/kg
By product	Energy consume	Unit

Figure 2.1 Input/output data show in inventory data section in LCSoft version 1.0.

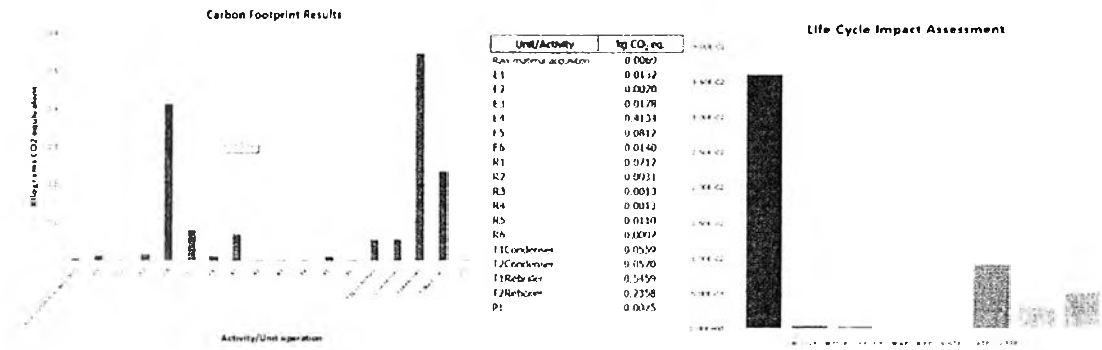


Figure 2.2 Carbon footprint and environmental impacts in LCSoft version 1.0.

2.1.3 Property prediction of environmental factors

The property estimation of organic chemicals have been employed to obtain the required property values where the property of a chemical is a function of structurally dependent parameters which determined as a function of the frequency of the groups representing the chemical and their contributions. Environmental factor estimation, one part of this work has been published within the study of " Estimation of Environment-Related Properties of Chemicals for Design of Sustainable Processes: Development of Group-Contribution$^+$ (GC^+) Property Models and Uncertainty Analysis" (Hukkerikar *et al,* 2012). The property prediction model to estimate the 11 characterization factors of organic chemicals employing Marrero and Gani (MG) method has the form.

$$f(x) = \sum_i N_i C_i + w \sum_j M_j D_j + z \sum_k E_k O_k \tag{2.1}$$

Where

f(x) = Function of property X

C_i = Contribution of simple groups (first-order group) of type-i that occur N_i times

D_i = Contribution of polyfunctional, polar or non-polar, and cyclic chemicals (second-order group)that occurs M_i times

C_i = Contribution of complex heterocyclic and polyfunctional acyclic chemicals (third-order group) of type-k that occurs O_i times

The MG method includes 220 first-order groups, 130 second-order groups, and 74 third-order groups to represent the molecular structure of the organic chemicals. In order to estimate the contribution of C_i, D_i, and E_i, simultaneous regression method is used. The statistical performance indicators, such as standard deviation (SD), average absolute error (AAE), average relative error (ARE), and coefficient of determination (R^2) are used in order to measure the reliability of property prediction models. For example, R^2 is closes to 1.0 indicated that the experimental data used in the regression have been fitted to a good accuracy.

The values of SD, AAE, ARE, and R^2 are 0.36, 0.26, and 4.87. They can be calculated using equation 4.2-4.4.

$$S.D. = \sqrt{\frac{(X_{pred} - X_{\exp})^2}{N}} \quad (4.2)$$

$$AAE = \frac{\sum |X_{pred} - X_{\exp}|}{N} \quad (4.3)$$

$$ARE\ (\%) = \frac{\sum |(X_{pred} - X_{\exp})/X_{\exp}|}{N}\ x\ 100 \quad (4.4)$$

$$R^2 = 1 - \left[\frac{\sum (X_{exp} - X_{pred})^2}{\sum (X_{exp} - M)^2}\right] \quad (4.5)$$

