Separation of fluorocarbon gases from a reactor plasma system

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DECLARATION

I, A.T. Grunenberg hereby declare that the thesis entitled: Separation of Fluorocarbon Gases from the Plasma-reactor System is my own work and that all sources and help obtained is acknowledged in either the references or the acknowledgements.

Signed: A.T. Grunenberg

Date:

ABSTRACT

South Africa has natural resources in mineral feedstock containing gold, manganese, chromium, vanadium, copper, antimony, phosphate rock, uranium, fluorspar and titanium. A high percentage of these ores are exported in unbeneficiated form. There are beneficiation opportunities to transform the raw materials to value-added products, thus increasing employment and stimulating the South African economy.

Fluorocarbon (C_xF_y) gases can be produced via high-temperature plasma processes, where fluorspar and carbon (CaF_2 + C) react at ~6000K. These gases are traditionally separated by means of costly and unsafe cryogenic distillation.

The focus of this project is to propose a feasible separation process and to interlink it to a plasma system in order to develop a conceptual plant that can produce 2500 t/a C_2F_4 and 625 t/a C_3F_6 safely and cost-effectively, both with 96% purity.

To execute the above a literature survey was done giving vital information on absorption and distillation systems as well as membranes that can be used to separate CF_4 from C_xF_y gas streams at acceptable pressures and temperatures.

The separation of a C_2F_4 -C_2F_6 -C_3F_6 mixture was investigated experimentally using a number of polymer membranes at 25^oC and trans-membrane pressures of 60 to 260 kPa. The AF 2400 Teflon-coated membrane was the only successful one with an optimized selectivity of 2.5 and a flux of 0.002 mole/m^2.s at 160 kPa. The unsaturated CF gases, C_2F_4-C_3F_6, permeated, whereas the C_2F_6 remained in the retentate. This presents an excellent opportunity to remove the impurity C_2F_6 from the valuable products C_2F_4 and C_3F_6, which can easily be separated from each other by means of cryogenic distillation. Increasing the transmembrane pressure leads to an increase in the permeance at 160 kPa from $25*10^{-6}$ to $100*10^{-6}$

mol/m^2.s.kPa. These data were used in the design of an ideal recycle cascade with 11 stages and a total membrane surface area of 6084 m^2.

By combining the plasma arc system with a hybrid separation process based on absorption, distillation, membrane separation and cryogenic distillation, a conceptual design was made for the production of 625 t/a C_3F_6 and 2500 t/a C_2F_4. The techno-economic analysis yielded good investment opportunities with a NPV of MR661 after 3.73 years, an attractive IRR of 29.17 %, with a turnover of MR240/a.

Key words
Fluorocarbon
Fluorspar
C_xF_y
CF_4
C_2F_4
C_2F_6
C_3F_6
Teflon-coated membrane
Plasma arc system
Membranes
High-temperature plasma

OPSOMMING

Suid Afrika is ryk aan natuurlike minerale, bevattende ondermeer goud, magnesium, chroom, vanadium, titanaan, koper, antimoon, fosfate, uraan en vloeispaat. ‘n Hoë persentasie van hierdie minerale word uitgevoer sonder enige waardetoevoeging, wat ‘n verlies aan moonlike inkomste en werksgeleenthede vir Suid-Afrika teweegbring.

Fluorokoolstof (C_xF_y) gasse word, onder andere, tans vervaardig deur ’n hoë-temperatuur plasmaproses, waar vloeispaat en koolstof (CaF_2 + C) by ~6000K met mekaar reageer. Hierdie gasse word dan deur middel van ’n lae-temperatuur tradisioneledistillasie proses van mekaar geskei. Hierdie skeiding word as duur en onveilig beskou.

Die fokus van hierdie projek is om ’n ekonomiese konsepsionele proses te ontwikkel wat veilig en prakties uitvoerbaar is, en wat gekombineer kan word met ‘n plasmastelsel om 2500 t/a, 96 % suiwer C_2F_4 en 625 t/a C_3F_6 as produkte te vervaardig.

Die literatuuroorsig het gefokus op ‘n skeiding van absorbsie-, adsorbsie-, distillasie- en membraan prosesse om suksesvolle metodes wat prakties toegepas kan word vir die skeiding van C_xF_y gasse by aanvaarbare temperature en drukke te kan ontwikkel.

Die skeiding van ‘n C_2F_4, C_2F_6, C_3F_6 gasmengsel is eksperimenteel ondersoek deur gebruik te maak van polimeermembrane by 25^oC en ‘n transmembraandruk van 260 kPa. ‘n AF 2400 Teflon-membraan van GKSS (Duitsland) was die enigste suksevolle membraan, met ‘n geöptimeerde skeidingsfaktor van 2.5 en ‘n vloed van 0.002 mol/m^2.s by 260 kPa. Die onversadigde C_xF_y gasse C_2F_4 en C_3F_6 het deur die membraan gepermeër terwyl die geperfluorineerde gas, C_2F_6, agtergebly het as die retentaat. Dit word gesien as ‘n deurbraak wat bewys dat C_2F_6 gas wel

van die ander C_xF_y produk gasse geskei kan word. Die res van die gasse kan teen ’n relatiewe lae koste deur middel van distillasie en adsorbsie geskei word.

Indien die permeasie verhoog word van $25*10^{-6}$ na $100*10^{-6}$ mol/m^2.s.kPa en ‘n transmembraandruk van 160 kPa gehandhaaf kan word, kan ‘n kaskadeontwerp voorgestel word wat 11 stadiums het, en wat n membraanarea van 6084 m^2 beslaan. ’n Hibriedskeidingsisteemkonsep is voorgestel waar absorbsie-, membraan- en distillasieskeidingsprosesse ingesluit is vir die produksie van 2500 t/a, 96 % suiwer C_2F_4 en 625 t/a C_3F_6 as produkte. Die tegno-ekonomiese evaluasie-analise het aangedui dat goeie kommersiële moontlikhede bestaan met ’n NHW (NPV) van MR661 oor 3.73 jaar, ‘n aanloklike IOK (IRR) van 29.17 %, en ‘n omset van MR240/a.

