Life Cycle Engineering in the Oil and Gas Industries, with Reference to Hydrodesulphurization of Gas Oil

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Introduction

The oil and gas industry was selected as a vehicle for studying Life Cycle Engineering because of the breadth and complexity of this sector of industry. Methods that work for the oil and gas industry will be generally applicable. It is not possible for any single study to trace the whole production process from cradle-to-grave. Modern developments in Life Cycle Analysis (LCA) thus concentrate on an incremental approach. Each step of the production process is analysed and the whole integrated to give a total life cycle impact. This research project adopts the incremental approach. One process, hydrodesulphurization of gas oil, is studied in detail. The research then establishes how this study can be integrated with other similar studies to give total life-cycle environmental impact.

There are sulfur impurities present in crude oil and natural gas. These impurities need to be removed before the oil can be converted to useful products such as fuel oil, motor oil, and petrochemicals. If they are not removed, they will give acid gases upon combustion, will damage motor and industrial catalysts, and are, themselves, very toxic. Thus, at some point in the refinery operations, these sulfur impurities have to be extracted from the oil to produce quality fuel oil products which have no major environmental impact. In principle, the sulfur could be removed at any point in the life-cycle, from the wellhead to the final product. In this limited study, we concentrate on one typical refinery desulphurization process. In this case, a gas oil hydro finer process for treating high-sulfur gas oil. The detailed life cycle engineering case study will then be generalized to reflect the possible routes of waste minimization, sulfur reduction and possible energy savings in the different stages of the processes involved in the petroleum industry.

In the oil and gas industry, movement towards sustainability requires an integrated approach to process/product design. Fossil fuel (crude oil), a non-renewable reserve, extracted, processed and used by the petroleum industry generally causes environmental problems from its extraction right through to the

production, consumption and final disposal or recycle (Finnegan 2002). It has been established from statistics that carbon dioxide (CO₂) is the predominant substance released during the burning of these fossil fuels, one of the main contributing factors to global warming (Besemer 2001). Other compounds such as oxides of sulphur, nitrogen and methane are also emitted by the petrochemical industries, which are contributors to acidification of rainwater and global warming respectively, thus damaging the soil and depletion of the ozone layer. Though it is generally known that carbon dioxide is the main hazardous compound emitted by the petroleum industry, there are still scientific debates on the certainty that the main cause of global warming is solely from anthropogenic emissions of carbon dioxide (Zwick).

Despite this fact, there is a great dependence on these non-renewable reserves now and in the future despite their harmful environmental effects. Data according to ABB report, 2002 shows that presently 16% of electricity is generated from renewable energy sources, which implies a larger amount, is from the use of non-renewable resources. There is therefore an essential need to shift from the use of non-renewable resources to a renewable energy supply (Klass 2003).

For the purpose of this research therefore, the methods of environmental critical assessment, process integration and eco-efficiency are adopted. These are used to establish a cost and emission trade-off as well as to minimize capital cost on utilities, and are the bases of the life cycle analysis/engineering tool.

Life Cycle Engineering Tools

Life Cycle Engineering (LCE) takes into consideration the technical, environmental and economic aspects of the life cycle of products and processes with the use of LCA and life cycle cost (LCC) tools. According to Keys (1990), "the principal unique aspect of life cycle engineering is that the complete life cycle of the product is kept in consideration and treated in each phase of the product development". LCE is a system-based tool and requires the **evaluation of alternative products** through decision support technology that is applied to determine **best** and most effective **alternatives** (Asiedu and Gu 1997).

The holistic nature of LCE enhances its use in the oil and gas industry, taking into consideration the upstream and downstream processes as well as the transportation and cost of the products and/or process. The products of the oil and gas industries are varied and numerous and most are used in the transport sector (as gasoline, diesel, petrol, engine oil and others) in heating and electricity generation (EPA 1998) and in the chemical industry which consumes most of the products. During the process of extraction, production, and transportation of raw materials, by-products and products, there are emissions involved that have negative impact environmentally, socially and economically. Thus an inventory of the substances is necessary using life cycling methodology.

Recently, petrochemical and petroleum companies, being also a business enterprise, are developing new tools of assessing the environmental impact of their processes and products, taking into consideration cost effectiveness. The life cycle engineering methods permit technical, economic and environmental analysis of processes, procedures and products and this is used by some oil and gas industries to optimise their product and production.

One of the leading chemical and petrochemical companies utilizing the life cycle engineering model is BASF that makes use of an Eco-efficiency analysis model developed by the WBCSD, to evaluate its products and processes. This idea by BASF is based on the fact that "to an increasing extent, environmental aspects of economic activity are being ranked alongside the financial issues" (Saling et al. 2002).

Tools and Models for Waste Minimization.

The tools of waste minimization as mentioned are varied in application. However, newly developing approaches to life cycle analysis and engineering involve the use of eco-efficient methodologies for the development of ecoefficient products, processes and competitiveness. Also other environmental models for product efficiency are being developed in the petroleum industries

Eco-Efficiency

The principal approach of eco-efficiency is environmental and economic viability.



The life cycle Eco-efficiency tool is designed to address not only strategic issues, but issues posed by the market place, politics and research. It is based on assessing environmental behaviour, environmental impact, possible impact on human health and the Eco-system and on the cost of products and processes from the cradle-to-grave" (Intl. J. LCA 2002).