Where

N = Number of data-point

X_{pred} = Estimated valued of the property X

X_{exp} = Experimental value of the property X

2.2 Sustainability analysis for process evaluation

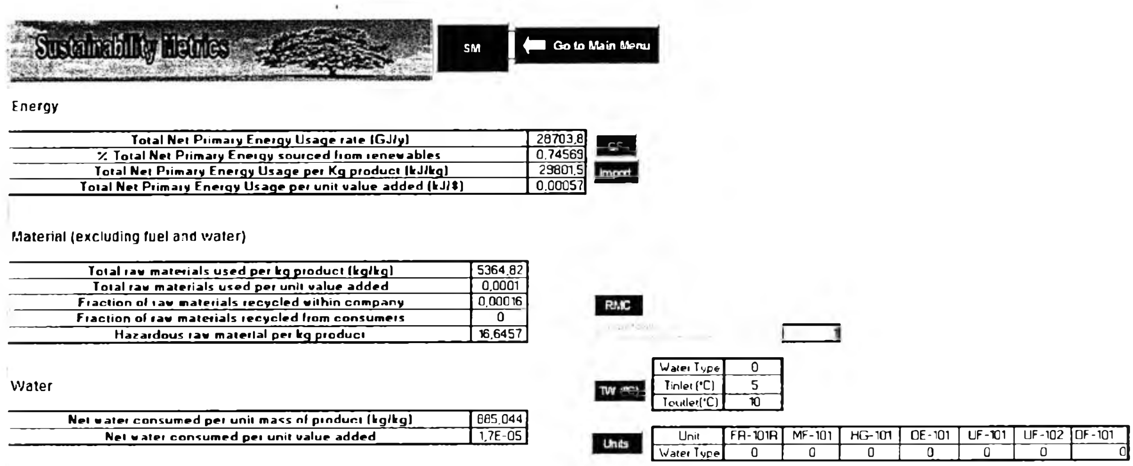
2.2.1 Concept of sustainability

Among several existing definitions of sustainable development, the most often quoted defined sustainable development as development that meets the needs of the present without compromising the ability of future generations to meet their own needs. The discussion about sustainability have increased significantly in the past few years, and most importantly comes the analysis if for instance a process is more sustainable than other. Recently has increased the search for methods and tools to make processes more sustainable. One of the great advances done in this area, regarding specifically chemical engineering industries, is the sustainability metrics created by the Institution of Chemical Engineers (IChemE). An overview of these will be given in the following section.

2.2.2 SustainPro-overview

SustainPro is an excel tool developed in Department of Chemical and Biochemical Engineering, Technical University of Denmark (Carvalho *et al.*, 2008) and it is first of all a tool to perform sustainability analysis of a process. Also it provides targets for improvement in order to make the process more profitable, safer , and more sustainable. It is easier to know what should be changed in order to obtain a better process design without having to formulate a complete process optimization which would be much more time-consuming, and that could even fail to give a solution. SustainPro allows for a quick and objective study of new design alternatives of a certain process with the purposes of improving environmental impacts, and also the safety and economy of the process. The purpose is to calculate a group of indicators which provide important information regarding which operation within a process flowsheet is comparatively more expensive than others. Taking this information one can set process points where high potential for improvements can be found, and these points will be targets for improvement. Through these indicators are generated process alternatives for new process designs and the new design alternatives will be made to match the designed targets.

The methodology involves calculating 49 sustainability metrics, and inherent safety indices so that a more complete evaluation and choice of the new alternatives can be achieved. The mass and energy balances from simulation results can be used to calculate the sustainability metrics (Figure 2.3) and safety indices (Figure 2.4). The sustainability metrics are a very good guideline to help engineers deal with issues of sustainable development in terms of economic, social and environmental aspects. Safety indices are to the compounds hazardous provided by MSDS.