Kern woorde:
Vloeispaat
Fluorokoolstofgasse
C_xF_y
CF_4
C_2F_4
C_2F_6
C_3F_6
Teflon-membraan
Membrane
Polimeermembrane

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Nomenclature

Symbol	Description	Unit
A	Absorption factor	-
$P_{atmospheric}$	Atmospheric pressure (87 kPa)	kPa
V_B	Boil-up ratio (V'/B)	-
B	Bottoms flow rate	kg/h
ΔT	Change in temperature (T_{out}-T_{in})	K or ^oC
D_c	Column diameter	m
D	Diffusion coefficient	m^2/s
D_d	Distillate flow rate	kg/h
K_n	Equilibrium ratio for vapor liquid equilibrium (y_n/y_x)	-
n	Exponent cost factor	-
F	Feed flow rate	kg/h
E	Fractional overall stage (tray) efficiency	-
K_N	Geometric mean of the K-values over N stages	-
Q	Heat	kW
ΔH^{vap}	Heat of evaporation	kJ/kmol
H	Henry's law coefficient	kPa^{-1}
b	Historical cost index	-
i	Index for the enrichment section	-
j	Index for the stripping section	-
c_i	Interface concentration	mol/m^3
L	Liquid mole flow rate	kmol/h
$\dot{m}$	Mass flow rate	Kg/h
u_v	Maximum allowable vapour velocity	m/s
l_M	Membrane thickness	m
N_{min}	Minimum number of equilibrium stages	-
R_{min}	Minimum reflux ratio (L_{min}/D)	-
x_B	Mole fraction in bottoms	mol/mol
x_D	Mole fraction in distillate	mol/mol
x_F	Mole fraction in feed	mol/mol
$\dot{M}$	Molar flow rate	kmol/h
n	Molar flow rate	mol/s
L'	Molar flow rate of solute-free absorbent	kmol/h
V'	Molar flow rate of solute-free gas	kmol/h
N	Molar flux	$mol/m^2.s$
y	Mole fraction at permeate side	mol/mol
x	Mole fraction at retentate side	mol/mol
X	Mole ratio of solute-free absorbent in liquid	mol/mol
Y	Mole ratio solute to solute-free gas in the vapor	mol/mol
M_R	Molecular weight	g/mol
N	Number of equilibrium stages	-
N_m	Number of membrane stages	-
P_A	Partial pressure of compound A	kPa
l_t	Plate spacing	m
P	Pressure	kPa
R	Reflux ratio (L/D)	-
S_e	Stripping factor	-
T	Temperature	K or ^oC
R	Universal gas constant (8.314 KJ/kg K)	kJ/kg K

V	Vapor mole flow rate	kmol/h
$\dot{v}$	Volumetric flow rate	mL/min
V_w	Volumetric vapor flow rate	m^3/s
Greek symbols		
α	Separation factor (Selectivity)	-
α^*_{AB}	Ideal selectivity of A over B	-
α_{AB}	Selectivity of A over B	-
λ	Latent heat	kJ/kg
ϕ	Cut (mole basis)	-
ϕ_S	Fraction in the liquid feed not stripped	-

1. Introduction

1.1 Background

South Africa has natural resources in mineral feedstock containing platinum group metals, gold, manganese, chromium, vanadium, copper, antimony, phosphate rock, uranium, fluorspar and titanium. A high percentage of these ores are exported in unbeneficiated form. There are beneficiation opportunities to transform the raw materials into value-added products, thus increasing employment and stimulating the South African economy.

Scientific and engineering skills are crucial to future technological growth; South Africa's technological skills are scarce and need to be developed (DTI 2005).

South Africa mines ~260 000 tonnes CaF_2 per annum, mainly for export, at a value of 100 USD per tonne. To come in line with government's drive and to add value to our mining resources, the opportunity exists to convert the fluorspar into useful products.

Fluorspar can be converted into intermediates HF or F_2 or into valuable end-products, including AlF_3, UF_6, NF_3 and various C_xF_y compounds.

C_3F_6 and C_2F_4 are valuable fluorocarbon gases used in semi-conductor industries. Currently DuPont (USA) and 3M-Dyneon (USA/Germany) are the main producers of these products using a process with refrigerant 22 (R-22) as their principal raw material.

With the production of C_3F_6, other valuable fluorochemicals-intermediates such as C_2F_4 and CF_4 are formed and sold as products to various markets. C_2F_4 is used for the production of PTFE (Teflon©) and other specialized high-value fluoropolymers, elastomers and fluorochemicals, which is being

researched at Necsa in conjunction with other international role-players (SPII, 2004).

Conventional methods, including cryogenic distillation, are used to separate and purify these products, which are costly, energy-intensive and dangerous to operate.

1.2 Aim and objectives

1.2.1 Aim

The aim of this research was to develop a conceptual design to separate C_xF_y gases produced from a CaF_2 plasma system, producing 2500 t/a C_2F_4 with purity 96%, and 625 t/a C_3F_6 with 96% purity.