'The eco-efficiency tool is designed to promote improving both environmental and economic performance at a company level by addressing the whole life cycle of a product or process'. (Azapagic and Perden 2000). From the view point of World Business Council for Sustainable Development (WBCSD), "Eco-efficiency is reached by the delivery of competitively priced goods and services that satisfy human needs and bring quality of life, while progressively reducing ecological impact and resource intensity to a level at least in line with the earth's estimated carrying capacity". (WBCSD Presentation 1995). However, in most cases, Eco-efficiency is taken to mean "ecological optimisation of overall systems while not disregarding economic factors" (von Weizsacker EU, Seiler-Hausmann 1999). "It is expressed as the ratio of economic creation to ecological destruction" (Hungerbuhler et al. 1999). Ciba Spezialitatenchemie, also states that the improvement of purely ecological factors, for example better utilization of resources through more efficient processes, is referred to as Ecoefficiency. It is a useful model for comparing products and processes in terms of their economic and environmental impacts, taking into consideration other factors such as toxicity level of products, as well as risk factors of both products

and processes. This is to ensure the health and safety of workers and consumers related to the products.

Oil and Gas Industry

The stages involved in the operations of crude oil processing can be categorized into two main categories: the upstream and downstream processes (Exxon Mobil 2002). The upstream side involves mainly the exploration and production processes, while downstream aspects of the operation include the refining, conversion, purification and distribution to end-users. Refining of crude is the most energy intensive stage of the refinery operations and it is further divided into other stages. Conversion, purification and separation are stages of the petroleum refinery operations.

According to Wittcoff and Reuben (1996), about 90% of products in the chemical industry and therefore for daily use originate from the petroleum and natural gas industry. These products range from the heavy oil products to the light gases. Statistics from Environmental Defence (1999) shows the distribution of refinery products below.



Figure 1 - Distribution of Refinery products.

Source: http://www.environmentaldefense.org/article.cfm?ContentID=1537



Oil and Gas impurities and Mitigation approaches

Considering the different emission reduction tools in use by the oil and gas industry, this project focuses on the gas oil desulfurization process as it is common knowledge that to a large extent, naturally occurring crude oil contains an amount of sulphur compounds (Ukoli; CONCAWE report 1998). In the extraction of crude oil, there are numerous organic compounds, which may occur as impurities. Among these is the sulfur atom and its associated compounds, nitrous oxides, particulates, and volatile organic compounds. These sulphur compounds exist as hydrogen sulphide (H₂S), elemental sulfur (S), mercaptans (R-SH), sulphides (R-S-R'), disulphides (R-S-S-R'), cyclic sulphides (S₈), thiophenes, Benzothiophenes, Bibenzothiophenes (Pfeiffer 1975). During the cracking and combustion of crude oil, these sulfur atoms undergo chemical reactions and form sulfur dioxide (SO₂), as well as other noxious and harmful gases formed from the combustion of carbon, and nitrogen atoms, such as carbon dioxide (CO_2) , carbon monoxide (CO), from incomplete combustion of hydrocarbons), nitrogen oxide as well as methane gas, and particulate. As discussed by van Ravenswaay, toxic these emissions arise at every stage of the petroleum industry processing, from extraction to the use stage. These include volatile organic compounds (VOC), carbon monoxide (CO), nitrogen oxide (NOx), oxides of sulfur (SOx), particulate matter (PM) and hydrogen sulphide (H_2S) as well as other organic matter.

The effect of emission of these substances into the atmosphere has detrimental impacts on humans and the environment if not treated before the products leave the manufacturer's gate. Some effects of pollutants include skin cancer, breathing impediments, acidification of rainwater, mortality and many other effects. (Kunzli et al. 2000).

Nevertheless, mitigation strategies are being developed to minimize the concentration of these pollutant as well as other above-mentioned substances as a result of strict legislations. (CONCAWE 1998). According to the CONCAWE report, sulfur atoms and their compounds in crude oil leave the refinery either in product form or are emitted to the atmosphere and these compounds are released from a number of sources. This is illustrated in the figure below. This sulfur undergoes combustion reaction to form oxides of sulfur, which have a toxic negative impact on the environment (Nagpal and Sen 2002) causing acid rain.



Figure 2: Sources of SO2 emission from refinery Source: CONCAWE report, 1998: http://www.concawe.be/Download/Reports/Rpt_02-10.pdf

Flue gas desulphurization (Nagpal and Sen 2002), is an essential part of the oil and gas purification process for gas oil products, which have uses in diesel power engines, fuels for ethylene plants and other uses. Nagpal and Sen, further discuss other methods of sulfur removal from crude oil.

Life Cycle Analysis and Responsible Care

Life cycle engineering, as earlier mentioned as an integrated approach to waste minimization, is useful in the identification of areas of possible emission, decision making on alternative steps of process and product design. This environmental tool ensures a holistic approach to design including energy and material balances of input and output resources.

The use of LCA in the petroleum/petrochemical industry has some shortcomings in terms of costing and allocation of emission burdens to multiple products and by-products. This is typical in the case of the multi-production section of which the oil and gas industry is a major part. The products and byproducts of crude oil are varied and may be feed to other industrial manufacturing sectors or may be used within the petroleum industry such as to generate electricity and heat. In order to trace the life cycle of these products, a continuous backward analysis needs to be undertaken to determine the feed and product from other process steps as well as their corresponding impacts, which is the essence of the cradle-to-grave nature of LCE. The case of the production of low sulphur gas oil is an example in which the process results in the production of desulfurized gas oil, naphtha products, fuel gas and hydrogen sulphide; which is later sent to the Claus plant for sulphuric acid manufacture for fertilizer and other chemical uses. Other products from the process include fuel oil, used as diesel fuel. In summary, the process equation is as follows:

Gas oil desulphurization = fuel gas + Naphtha + Purified gas oil + Hydrogen sulphide To conduct a life cycle engineering assessment of this simple process, information on the emission, energy use in the crude oil extraction and transportation processes are needed as well as the potential uses of the products, up to their disposal stage.

Eco-Efficiency Methodology

This analysis compares alternatives by considering both the environmental profile and the economic cost of the process. It provides a series of ways of visualising the relative impact and cost, so that the best compromise is achieved. BASF has utilized this tool on a number of its products with a published case study of indigo dye manufacturing process.

The first step to the use of this methodology is the generation of realistic alternative options of processes or products.