Energy

Total Net Primary Energy Usage rate (GJ/y)	28703.8
% Total Net Primary Energy sourced from renewables	0.74569
Total Net Primary Energy Usage per Kg product (kJ/kg)	29801.5
Total Net Primary Energy Usage per unit value added (kJ/$)	0.00057

Material (excluding fuel and water)

Total raw materials used per kg product (kg/kg)	5364.82
Total raw materials used per unit value added	0.0001
Fraction of raw materials recycled within company	0.00016
Fraction of raw materials recycled from consumers	0
Hazardous raw material per kg product	16.6457

Water

Net water consumed per unit mass of product (kg/kg)	885.044
Net water consumed per unit value added	1.7E-05

Water Type	0
Tinlet (°C)	5
Toutlet(°C)	10

Unit	FA-101R	MF-101	HG-101	DE-101	UF-101	UF-102	DF-101
Water Type	0	0	0	0	0	0	0

Figure 2.3 Sustainability metrics.

Total inherent safety index (ISI)			
Chemical inherent safety index,Ici	Score	Process inherent safety index,Ipi	Score
Subindices for reactions hazards		Subindices for process conditions	
Heat of the main reaction,Irm	4	Inventory,Ii	4
Heat of the side reactions,Irs	0	Process temperature,It	0
Chemical Interaction,Iint	2	Process pressure,Ip	0
Subindices for hazardous substances		Subindices for process system	
Flammability,Ifl	4	Equipment,Ieq	
Explosiveness,Iex	1	Isbl	3
Toxicity,Itox	6	Osbl	1
Corrosivity,Icor	1	Process structure,Ist	2
Ici	18	Ipi	10

ISI	28

Figure 2.4 Safety indices.

Mass and energy balances are converted to open paths (OPs) and closed or recycling paths (CPs). This decomposition in OPs and CPs is based on graph theory, being the units of the flowsheet called vertices are referred as the supply flows, and what is leaving the vertices is referred as the demand flow, after having the graphs, they have to be decomposed in OPs and CPs and for this there is an algorithm in SustainPro which detailed explanation is outside the scope of this work. Table 2.1 are displayed the main indicators in SustianPro and their definition. Total value added is related with the first two, MVA and EWC have the purpose of maximizing the economic efficiency of a process through the identification of where the process are high accumulation and high cost. MVA is the value generated from the feed to the demand of a certain compound in a certain OP. In the MVA definition, M stands for mass of the component, P_{sale} is the sale price and P_{cost} is the purchase price. EWC can be divided into two parts as it is given by the sum of the energy and waste cost indicator. The waste cost being the mass of waste times the treatment cost. The energy cost is calculated like it is displayed in the table, with E standing for duty, P_E is the unit price of the utility needed in sub-operation i, and ß is a characteristic physical property that depends on the unit operation. The input paths determined and additional information about compound properties, prices are used in this step. The indicators showing higher potential for improvements were selected and they are presented in **Error! Reference source not found.**.2. For this example results of indicator calculation, this process, OP31, OP34, OP37, OP114, OP118 and OP121 have very negative values of MVA. This means that money is being lost across the entrance the exit of those compounds in the process. The MVA value improves when its value increases. It can be also seen that OP125 shows high value of EWC, which means high energy consumption through that open-path. The EWC (Energy and Waste Cost) value should be reduced in order to improve the process.