1.2.2 Objectives

In order to achieve this aim the following objectives were defined at the start of the project:

- Define a plasma system that will be suitable and cost-effective to produce C_xF_y gases;
- Separate CF_4 from a C_xF_y plasma mixture (low-value high-inert gas) using absorption;
- Use membrane technology to separate C_2F_6 from a C_xF_y gas mixture, thereby, simplifying and reducing cost in comparison to traditional difficult and unsafe cryogenic distillation;
- Use distillation to separate C_2F_4 and C_3F_6 as final product at a pressure below 200 kPa;
- The final objective is to develop a process and arrive to a first-order cost estimate.

1.3 Scope of the Thesis

The scope of this thesis was to evaluate the different types of separation systems to meet the objectives.

A literature study was done to become familiar with and understand the markets of C_xF_y gases, in particular CF_4, C_2F_4, C_2F_6 and C_3F_6, using CaF_2 as raw material. Plasma methods proposed to produce these C_xF_y gases will be investigated and the best technology selected. Several separation methods namely distillation, absorption, adsorption, and membrane separation including the thermodynamics of these C_xF_y gases were studied and used in the conceptual design to compile a first-order plant cost estimation. This information is reported on in Chapter 2.

Experimental work was done on selected membranes to see if they can be used to separate C_2F_6 from the C_xF_y gas mixture, thus simplifying and reducing cost in comparison to the difficult and unsafe cryogenic distillation. The results of these tests were analysed to choose a suitable membrane and to define the design parameters to be used in the conceptual design phase. Experimental membrane work is reported on in Chapter 3.

A conceptual plant design was proposed by reviewing above-mentioned technologies and choosing an acceptable process to produce 2500 t/a C_2F_4 (96%) and 625 t/a C_3F_6 (96%) product gas. Basic size requirements were calculated to get sufficient information to perform a cost evaluation of the proposed plant. The conceptual plant design is reported on in Chapter 4

Cost estimation was done using a proven method developed by Necsa management to calculate the IRR, NPV and payback times of C_xF_y gas manufacturing plants. The basis of this method is to estimate capital equipment cost by using previous examples (previous or similar plants built) and multiplying them with cost indexes to be used as 2008 cost prices. The cost evaluation is reported on in Chapter 5.

All conclusions, future work and recommendations are summarised and reported on in Chapter 6 to be used as a basis for the design of a detailed (pilot) plant.

2. Literature study

2.1 Introduction

This chapter will present a study of the various separation methods in order to design and propose a feasible separation process for various fluorocarbon mixtures. The aim is not to revise all theory of the specific separation unit operations, but only to highlight the fundamental basics of separation methods to be used in order to propose a conceptual design for the separation of fluorocarbon gases produced by the CaF_2 plasma process. This forms part of the fluorspar beneficiation project currently funded by the Innovation Fund.

Due to the fact that more than one process can be used to produce fluorocarbon gases, the aim was to formulate a separation process that is feasible and compatible with a specific plasma process. The fact that some of these plasma systems are highly dependent on recycle streams, implies that one cannot separate the plasma system from the separation unit operation.

The following two fluorocarbon manufacturing methods can be considered:

- (CaF_2 + C) transfer-arc plasma to produce C_2F_4 and C_3F_6;
- (CaF_2 + C) non-transfer-arc plasma using N_2 or CF_4 recycle gas to produce C_2F_4 and C_3F_6.

For the separation of the C_xF_y gases, the following separation methods were considered:

- Traditional **cryogenic distillation**. Due to the fact that it is a method that has been proven and is widely used by well-known PTFE manufacturers (Dyneon and DuPont), this method will be used as a starting point to find solutions to reduce energy consumption and to solve safety and feasibility problems;

- **Absorption** is a well-known and defined method for gas purification and will be investigated as a possible separation method;

- **Adsorption** which is used as a separation method in separating various C_xF_y gases;

- New technological developments in the manufacturing of high-density polymer **membranes** stimulated curiosity regarding the possibility of membrane separation of C_xF_y gases as a feasible and practical separation method, particularly with respect to the difficult C_2F_4/C_2F_6 separation.

2.2 Fluorocarbon gases: markets, applications and safety

2.2.1 Markets

Present estimates indicate a potential to increase fluorochemicals turnover from R150 million per annum to over R1 billion per annum within the next 9 years with a portfolio of high-value and high-purity products in different markets. Agricultural, refining and steel industries (HF), performance fluids and solvents (fluorinated-liquids), performance elastomers (perfluoro-monomers) and the semiconductor industry (fluorine-based F-gases) are the main role players. More than 90% of the revenue will be from international markets, which would have a big positive impact on the South African chemical trade balance. (DTI, 2005)

Fluorspar is currently exported at a price of 100 $/tonne (USD), while the opportunity exists to beneficiate more locally by the manufacturing of downstream products such as tetrafluoroethylene (C_2F_4), the monomer for polytetrafluoroethylene (PTFE or Teflon©), hexafluoropropylene (C_3F_6) at up to 80 R/kg (Freedonia, 2000), and advanced electronic gases such as C_xF_y which sell at prices between 2 and 4 USD/kg. Hundreds to thousands of tons are

currently needed for the world market that grows at 6-8 % per annum. The conventional manufacturing processes for fluorocarbon products are expensive and unsafe and environmentally-unfriendly (Van der Walt, 2007), (Freedonia, 2000).

2.2.2 Applications

C_2F_4 and C_3F_6 can be used to produce various type of polymers, including PTFE (Teflon ©). It is copolymerized with hexafluoropropylene, ethylene, perfluorinated ether, isobutylene and propylene. C_2F_4 and C_3F_6 are also used to produce low-molecular-weight polyfluorocarbons which are used in situ on metal surfaces.