The second step in Eco-efficiency analysis is the determination of environmental impact of the various alternatives and the calculation of these impacts based on the International Standardization Organization (ISO 14040). Environmental impacts are determined on the basis of 5 main aspects. These include:

- Raw material consumption
- Energy consumption
- Toxicity potential
- Abuse and risk factor
- Resulting emissions

The emissions considered are:

- Emission to land
- Emission to air and
- Emission to water.

These aspects are tackled individually to analyze the effect of each product and process on the environment, which will assist in deciding the optimum option.

Environmental Impact

The emissions to air, land (soil) and water are determined individually and the results for each are aggregated following normalization to obtain the ecological fingerprint. The emission potential of a substance to air is assessed following an inventory analysis of the various substances and the impact affected. These inventories are categorized in a tabular form with the calculated impact categories. The categories are the global warming potential (GWP), ozone depletion potential (ODP), photochemical ozone creation potential (POCP), acidification potential (AP).

Factors	GWP (g)	ODP(g)	POCP(g)	AP(g)
Categories				
CO ₂	1			
SO ₂				1
NO _x				07
CH ₄	0.009		0.007	
HC	0.000022	1	0.416	
NH ₃	0.0037			1.88
N ₂ O				
HCL				0.88
HF				1.2

Table 1 - Impact potential for air emissions

Source: International LCA Journal, 2002 (BASF report pg. 4)

http://www.basf.de/basf/img/umwelt/oeko/LCA_2002_OnlineFirst_Saling.pdf?id=*C2yHMo**bsf9 00

 CO_2 is carbon dioxide, SO_2 is sulfur dioxide, HC is hydrocarbons, N₂O is nitrous oxide, HF is hydrogen fluoride, NO_x is oxide of nitrogen. The values obtained each are plotted graphically for the various alternatives. This gives a picture of the process with the highest potential emission hazard for

a particular factor, for example CO₂.

The emission to water is determined from the inventory use of chemical oxygen demand (COD), biological oxygen demand (BOD), the compounds of ammonia, hydrocarbons, phosphate, absorbable organic halogens, and heavy

metals. The extent to which each of these compounds contaminates surface water is evaluated using the critical volume for discharge to surface water. The regulation on discharge of wastewater into surface water is used to determine the limit of surface water contamination. Each of the alternative options has varied potential of emitting the above listed compounds to water, and it is the extent to which these compounds are present in the alternative and the ability to contaminate water, that is calculated. Also ¹the amount of clean water needed to dilute the contaminated water back to the acceptable limit is estimated. The larger the hazard caused by a compound, the lesser its limit. These limits are then expressed as reciprocals to ensure that the most problematic contributor is given a large critical value, expressing this fact.

	Limit	Factor (1/limit)
COD	75	.013
BOD	15	0.067
N-tot	18	.056
NH₄ ⁺	10	0.1
P-tot	1	1
AOX	1	1
HMs	1	1
HC	2	0.5
SO ₄	1000	0.001
Cl	1000	0.01

Table 2 - Potential Impact for emission to water

Source: International LCA journal LCA, 2002 (BASF report, pg. 5)

The sums of these emissions are calculated to arrive at a total emission value that is then normalized. Determination of the product or process with the most emission to water is determined easily from a graphical plot of the impact to water of the individual alternatives.

¹ COD is chemical oxygen demand, BOD is biological oxygen demand, N-tot is total nitrogen

The potential impact of the various products to soil is estimated from the average cost of waste disposal and these wastes are categorized into 3 aspects: Special waste, building material waste and domestic waste. The costs for the disposal of the various categories are calculated and factored. The values obtained are combined to determine the contributing factor of each alternative.

Material consumption needed for the processes or products are obtained by inventory analysis. This results in the weighting (scientifically and socially) of the various identified materials based on their reserves i.e. the length of time a particular raw material will be productive considering the present economic methods. It is on the basis of these reserves that estimation of the factors for each material inventory of product and processes are made.

The chemical industry uses the classification and labelling guidelines of the German Chemical Act to determine the toxicity potential of alternatives under consideration, in which each product to be calculated is balanced from the cradle to grave. The toxicity of a particular product is labelled using hazard symbols with arithmetic factors based on a logarithmic scaling LD₅₀ (lethal dose at 50% mortality). As with the other impact evaluations, the individual processes are tackled separately and weighting is done on various toxicity factors. Cases where there are direct contacts and impacts on humans are given more attention as opposed to those in which humans have limited exposure. The potential of the alternative products/processes is also displayed graphically to determine the most toxic substance to humans.

Energy consideration is factored in for the entire life of the products and processes. Each of the different sectors such as steam generation, are evaluated on the basis of energy consumption for each alternative considered. The aggregate of the various energy uses is then normalized with respect to the others resulting in the least favorable alternative having the highest value of one. The abuse and risk potential of environmental impact is based on probability of occurrence of risk from the extraction through the transportation to the recycle or disposal stage. Information on this is obtained from workplace statistics of accidents from the insurance companies.

The information obtained from the environmental impact of the various alternatives is combined following scientific and social weighting, coupled with normalization. The result is represented on an ecological fingerprint. This plot shows the ecologically sound alternatives to consider, points out the least environmentally Eco-efficient alternative and displaces areas where necessary optimization is needed for a better product. A typical ecological fingerprint is shown below:



Figure 3 - Ecological fingerprint of various alternatives

Sources: International LCA Journal, 2002 (BASF website, 2002)

The pentagonal shape of the fingerprint is drawn in 3 dimensions to represent the 5 environmental impact considerations and each of these is independent of the other. An alternative with a value of one for a particular impact is least favorable while that with zero is the most eco-efficient product/process. The goal of all petrochemical companies is to tend towards the centre with **ZERO** environmental impact.