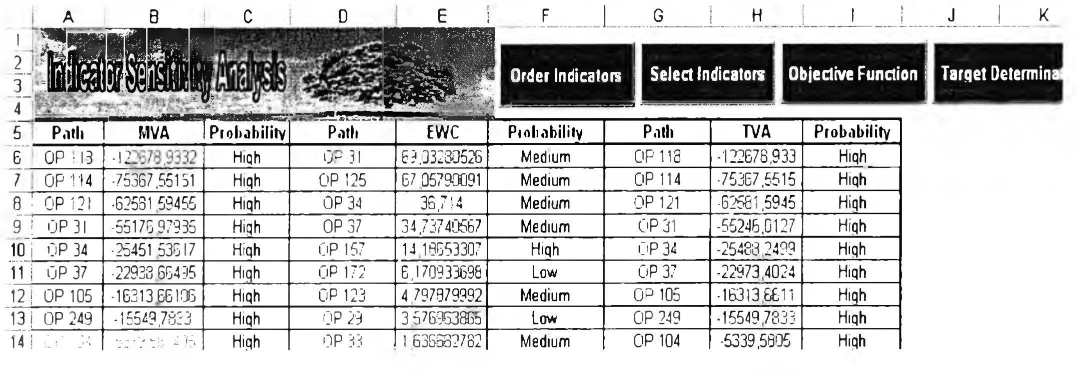
SustainPro orders the indicators taking into account their values. The paths, which correspond to the most negative values of MVA, RQ and TVA and the highest values of AF and EWC indicate higher potential for improvements and are at the top of the table (see Figure 2.5). From the top to the bottom the user can screen all the indicators from an ordered list of indicators to select the ones with the highest potential for improvement. SustainPro performs a complete indicator sensitive analysis, automatically, and presents the results in terms of scores for each of the selected indicators.

Table 1.1 Indicators calculated by SustainPro

Indicator	Description	Definition
MVA	Material value added	$MVA = M_T \times (P_{sale}-P_{cost})$
EWC	Energy and waste cost	$EWC = E \times P_E \times M_i ß_i / (\sum_i M_i ß_i)$
TVA	Total value added	$TVA = MVA-EWC$

Table 2.2 Most sensitive indicators

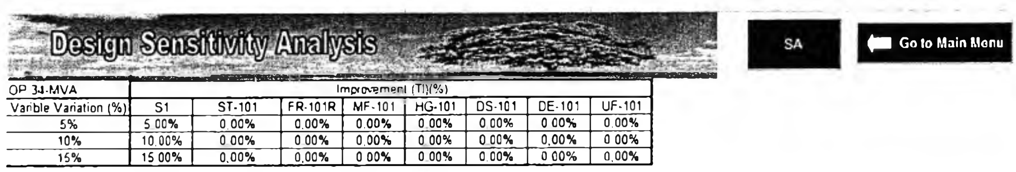
OP	Path	Component	Flowrate (kg/h)	MVA (10^3\$/yr)	EWC (10^3\$/yr)	TVA (10^3\$/yr)
OP 31	S1-S21	H_2O	33158	-55177	69	-55246
OP 34	S1-S34	H_2O	15295	-25451	37	-25488
OP 37	S1-S47	WFI	14472	-22939	35	-22973
OP 114	S41-S42	WFI	95438	-75367	0	-75367
OP 118	S44-S45	WFI	155349	-122679	0	-122679
OP 121	S63-S62	WFI	72043	-62582	0	-122679
OP 125	S10-S14	N_2	33684	0	67	-67



Path	MVA	Probability	Path	EWC	Probability	Path	TVA	Probability
OP 118	-122678,9332	High	OP 31	69,03230526	Medium	OP 118	-122678,933	High
OP 114	-75367,55151	High	OP 125	67,05790091	Medium	OP 114	-75367,5515	High
OP 121	-62581,59455	High	OP 34	36,714	Medium	OP 121	-62581,5945	High
OP 31	-55176,97935	High	OP 37	34,73740567	Medium	OP 31	-55246,0127	High
OP 34	-25451,53617	High	OP 157	14,18653307	High	OP 34	-25488,2499	High
OP 37	-22938,66495	High	OP 172	6,170933698	Low	OP 37	-22973,4024	High
OP 105	-16313,66106	High	OP 123	4,797879992	Medium	OP 105	-16313,6611	High
OP 249	-15549,7833	High	OP 29	3,576953865	Low	OP 249	-15549,7833	High
[illegible]	[illegible]	High	OP 33	1,636682782	Medium	OP 104	-5339,5805	High

Figure 2.5 Top indicators ordered by their potential for improvement

SustainPro performs a design sensitivity analysis in order to determine the target variables for the selected target indicators that would produce the best improvements in the target indicators. From sensitivity analysis of the operational parameters influencing the target indicator (MVA – OP34 and OP37) it was found that the most significant operational parameters are respectively the flow rates of OP34 and OP37. The Interface for the design sensitivity analysis is shown in Figure 2.6. For the batch indicators the flow rate of the accumulation-path was found to be the most sensitive variable, and consequently, for a decrease of the operation time there should be an increase on the operational flow rate.