Product requirements are summarized in Table 2-1. (Van der Walt, 2001)

Table 2-1: Product market specification

Product	Purity	Other impurity specifications
C_3F_6	Min 95%	C_xF_y gases making up the rest of the 5 %stream
CF_4	Min 95%	The CF_4 is recycled back as a recycle gas, C_xF_y gases making up the rest of the 5 % stream
C_2F_4	C_2F_4 is not a commercially-traded product due to its highly hazardous nature. All C_2F_4 produced globally is solely for captive use for the production of fluoropolymers or other fluorochemicals. However it would typically be of a purity of 96 % with a combination of C_xF_y gases used for polymerisation. The C_2F_6 concentration must be as low as possible due to the fact that it interferes with the polymerisation reaction.	

2.2.3 Safety

The safety aspects of C_2F_4 and other C_xF_y gases have been publicised by Du Pont and Dyneon. General rules of thumb as suggested by these manufacturers (Du Pont, 1996) are summarised below:

- C_2F_4 below 220 kPa is safe;
- C_2F_4 below 60 % concentration at higher than 220 kPa is safe;
- Pure liquid C_2F_4 at pressures above 220 kPa (a) and temperatures below -80 ^oC is considered safe;
- Air contamination caused by leaks must be kept below 1 %;
- Avoid uncontrolled adsorption on zeolite or activated carbon traps, heat of adsorption may cause explosion;
- Process temperatures should always be kept below 100 ^oC;
- C_2F_4 system are Zone 1 or 2 classified (explosive mixture), 3.5 mJ required for ignition above 8 mole %.

The main risk of C_2F_4 is deflagration according to the exothermic reaction:

C_2F_4 (g) = CF_4(g) + C (s) + 66 kcal/mol.

Figure 2-1 illustrates the flammability region of C_2F_4 / air mixtures at 25^oC and 100 kPa (Du Pont, 1996).

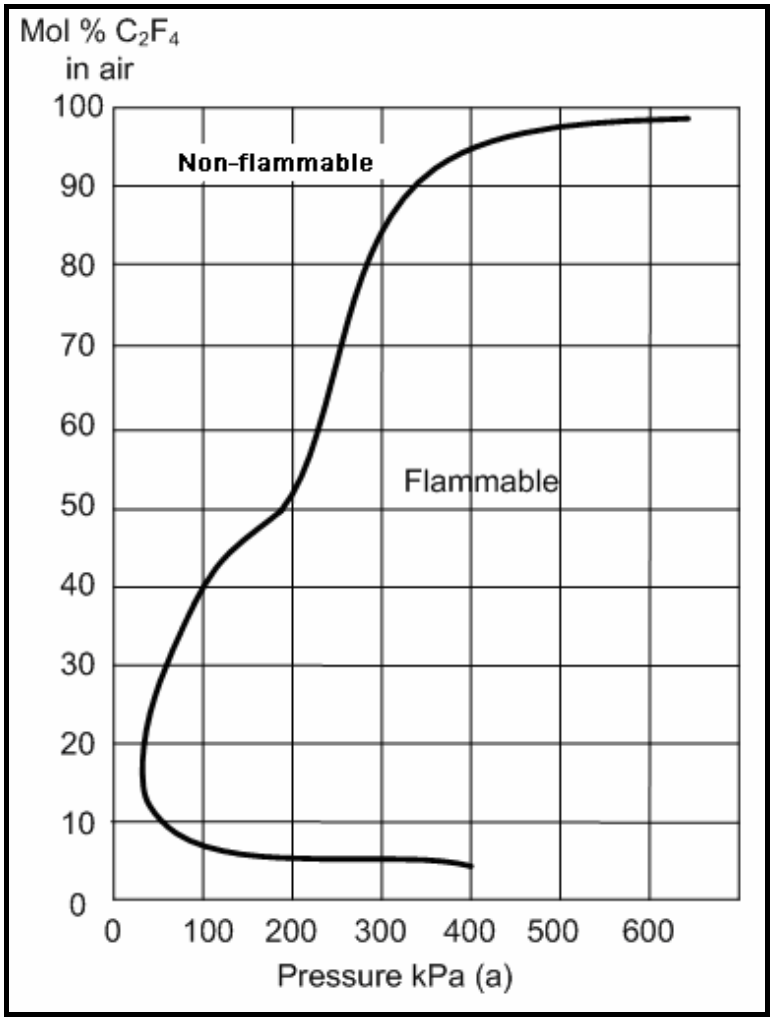

Figure 2-1: Flammability of a C_2F_4 / air mixture at 25 °C (Du Pont, 1969)

2.3 Plasma reactors

2.3.1 Introduction

Two types of plasma systems were considered: (i) a non-transfer-arc and (ii) a transfer-arc plasma. Both systems will produce C_xF_y gas mixtures. The composition of the gas mixtures is mainly determined by the operating pressure and quenching rate (Moore, 1997).

Each system is unique even if the basic chemistry follows the same thermodynamics, kinetics and principles.

In this study three plasma systems and their associated products were evaluated with regard to separation aspects. These systems were:

- Nitrogen plasma (non-transfer-arc plasma)
- CF_4 Plasma (non-transfer-arc plasma)
- Transfer-arc plasma (no carrier or plasma gas)

An overview of different plasma systems is given by MD Smith in Kirk-Othmer Encyclopaedia of Chemical Engineering (Smith, 2000).
The electron region of plasmas with respect to temperature and density is illustrated in Figure 2-2, which forms the basis of conceptual design.