Economic Impact

The ecological operational and capital costs and total cost of the alternative products are calculated based on real cost data. This gives the overall cost. For a comprehensive representation of the most eco-efficient product, the 'Eco-Efficiency Portfolio' model was adopted, which displays the environmental as well as economic potential of each system, product or process on an x/y graph. The most Eco-efficient process or product is situated on the upper right hand side with the lowest total cost and lowest environmental impact. The adoption of the diagram plot with point (0, 0) on the top right-hand corner, does not give a comprehensive illustration, therefore, the point (0, 0) at the bottom left-hand side of the Cartesian co-ordinate system is used in this study. An illustrative example is given below.



1.0

1.8 1.8

Emissions (tonne/yr)



0.2

Alternative 3

Alternative 2

1.0

Total costs (normalized)

Source: BASF in North America, 2002. (http://www.basf.com/newsinfo/pdffiles/EcoEfficiency.pdf) This is a hypothetical "Pareto curve", in with points generated at the top right-hand corner are feasible options, and can be modified towards the lower left-hand corner. However, below this line, are infeasible points because no other point can be better that the Pareto optimum. Furthermore, the ecoefficiency tool has no methodology for computing the Pareto line, but from the generation of alternative processes, it is possible to identify the most feasible path of the curve.

Modification of the points and curve obtained results in the identification of processes with low environmental impact and high profits. There is the possibility of designs that lie on the curve with improved economic and environmental performance. However, a point on the line, with better economic impact cannot be further improved without possible detrimental effect on the environmental impact, thus, the need for an established trade-off between the impact factors.

Therefore, it is the goal to identify a design that lies on or close to the line and the location of this line is determined to a large extent by compromise between environmental impacts and economic profit. A high economic priority design will cause the line to lie towards the right-hand curve, while high environmental priority design results in the curve tending towards the left-hand corner of the plot.

Central to the success of any eco-efficiency study, is the ability to generate feasible designs in order to determine a design close to the Pareto curve. The next section describes how the points on the eco-efficiency diagram can be generated and possible ways that the Pareto curve might be computed.

Model Description and Development: Hydro-desulphurization of Gas Oil Process

The hydro-desulphurisation process, sometimes the fourth stage of crude oil manufacture from raw material, is an essential part of the supply chain of the petroleum industry. This is a process whereby sulphur compounds in all its forms are removed from the products of crude oil distillation process, with the use of gas fuel, with a high percentage of hydrogen and an amine compound. This occurs in a two-stage process. In the first stage, sulphur in the crude oil is converted into hydrogen sulphide by the reaction with the high content hydrogen gas. The second stage is the removal of the hydrogen sulphide from the hydrocarbon mixture by the use of an amine compound. These amine compounds may include mono-ethanolamine, di-ethanolamine or triethanolamine. The reaction takes place in the presence of a catalyst, which breaks down the bond between the carbon and sulphur atoms of the fuel.

The model used for this research work is based on an existing refinery process of the Gas Oil hydro finer for the removal of sulphur and its compounds from the gas oil feed. The original model design was part of an undergraduate design project. The gas oil feed has 1.0 %wt sulfur content with the aim to reduce this to 0.05 %wt sulfur gas oil content. The processes of desulphurization consist essentially of two sections:

- The Reaction section
- The stripping section

The reaction section involves the hydro treating of the gas oil mixture with a rich treat gas feed, while the stripping section deals with the separation of oil and gas mixtures resulting from the treatment with an alkaline.

The hydro finer process has two main feed streams, the high sulfur content gas oil feed and the treat gas feed. This treat gas has a high hydrogen content to desulfurize the gas oil feed. This feed gas comes in at a temperature of about 43°C and is preheated to 112.5°C, by two condensers and two heat exchangers. The gas oil feed exits the fourth side-stream of the crude oil distillation column at a temperature of 88°C, and it then undergoes through two heat exchangers, the first at 240°C and the second at 270°C. This is followed by heating from a fire heater, which operates at 300°C. The heated gas oil feed

is then mixed with the preheated treat gas and both are reacted in the reactor at 292°C.

The reaction is endothermic in the presence of a cobalt molybdenum catalyst, with high to medium desulfurization potential. The chemical reaction is shown below. The desulphurization reaction occurs in the reactor with most of the carbon-sulphur broken to for hydrogen sulphide. The reactor products are then cooled by counter current heat exchangers to 270°C at which temperature they enter the hot flash drum. The liquid and gas products from the reactor are separated in this column at the same temperature. Two other heat exchangers and a small air cooler cools the gas phase before entering the second flash drum at a lower temperature of 38 °C. Most of the hydrogen sulphides are contained in this tail gas, which are routed to the amine scrubber. This strips the hydrogen sulfide from the treat gas. The later is then recycled back into the process.

The liquid phase from the flash drum flows to the distillation column in the presence of steam at 200°C. The gas oil product is then separated from the light gases. Some naphtha products are produced from this column at 38°C. The liquid phase of low content sulphur is cooled to 90°C where another flash drum separates the liquefied gas oil product with 0.05 %wt sulfur from the other naphtha product at 38°C.

The amine used in this model is mono-ethanolamine and this absorbs the hydrogen sulfide in the scrubber and is removed from the system. The sulphide is routed to the Claus plant, which is not included in this model.

This model desulfurization plant operates for 8,760 hr/yr and the annual production for the products are as follow:

- 1. Gas oil = 1,601,958 ton/yr
- 2. Wild naphtha = 5416 ton/yr
- 3. fuel gas = 59,635 ton/yr

Also the costs of products are as follows:

Feed and product	Price (US\$)
Hydro fined Gas oil Product	\$230 per tonnes
Wild Naphtha	\$240 per tonnes
Fuel gas	\$120 per tonnes
Gas oil feed	\$215 per tonnes
Treat gas feed	\$150 per tonnes

Table 3 - Product and feed costs

Results and Data Analysis

This section gives the results in three parts with an overall analysis of the life cycle engineering of the hydro-treating process of the oil and gas industry.