OP 34-MVA	Improvement (TI)(%)							
Varible Variation (%)	S1	ST-101	FR-101R	MF-101	HG-101	DS-101	DE-101	UF-101
5%	5.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
10%	10.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
15%	15.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%

Figure 2.6 Design sensitivity analysis.

2.3 Economic evaluation for process evaluation

Economic is a normal term presented in our lives relating to trade, industry and creation of wealth. Economic analysis is very important for an acceptable process design that must represent a plant. The process produces a product which will be sold for a profit. This design is desired physical and/or chemical transformation of materials. Process design can be the design of new facilities or modification of the existing facilities. The design starts at a conceptual level or preliminary level and finishes in the construction plans. Process design is distinct from equipment design, that part of unit operation. Processes often include many unit operations. This work we will focus on preliminary designs that are used as a basis for determining whether further work should be on a proposed process. The design is based on approximate process methods, and approximate cost estimates are prepared. If preliminary design's result can be accepted, next step of design will be developed.

2.3.1 <u>ECON-overview</u>

ECON is computer-aided tool for processing cost analysis, including calculating equipment cost, capital cost, utility cost, operating cost (Saengwirun, 2011). The economic analysis of a process design is given in term of PIE charts and sensitivity analysis that points to areas of the process design where further improvements in terms of cost benefits may be possible.

The data required to use ECON are process type, quantities and costs of raw material and product, sizes and specification of equipment, utility prices, and operation time. ECON will calculate the purchase costs for all equipments and the utility costs. Pie chart represents fractions of equipment cost and utility cost, as shown in Figure 2.7. Capital cost is calculated based on the purchase cost. The results from this step contain the direct capital cost, indirect capital cost, working capital cost and total capital cost as shown in Figure 2.8. Operating cost calculation is based on utility cost, catalyst cost, labor cost, and raw material, variable cost, fixed charge cost, plant over head, general expense, and total product cost calculation. The results are shown in Figure 2.9.Economic analysis will be done. Economic evaluation parameters such as NPW, DCFR, ROI, PBP and R_n will be calculated after entering construction inflation rate, product price inflation rate, TPC inflation rate, minimum acceptable rate of return, taxes, project life time and land cost, as shown in Figure 2.10.

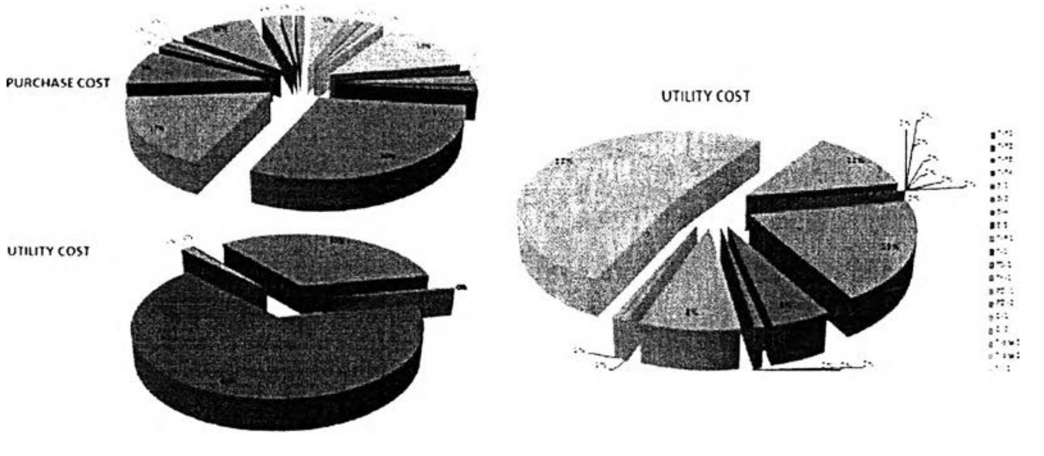


Figure 2.7 ECON pie chart of equipment cost calculation.