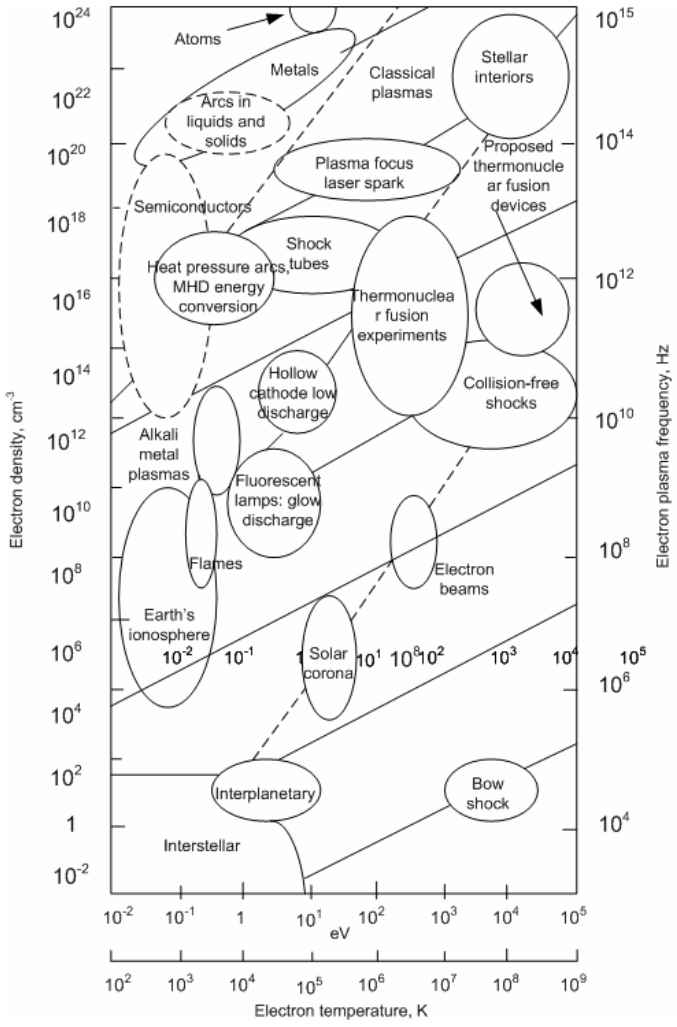

Figure 2-2: Electron region of plasmas (Smith, 2000)

Figure 2-2 indicates that the plasmas that will be considered works in the liquid and solid arc region at 6000K, with an electron density of 10^{20} cm^{-3} and frequency of approximately 10^{14} Hz.

Non-transfer-arc plasma is defined as a plasma system which has a water-cooled, non-consumable anode and cathode. The plasma arc is generated by means of a high-frequency spark generator between the cathode and anode. An open-circuit potential difference between the two electrodes and an appropriate power supply will then sustain the plasma (a welding arc can be used as example to visualise the concept). The reactants can be fed into the plasma arc or into the tail flame, depending on the plasma torch used, and will be heated sufficiently to atomize them (Smith, 2000).

The transfer-arc plasma consists of continuous consumable, hot carbon electrodes and has the advantage of the one arc attachment point being positioned into a molten pool of electrically-conductive reactant. Due to the high thermal energy generated by the plasma arc and the resistance of the molten bath reactant, a potential difference across the electrodes causes a current to flow. This in turn generates a high amount of heat in the molten bath causing the reactants to ionize and react with each other forming the C_xF_y species required (Cotchen, 2000).

The quench probe is an inherent part of the plasma system, quenching from up to 6000 down to < 500 K, forming various species of C_xF_y gases.
Plasma systems have the capability to produce C_2F_4 and C_3F_6 species at different yields by manipulating pressures and quenching rates (Van der Walt, 2007). Previous experience showed that the C_2F_4 and C_3F_6 yields differ slightly from system to system. Ten to fifth teen percent differences in the C_2F_4 and C_3F_6 yields are achieved by manipulating process conditions, such as pressure and quenching rates.

The separation of the different fluorocarbon products is conventionally done by distillation columns were high recycle rates of carrier gas (CF_4 or N_2), is part of

the separation train and is recycled to sustain the plasma arc. The main advantage of these systems is that gases, that are normally an environmental risk, can be recycled back to the plasma to be converted to useable products.

Energy requirements for producing these gases are not a straightforward conclusion and still need to be clarified and verified through experimental work. A safe and practical assumption that can be made from production units and experimental systems at Necsa, Pelindaba, is that **10 kW** is needed to produce **1 kg** of $\mathbf{C_xF_y}$ gas.

2.3.2 CF_4 Plasma system

The solid feed of CaF_2 and carbon reagents is preheated and fed to the plasma reactor continuously into the high-temperature zone. By carefully selecting the quenching conditions, desired end-products like CF_4, C_2F_4, C_2F_6, C_3F_6, etc., can be produced from a CF_4 non-transfer-arc plasma system.

A typical composition from a non-transfer-arc and transfer-arc plasma system is shown in Table 2-2.

Table 2-2: CF_4 plasma mixture composition mole% of non-transfer-arc and transfer-arc plasma (Moore, 1997)

Product	% Yield
CF_4	65
C_2F_4	25
C_2F_6	7
C_3F_6	3

The basic reaction in a CF_4 non-transfer-arc plasma and quenching system is:

CaF_2 (s) + C (s) at 4000K to 6000K in a CF_4 plasma system (Moore, 1997):

C (s) + CaF_2 (s) + CF_4 (g) = C_xF_y (g) + C (s) + CaC_2 (s).

A solid residue, CaC_2 and unreacted CaF_2 is separated by a filter system. The plasma gas is compressed and fed to a lights removal column separating light gases (e.g. CF_4) from the rest of the product mixture.