The stepwise results from the process simulations are presented illustrating a comparison with the base case. This is used in the eco-efficiency plot from which it is possible to select a process design, demonstrating the "best" compromise between cost and emission.

The environmental impact of the process is then analysed with the use of the stream data and critical assessment forms. This shows the environmental areas of concern as well as the mitigation suggestions for consideration and possible benefits.

The energy and cost conservation analysis, using the pinch analysis is illustrated to demonstrate ways of minimizing energy use by maximizing heat recovery which result in the modification for use of minimum number of heat exchanger network, thus reducing cost. The comparison is made with respect to the base case. The overall analysis and correlation of all the tools used is summarized and analyzed, to show the relevance and correlation of the use of these tools in the industrial sector of concern.

Process Simulation

The process of simulating the gas oil hydro finer model was conducted on a knowledge basis i.e., physical condition changes were made to the process to generate possible alternative designs based on different alterations.

The base case consists of two inlet streams, each has life cycle costs from the process prior to the desulphurization process. Calculations of the cost of the feed streams are based on the individual mass flow rates and the cost per tonne of feed. The calculations are as follows: Cost of gas oil feed = 215/tonne Cost of treat gas feed = 150/tonne Mass flow rate of gas oil = 203814.517 Kg/hr Mass flow rate of treat gas = 9360.892 Kg/hr \therefore Cost of gas oil feed = 215/tonne * 203.8145 tonne/hr * 7440 hr/yr = 326,021,674/yr \therefore Cost of treat gas = 150/tonne * 9.36089 tonne/hr *7440 hr/yr = 10,446,755.6 /yr

Total feed cost = \$ 336,468,429.8/yr

The energy cost used in the running of the plant includes electricity and steam cost at \$58.1 MWh and \$ 12.1/ tonne respectively (obtained from gas oil hydro finer process description). These are used as utilities in the operation of the compressors, fire heater, pumps and boilers. The cost allocation to each of this equipment is based on the heat loads. The life cycle cost is as follows: Electricity cost = \$58.1 MWh

Steam cost = <u>\$ 12.1/ tonne</u>

There were a total of 7 simulations excluding the base case. These resulted in changes in energy use as well as cost of equipment. The alterations

come from the changes in temperature, resulting in different fire heater heat load tabulated below.

Table 4:

	Base	Sim1	Sim2	Sim3	Sim4	Sim5	Sim6	Sim7
	case							
Heat	16826.6	19546.1	16855	32210.5	18919.6	5743.98	16825.2	22245.2
loads								
MJ/h								

A table of the different simulations and their corresponding equipment capital cost are tabulated below. The capital cost is calculated using the ChemCad software by the input of heat transfer coefficient data for each stream. These capital costs are used in the calculation of the overall plant profit.

	Base	Sim1	Sim2	Sim3	Sim4	Sim5	Sim6	S7
HX1	5.09	0.222	2.54	0.348	1.286	1,374	0.742	2.623
HX2	2.45	0.225	0.142	0.117	0.129	0.644	0.109	0.301
HX3	0.036	0.0045	0.0797	0.1166	2.573	0.355	1.484	5.246
HX4	0.268	0.377	0.337	0.433	2.573	0.2553	0.377	0.255
HX5	0.098	0.0494	0.0392	0.0502	0.0401	0.0936	0.040	0.0936
HX6	0.678	0.207	0.202	0.206	0.228	0.651	0.206	0.651
Column	0.591	0.370	0.370	0.370	0.370	0.370	0.370	0.370
Heater	0.373	0.432	0.341	0.663	0.380	0.151	0.483	0.483
Reactor	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
Compressors	2.7	2.9	2.93	2.902	2.902	2.902	2.902	2.902
Pumps	0.087	0.094	0.094	0.094	0.094	0.094	0.094	0.094
Drums	1.716	1.078	0.333	1.078	1.078	1.078	1.078	1.078
Total	14.2	6.041	7.458	6.457	11.732	20.10	7.965	14.178

Table 5 - Equipment Capital costing in millions of US\$

The costs of the different product streams are also taken into consideration. The product streams include the desulfurized gas oil, fuel gas, as well as some wild naphtha products.

The production rate of gas oil is estimated at 1,601,958 tonnes per year at a value of \$230 per tonne. The wild naphtha product is at the rate of 5416 tonnes per year while the fuel gas is at 59,879 tonnes per year. Therefore, the total amounts of product taken into consideration are as follows:

Cost of gas oil per year = 1601958 tonnes/yr. * \$230/tonne = \$ 368,450,340/yr

Cost of Wild Naphtha per year = 5416 tonnes * \$240/ tonne = \$ 1299, 840/ yr. Cost of Fuel gas = 59879 tonnes/yr. * \$ 120 tonnes = \$ 7,185,480/ yr.

Each of these products has environmental emission potentials and this has to be taken into consideration in the life cycle of the process. This study looks mainly at the environmental impact of producing the products, while the estimation of the cost of the product is done by the end users. Therefore, for the users to conduct environmental impact estimation; values from this study are adopted.

The emissions taken into consideration are the carbon dioxide, sulphur dioxide, hydrogen sulphide emissions, and monoethanolamine. The life cycle costs of these pollutants are calculated based on the amount of tonnage of gases emitted during the use of electricity and steam in the equipment. These calculations are carried out for all the simulations that follow as well as the individual heat loads for potential emission area. These heat loads are obtained from the ChemCad simulation process and Table 6 gives the different alteration.