Manufacturing Fixed-capital Investment (Direct Cost)	% Delivered-equipment Fluid Processing Plant		Result
Purchased Equipment Delivered	1.1	$	543,106.30
Purchased Equipment Installation	0.47	$	255,259.96
Instrumentation and Controls (installed)	0	$	-
Piping (Installed)	0	$	-
Electrical Systems (Installed)	0	$	-
Buildings (Including Services)	0	$	-
Yard Improvement	0	$	-
Service Facilities (Installed)	0	$	-
	0.47		
	Total Direct Cost	$	798,366.26

Nonmanufacturing Fixed-capital Investment (Indirect Cost	% Delivered-equipment Fluid Processing Plant		Result
Engineering and Supervision	0	$	-
Construction Expenses	0.41	$	222,673.59
Legal Expenses	0	$	-
Contractor's Fees	0.22	$	119,483.39
Contingency	0.44	$	238,966.77
	1.07		
	Total indirect cost	$	581,123.74

Fixed-capital Investment	% Delivered-equipment Fluid Processing Plant		Result
Fixed-capital Investment (FCI)		$	1,379,490.00

Working Capital Investment	% Delivered-equipment Fluid Processing Plant		Result
Working Capital Investmenst (WC)	0.89	$	483,364.61

Total Capital Investm	$ 1,862,854.61

Figure 2.8 Capital cost.

Fixed Capital Investment	$ 1,379,490.00	
Plant Capacity	600000	kg/day
Processing Step	0	

Items of Operating Cost	Factor (can change by user)	Basis		Cost, $/year
Raw Material	0		$	124,398,001.00
Operating Labor	0.039999999	Fixed Capital Investment	$	49,329.45
Operating Supervision	0.1	Operating Labor	$	4,932.94
Utilities	0		$	1,399,136.00
Maintenance and Repairs	0.06	Fixed Capital Investment	$	73,994.16
Operating Supplies	0.15	Maintenance and Supplies	$	11,099.12
Laboratory Charges	0.15	Operating Labor	$	7,399.42
Royalties	0	Total Product Cost	$	-
		Variable Cost	$	125,943,892.09
Property Taxes	0.02	Fixed Capital Investment	$	24,664.72
Financing (interest)	0	Fixed Capital Investment	$	-
Insurance	0.01	Fixed Capital Investment	$	12,332.36
Rent	0	Fixed Capital Investment	$	-
		Fixed Charges	$	36,997.08
Plant Overhead	0.6	ıbor + Supervision + Maintena	$	76,953.93
		Manufacturing Cost	$	125,980,889.17
Administration	0.2	ıbor + Supervision + Maintena	$	25,651.31
Distribution & selling	0.02	Total Product Cost	$	2,599,659.68
Research & Development	0.01	Total Product Cost	$	1,299,829.84
		General Expense	$	3,925,140.83
		Total Product Cost with Out Depreciation	$	129,982,984.00

Figure 2.9 Operating cost and total product cost.

Profitability	
not include time value of money	
Rate of Return	-66%
Pay Back Period	-1.234953933
Net Return	$ (7,202,657.83)
include time value of money	
Annual Ene of Year cash flows and discounting	
Net Present Worth	$ (29,768,174.00)
DCFR	0.15001
Continuous cash flows and discounting	
Net Present Worth	$ (31,947,202.46)
DCFR	0.139786392

Figure 2.10 Economic evaluation.