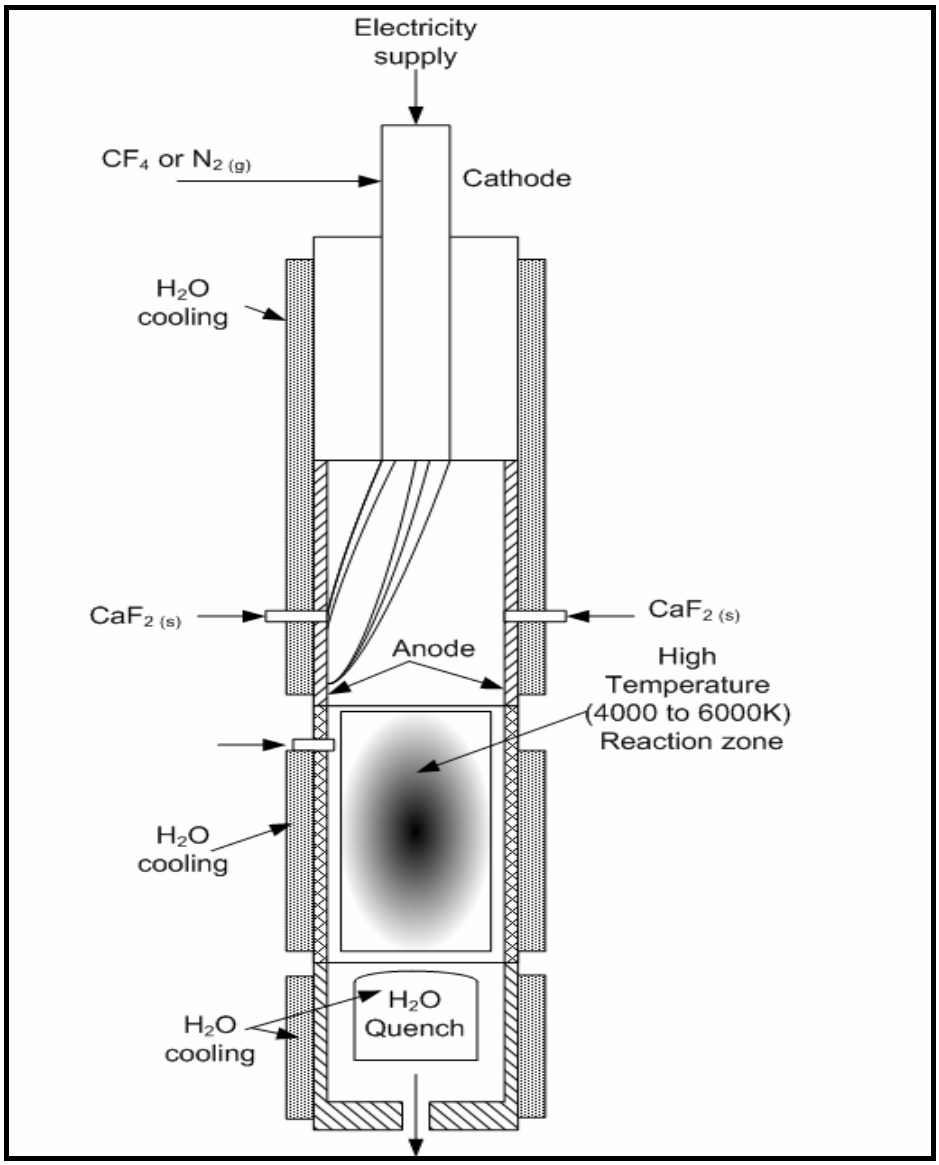

Figure 2-3: The non-transfer-arc plasma system

The C_xF_y gas mixture from the quench probe is the feed stream to the hybrid separation section where the C_2F_4 and C_3F_6 are recovered as end-products and the CF_4 and C_2F_6 as recycle gases to the plasma reactor.
Figure 2-3 shows the non-transfer-arc plasma configuration using CF_4 or N_2 as carrier gas.

A typical flow sheet and stream table of the non-transfer-arc plasma are given in Figure 2-4. The mass balance is based on a 300 working days/year, 2500 tonnes/annum C_2F_4, and 500 tonnes/annum C_3F_6 plant.

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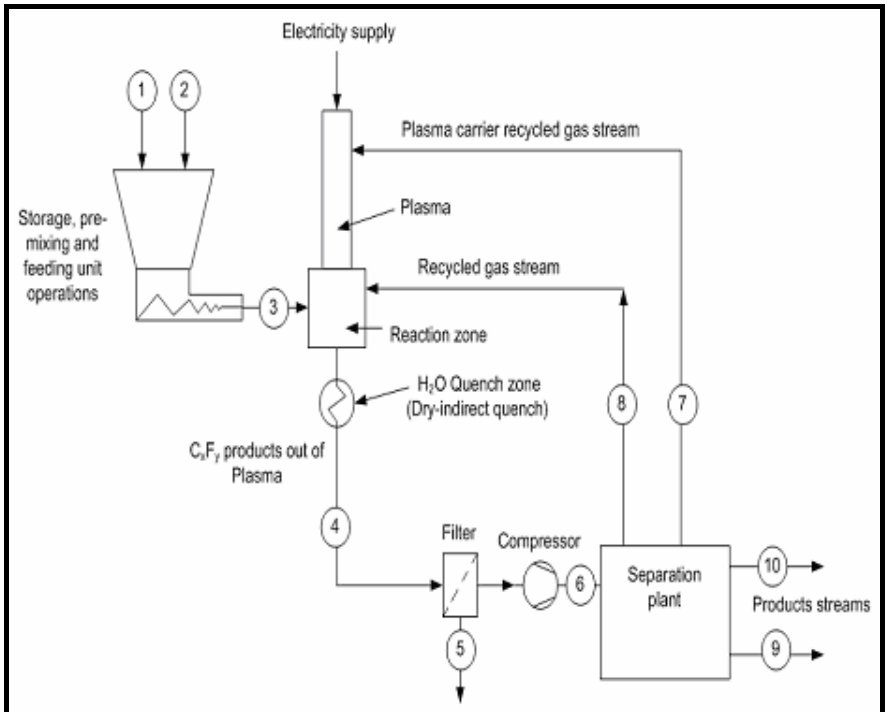