Table 6 - Table of heat loads for potential emission areas for the different simulations

	Compressor 1	Compressor 2	Heater	Pump1	Pump2	Boiler
Base case	578336.31	1717619.6	16826599.4	876658.	202438	1938
Sim1 (KJ/hr)	578336.31	1717536.1	19546400	8766568	202438	1938
Sim2 (KJ/hr)	578336.31	5144090	16855000	8766568	202438	1938
Sim3 (KJ/hr)	578336.31	171238.25	32210500	8766568	202438	1938
Sim4 (KJ/hr)	578336.31	1717536.1	18919600	8766568	202438	1938
Sim5 (KJ/hr)	578336.31	2451457.1	5743980	8766568	202438	1938
Sim6 (KJ/hr)	578336.31	2451457.1	16825200	8766568	202438	1938
Sim7 (KJ/hr)	578336.31	2451457.1	22245200	8766568	202438	1938

Assuming the use of a 16-carbon hydrocarbon as fuel for the running of this equipment, the amount of CO_2 found in a kilogram of combustion fuel is determined from the molar equations.

 $C_{16}H_{34} + 23/2O_2 \longrightarrow 16 \text{ CO}_2 + 17 \text{ H}_2\text{O}$ $\Delta \text{ H}_c = -4.587^*10^4 \text{ KJ/Kg}$

This implies 1nKg of the hydrocarbon => 16nKg of CO₂ i.e. 226 Kg C₁₆H₃₄ => 704 Kg CO₂ in the fraction 3.115 Therefore the amount of CO₂ in the fuel = $1 \div 4.587E-4$ Kg/KJ * 3.115 = 0.0679 Kg of CO₂/KJ of fuel.

It is assumed that the compressors have 70% efficiency. Therefore the amount of CO_2 per KJ of fuel would be 100/70 * 0.0679 Kg of CO_2 = 0.097 Kg of CO_2/KJ of fuel.

For the emission of SO_2 resulting from the conversion of elemental sulfur to its oxide, the quantity is calculated. From literature, the gas oil feed has 1 %wt sulfur content. Therefore, there is 0.01 Kg of sulfur per Kg of gas oil The mass flow rate of the gas oil is 203814.5Kg/hr, which gives 2038.1 Kg of Sulfur.

A 1:2 ratio exists between sulphur and sulphur dioxide considering the equation: $S_{(g)} + O_{2(g)}$ $SO_{2(g)}$ 32 Kg of S gives 64 Kg of SO₂ => 2038.1 Kg of S = 4076.3 Kg of SO₂ \therefore The ratio of SO₂ to fuel is 1:50 = 0.02 Heat of combustion of the fuel is 4.587E4 The Kg of SO₂ per KJ of fuel therefore is $1 \div 4.587E4$ Kg/KJ * 0.02 This gives = 4.36 E-7 Kg of SO₂ per KJ of fuel.

Monoethanolamine (MEA) losses are based on the amount of the difference in inlet and outlet flow rate from the process, which is 356.444 tonnes of MEA per year.

Hydrogen sulphide quantities are calculated from the molecular weight of the compound and the heat of combustion of the 16-carbon atom fuel at –4.587 exp 4 KJ/Kg.

Molecular weight of $H_2S = 34$ Kg/mol

226 Kg of $C_{16}H_{33}S => 34$ Kg H_2S

- ⇒ 34 / 226 = 0.15
- \Rightarrow 1 / 4.587exp 4 *0.15 = 3.27 exp –6 Kg of H₂S per KJ of fuel
- Assuming a 70% efficiency of compressors, the amount of H₂S per Kg of fuel would be 3.27 exp –6 Kg/KJ * (100 /70)
- \Rightarrow = 4.67 exp –6 Kg of H₂S per KJ of fuel.

Results for the emission of CO_2 , H_2S , SO_2 and Monoethanolamine are tabulated below:

	Base	Sim1	Sim2	Sim3	Sim4	Sim5	Sim6	Sim7	Total
	case								
CO ₂	1960.9	2681.1	2830.9	3541.0	2638.6	1743.9	2496.4	2864.37	21,292.8
SO ₂	1.26	1.58	1.47	2.13	1.54	0.77	1.25	1.49	11.49
MEA	356.44	356.44	356.44	356.44	356.44	356.44	356.44	356.44	2851.55
H ₂ S	0.11	0.103	0.111	0.15	0.10	0.06	0.09	0.112	0.84

Table 7 - Emission losses from the different simulations

This gives the total emission of each simulation in tonnage per year. The major emission from the overall simulation processes and thus the highest pollutant of the process can be determined and compared graphically.



Figure 5 - Emission comparison from gas oil processes

Efficiency Envelope

The establishment of a trade-off between the emission cost and profit assist in the decision making process as a tool in the petroleum and petrochemical industry. This entails the use of the life cycle engineering, ecoefficiency tool.

In the calculation of the profit made from the process, the feed, utility and capital costs are deducted from the total profit cost. For the calculation of the capital cost, the equipment costs are taken into consideration excluding the labor cost, taxes and other miscellaneous costs, because that in the analysis of the emission impacts of a process, these costs, which are constant, do not have significant impact on the environmental and total profit trade-off.

In the calculation of the total profit, the equation used is:

Total profit = totals product value – raw material cost – 0.2 (capital cost) The capital costs are annualized with the multiplication of the factor 0.2, which can be computed using discounted cash flow. This cost is based on the equipment costing shown in table 6 above, which does not include the discount factor. Table 9 below gives the annualized values for the capital costs, which are also based on the equipment costing shown in table 6 above multiplied by the discount factor of 0.2, i.e. (0.2 * equipment capital cost).

	Base	Sim1	Sim2	Sim3	Sim4	Sim5	Sim6	Sim7
	case							
Cost	2.840	1.208	1.492	1.407	1.907	1.546	1.593	2.836
(Million								
US\$)								

Table 8 - Annualised capital cost values

Operating cost for the process analyses includes the utility cost and the feed cost. Maintenance costs are not taken into consideration in this study. The feed costs are calculated in page 45 for the gas oil and treat gas feed, at a total cost of \$336,468,429.8/yr for each of the seven simulations, as they have the same feed streams at equal flow rates.