	Streams	Units	1	2	3	4	5	6	7	8	9	10
Mass Flow	Molar mass											
CaF_2 (s)	78.00	kg/h	23719.0		23719.0	19765.8	19765.8					
C (s)	12.00	kg/h		5982.6	5982.6	4985.5	4985.5					
C_2F_4	100.00	kg/h				578.7		578.7	11.6	228.7	350.0	
C_2F_6	138.00	kg/h				162.0		162.0	1.6	1.6		
C_3F_6	150.00	kg/h				69.4		69.4	1.4	1.4		68.1
CF_4	88.00	kg/h				1504.6		1504.6	1429.4	1.5		
CaC	52.00					2635.4	2635.4					
Total			23719.0	5982.6	29701.6	29701.6	27386.7	2314.8	1444.0	233.2	350.0	68.1
Streams	Molar mass	Units	1	2	3	4	5	6	7	8	9	10
Mass Flow	kg/kmol											
CaF_2 (s)	78.00	kmol/h	304.090		304.090	253.408	253.408					
C (s)	12.00	kmol/h		498.546	498.546	415.455	415.455					
C_2F_4	100.00	kmol/h				5.787		5.787		2.287	3.500	
C_2F_6	138.00	kmol/h				1.174		1.174		0.012		
C_3F_6	150.00	kmol/h				0.463		0.463		0.009		0.454
CF_4	88.00	kmol/h				17.098		17.098	16.243	0.017		
CaC	52.00	kmol/h				50.682	50.682					
Total			304.090	498.546	802.636	744.067	719.545	24.522	16.243	2.325	3.500	0.454
Proces parameters												
Temperature		°C	25	25	25	250	250	25	-75/25	-75/25	<-50	25
Pressure (a)		kPa	87	87	-40	-40	87	1600	1600/150	250/150	<220	150

Figure 2-4: CF_4 Plasma system, flow sheet and stream table

From the above flow sheet it can be seen that the recycle streams are large in comparison to the end-products, which is a clear indication of energy requirements required. The above traditional cryogenic distillation system is

clearly uneconomical if you look at the temperature differences of the separation system.

2.3.3 N_2 non-transfer-arc plasma system

The reactions are the same as described above in the CF_4 plasma section. The main difference is that N_2 gases are fed to the plasma, sustaining the plasma arc, see Figure 2-3 for details. As demonstrated, the CF_4 yield is lower than in the CF_4 plasma.
Typical N_2 plasma system yields are indicated in Table 2.3, assuming that the N_2 does not take part in any reactions in the plasma system.

As illustrated in Table 2.3, the N_2 carrier gas comprises of 80 % of the total stream, where the 20 % C_xF_y gases make up the rest, typically with the same composition as for the CF_4 plasma, if the same quenching conditions are applied.

Table 2-3: Typical composition of the product of a N_2 non-transfer-arc plasma (Moore, 1997)

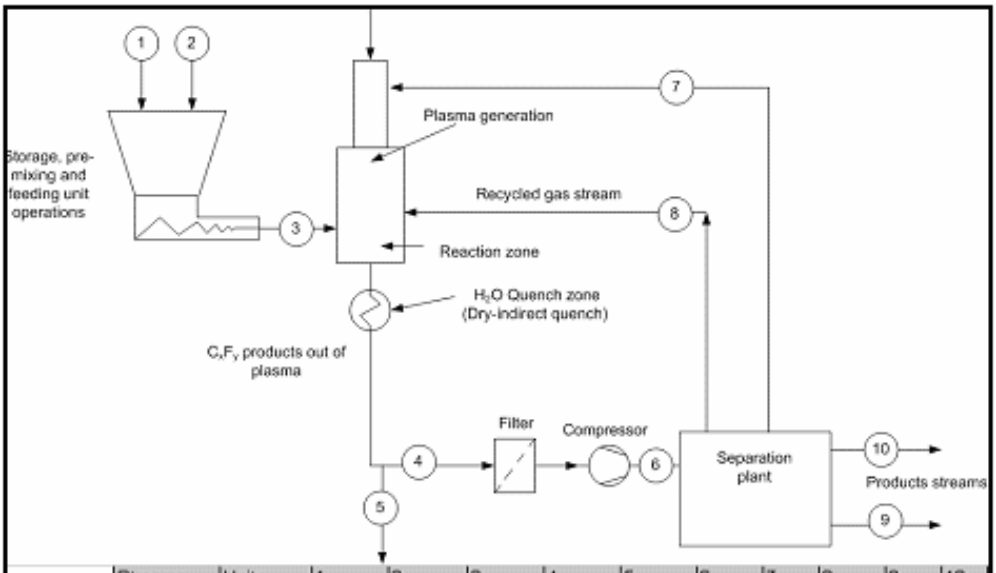
Product	% yield
N_2	80
CF_4	13
C_2F_4	5
C_2F_6	1.4
C_3F_6	0.6

The CF_4 as well as other non-product C_xF_y gases will be recycled into the plasma tail-end area as depicted in Figure 2-3.

Reaction of CaF_2 (s) + C (s) at 4000K to 6000K in a N_2 plasma system:

C (s) + CaF_2 (s) + N_2 (g) = C_xF_y (g) + CaC_2 (s) + N_2 (g).

A typical flow sheet and stream table for the N_2-plasma system is given in Figure 2-5. The mass balance is calculated on the same basis as the CF_4-plasma.