Also the calculation for utilities at \$ 58.1/MWh and \$12.1/tonne for electricity and steam respectively, for each simulation are given earlier. However, the overall results from the calculation are as follows:

Table 9 - Utility Costs per annum (Million US\$) for the different simulations

	Base	Sim1	Sim2	Sim3	Sim4	Sim5	Sim6	Sim7
	case							
Electricity	\$3.608	\$3.992	\$4.095	\$5.778	\$3.903	\$2.045	\$3.608	\$4.344
Steam	\$0.458	\$0.458	\$0.458	\$0.458	\$0.458	\$0.458	\$0.458	\$0.458
Total	\$4.067	\$4.450	\$4.554	\$6.236	\$4.361	\$2.962	\$4.066	\$4.805

Therefore total operating cost for the process is the sum of the feed cost and the above utility costs to give the figures in Table 10.

	Operating Costs
	(US\$)
Base	340,535,185/yr
Case	
Sim1	340,918,703/yr
Sim2	340,022,147 /yr.
Sim3	342,704,871/yr
Sim4	340,830,363/yr
Sim5	339,430,410/yr
Sim6	340,534,977/y
Sim7	341,273,692/yr

 Table 10 - Total Operating Cost

The total profit, therefore made in each simulated process is equivalent

Base Case: Product value –raw material cost – 0.2 (equipment capital cost)

= \$376,935,600 /yr. - \$340,535,185/yr - \$2,840,000/yr

= \$ 33,560,415 /yr.

This is conducted for each of the simulations to arrive at total profit per year illustrated in the table below.

	Profit
Base Case	\$ 33,560,415 /yr.
Sim1	\$ 34,808,744/yr.
Sim2	\$ 35,421,777/yr
Sim3	\$ 32,823,508
Sim4	\$ 34,197,970
Sim5	\$ 35,959,546
Sim6	\$ 34,807,534
Sim7	\$ 32,826,390

Table 11 - Total profit of simulation processes.

The decision making ability of a refinery process operation is based on the ability to establish a trade-off between the environmental and economic efficiencies for the best design process. This can be illustrated on the x/y eco-efficiency curve. This gives the eco-efficiency of each process relative to the base case. The plot of this curve assists in the choice of the best available design option for a segment of the oil and gas industrial processes.

Table 12 - Plotted	emissions vs.	Profit
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	Base	Sim1	Sim2	Sim3	Sim4	Sim5	Sim6	Sim7
	Case							
Profit	33.6	34.8	35.4	32.8	34.2	36	34.8	32.83
Emission	2318.71	3039.2	3188.92	3899.73	2996.64	2101.20	2854.13	3222.41



Figure 6 - Environmental and economic financial Analysis plots.

Interpretation of Result

The significance of this plot is used in the selection of a preferred process design. The seven different simulations are compared with the base case and the results can be summarized in the plot above.

As calculated from above, the different processes and their corresponding economic profits as well as environmental emission costs show that the fifth simulation process with co-ordinated (36, 2101.20) can be a better hydro finer design process, compared to the base case in terms of both profit and emissions. The other processes however do not prove to be environmentally viable options. From the plot above, a comparison of the base case with the other simulation, i.e. 1, 2,3,4,6 and 7 shows that the base case emits fewer pollutants compared to the others. The case with profit 32.83, 33.6 and 36 are all candidates for the "best process" design depending on the balance of profit and pollution.

In terms of profit, simulation 5 is also the process with the most beneficial cost effectiveness while the 3rd and 7th process designs are the least profitable design. This is mainly as a result of the high utility cost and the high capital cost respectively for the two processes. The implication of this in the life cycle of the gas oil desulphurization process is to illustrate the process simulation that has the most environmental impact, so as to take necessary mitigation steps to minimize or avoid these emissions. This is also useful in this project case, for the re-design of processes.

For the avoidance of these emissions summarized in the eco-efficiency plot, and to conform to the environmental regulations, the environmental critical analysis tool is used to determine the areas of possible potential environmental concerns as well as the pollutants to consider in this process. Alternatives and mitigation options are also suggested.

Environmental Critical Assessment Review

The goal of the critical review is to generate environmental variants that are of concern in this process. This analysis generated a number of possible environmental issues and possible emitted pollutants, which have adverse effects, such as global warming, acidification and other effects.

The critical analysis considered variants such as carbon dioxide releases, hydrogen sulphide losses, sulphur dioxide losses, damages to equipment, and possibility of explosion. These were considered relevant to the reference case of a hydro finer process as a result of the presence of toxic gases.

The use of a stream date form helped to determine physical and chemical properties of streams that were considered to have an impact on the process design. Data extraction is based on the ChemCad software package used in the design process. The information on the data form gives an indication of the tendency of the stream to cause hazard and also shows possible mitigation strategies.

The analyses are provided in an environmental critical assessment review illustrated in Table 13.

Table 13 - Environmental critical assessment review							
Project Title	Gas Oil Hydro finer Process (Desulphurization	Page No.					
Action Ref.	Concerns	Mitigation steps	Possible Benefits	Comments/Action			
				S			
GO001	 CO₂ release Fired Heater Boiler or steam generation Electricity supply for condensers, pumps 	 Reduce energy use Conduct a heat integration and recovery process Ensure energy efficiency 	 Conserves natural resources Saves cost on utility and cost of emissions 	This is done in the project by the use of pinch analysis to reduce the amount of heat requirement and therefore reduction in capital cost.			
		Alternative reactor designUse of Biotechnology					
		Enhance the use of CO ₂ sequestration	Generally reduces global warming	Ongoing research in the area			

GO002	• Fugitive emission from pumps,	•	Monitoring and	•	Reduces the rate of	
	valves, and seals		maintenance of		explosions in	
			equipment.		process plant	
		•	Install mechanical	•	Ensure safety of	
			and dual seals		workers and the	
					environment	
GO003	• SO ₂ and H ₂ S emissions	•	Reduced Fugitive	•	Improved health and	
			emissions		safety of workers	
					and the environment	
					in general	
		•	Change to the use of	•	Reduced emission	No used in the
			bio-catalytic		and complete	study
			desulphurization		conversion of	
			using irradiation		sulphur atoms to	
			techniques		hydrogen sulphide	
GO004	Possibility of explosion	•	Reduce the flow rate	•	Safer working	
			of light gases from		environment.	
			process streams			
GO005	Disposal of sour water	•	Treatment of waste	•	Preservation of	
			water before		aquatic life as well	
			disposal		as safer domestic	
					water use	
				1		

Conclusive Thoughts

The use of environmental assessment tools such as life cycle assessment is useful only in the analysis of environmental aspects of processes and products in the supply chain. However, an extension to the use of the engineering approach to products and processes further enhances sustainability.

This study on the life cycle engineering the oil and gas industry was tackled using the responsible care approach to systems, with the aim of accumulating environmental impact at each stage of the industrial process. The goal of the study was to use life cycle engineering tools to determine the efficiency of industrial processes, conservation of energy and material, to determine emissions impacts and cost. This was carried out in collaboration with other environmental tools: process simulation, environmental critical assessment and pinch analysis.

To demonstrate the use of these tools in the petroleum industry, a process from the refinery supply chain was dwelt upon, gas oil desulphurization, mainly as a result of its availability. As a result of these tools, it was established that possible savings in energy use is possible by the simulation of industrial process (changing physical conditions such as temperature and heat loads) as well as the use of the process integration (pinch analysis) approach. This saving in energy use results in the reduction of environmental emission from the processes.

Systems approaches side-by-side with business-oriented context can lead to a systematic approach to new designs and solutions. Possibilities of improvement with evolving technology can also be achieved with the environmental critical analysis tool, which suggests alternatives to processes and mitigation potentials for emission. As a result of these steps, environmental impacts are then calculated for two acid gas emissions to assess the environmental impact of products. The aim of this is to ensure the accurate allocation of environmental costs by end users to products.

This study is not extensive as it were and further work on the extension of this model to the entire petroleum process is required.

References

.

ABB Group (2000). *Life cycle assessment tool for eco-efficient products*. Annual report, Technology report.

Asiedu , M. Y., and Gu. P. (1998). *Product life cycle cost analysis- the state of the art review. Int. J. Prod. Res., vol. 36, No. 4, 883-908.*

Azapagic, A., and Perden, S. (2000). Indicators of sustainable development for industry: A general framework. *Trans Ins. Chem. Eng.* Vol. 78, B4, pp. 243-261.

Barwis, J. H., Sustainability and the oil & gas industry: the role of technology in minimizing environmental impacts.

http://www.copernicus.org/EGS/egsga/nice01/programme/abstracts/aac7349.pdf

Besermer, J. J. (2001). Global Warming: The Big Picture. http://www.ocs.orst.edu/forum/BigPicture.htm

CHEMCAD, Chemstations INC. (2003). *Chemical Process Simulation* http://www.chemstations.net

Ciba Spezialitätenchemie, Umwelt, Gesundheit und Sicherheit– Innovationen im Umweltbereich

CONCAWE report (1998). Sulphur dioxide emissions from oil refineries and combustion of oil products in Western Europe and Hungary.

Environmental Defence (1999). Oil refining main page http://www.environmentaldefense.org/article.cfm?ContentID=1537

Finnegan, L. (2002). *The Environmental Effects of Fossil Fuel.* http://www.personal.psu.edu/users/l/a/laf208/environmental_effects_of_fossil.htm.

Hungerbühler K, J. Ranke, T. Mettier (1999). *Chemische Produkte und Prozesse. Springer Verlag Berlin, ISBN 3-540- 64854-2.*

Keys, L. K. (1990). System life cycle engineering and DF, 'X. IEEE Transactions on component, Hybrid and Manufacturing Technology, **13**(1), 83-93.

Klass, D. (2003). A critical assessment of renewable energy usage in the USA. Energy policy 31 (2003) 353-367. Presented at the online conference "Energy Resource", 2001.

Kunzli, N., et al. (2000). Public-health impact of outdoor and traffic-related air pollution- a European assessment. *The Lancet*, vol. 356. September. 795-801.

Nagpal, S., and Sen, P.K. (2002). Selecting the solvent for SO₂ removal absorption. *Environmental Management: Air-Pollution Control*

Pfeiffer, J. B. (Ed) (1975). *Sulfur Removal and Recovery from Industrial Processes* (*Advances in Chemistry Series: No 139*). Oxford University Press.

Saling, P., A. Kicherer, B. Dittrich-Krämer, R. Wittlinger, W. Zombik, I.Schmidt, W. Schrott and S. Schmidt: *International LCA Journal: Eco-efficiency by BASF, The Method (International LCA Journal, 2002)* (http://www.basf.de/basf/img/umwelt/oeko/LCA) SETAC (1993) *Guidelines for life cycle assessment. A code of practice.* http://www.setac.org/guidelife.html

Ukoli, M. K., *Environmental factors in the management of oil and gas industry in Nigeria*. http://www.cenbank.org/out/annual/ACZRU/2001/Owe-01-2.pdf

van Ravenswaay, E. O. PRM 255 Pollution prevention case study on petroleum refining.

Von Weizacker EU, Seiler-Hausmann J. (Ed) (1999): Ökoeffizienz Management der Zukunft.

WBSD Presentation (1995).

Welford R. (1998). Corporated Environmental Management, Earthscan publication.

Wittcoff, H. A., and Reuben, B. G. (1996). Industrial organic chemicals.

Zwick, A., *Decisions in a climate of uncertainty - Addressing CO2 issues.* http://www.jrc.es/iptsreport/vol02/english/art2.doc