	Streams	Units	1	2	3	4	5	6	7	8	9	10
Mass Flow	Molar mass											
CaF_2 (s)	78.00	kg/h	29885.9		29885.9	29885.9	24905.0					
C (s)	12.00	kg/h		7538.0	7538.0	7538.0	6281.7					
N_2	28.00	kg/h				437.5		437.5	437.5			
C_2F_4	100.00	kg/h				729.2		729.2	14.6	379.2	350.0	
C_2F_6	138.00	kg/h				204.2		204.2	2.0	2.0		
C_3F_6	150.00	kg/h				87.5		87.5	1.8	1.7		85.8
CF_4	88.00	kg/h				1895.8		1895.8	94.8	1711.0		
CaC	52.00					3320.7	3320.7					
Total			29885.9	7538.0	37424.0	44098.8	34507.3	3354.2	550.7	2093.9	350.0	85.8
Streams	Molar mass	Units	1	2	3	4	5	6	7	8	9	10
Mass Flow	kg/kmol											
CaF_2 (s)	78.00	kmol/h	383.15		383.15		319.29					
C (s)	12.00	kmol/h		628.17	628.17		523.47					
N_2	28.00	kmol/h				15.63			15.63			
C_2F_4	100.00	kmol/h				7.29		7.29	0.15	3.79	3.50	
C_2F_6	138.00	kmol/h				1.48		1.48	0.01	0.01		
C_3F_6	150.00	kmol/h				0.58		0.58	0.01	0.01		0.57
CF_4	88.00	kmol/h				21.54		21.54	1.08	19.44		
CaC	52.00	kmol/h				63.86	63.86					
Total		kmol/h	383.15	628.17	1011.32	110.38	906.63	30.90	16.87	23.26	3.50	0.57
Temperature		°C	25	25	25	250	250	25	-75/25	-75/25	<-50	25
Pressure (a)		kPa	87	87	-40	-40	87	1600	1600/1	250/150	<220	150

Figure 2-5: N_2 Plasma system, flow sheet and stream table

As for the CF_4 plasma system, the recycle streams are huge in comparison with the product streams. The same arguments are true as for the CF_4 system, causing this system to be highly energy-intensive.

2.3.4 Transfer-arc plasma

The difference between the transfer-arc plasma and the conventional non-transfer-arc plasma is that the arc is directly attached onto the reactants which act as an anode, as indicated in Figure 2-5.

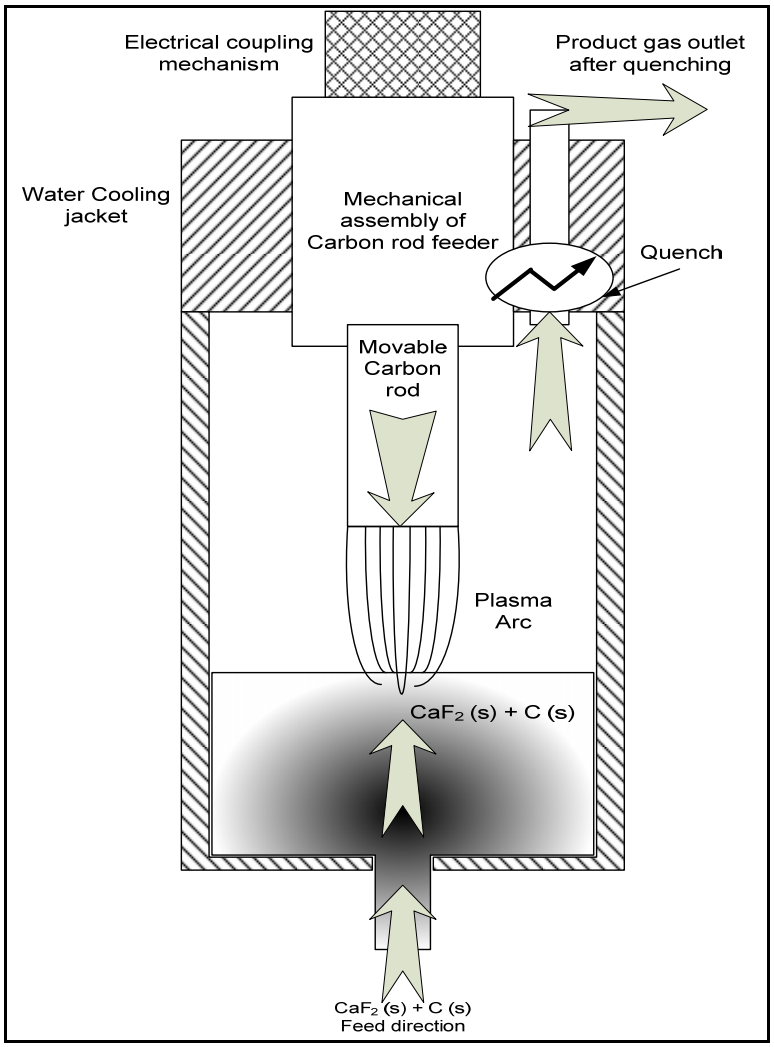


Figure 2-6: The transfer-arc plasma

The premixed CaF_2 (s) and C (s) powder (minimum) will be fed into a chamber that also acts as the cathode or positive electrode. A carbon/graphite rod is the consumable electrode (anode) and is constantly fed into the reaction chamber as it is consumed. An electric arc will be generated between the cathode (reagent containing chamber) and anode (Cotchen, 2000).

Heat will be generated up to 6000K, causing evaporation of the mixture and subsequent dissociation. The gas is then quenched at a rate of approximately 10^6 K/sec to produce various compositions of C_xF_y gases. A transfer-arc plasma system doesn't use a carrier gas to stabilize the plasma arc. It will be safe to assume yields of C_2F_4, and C_3F_6, as indicated in Table 2-4.

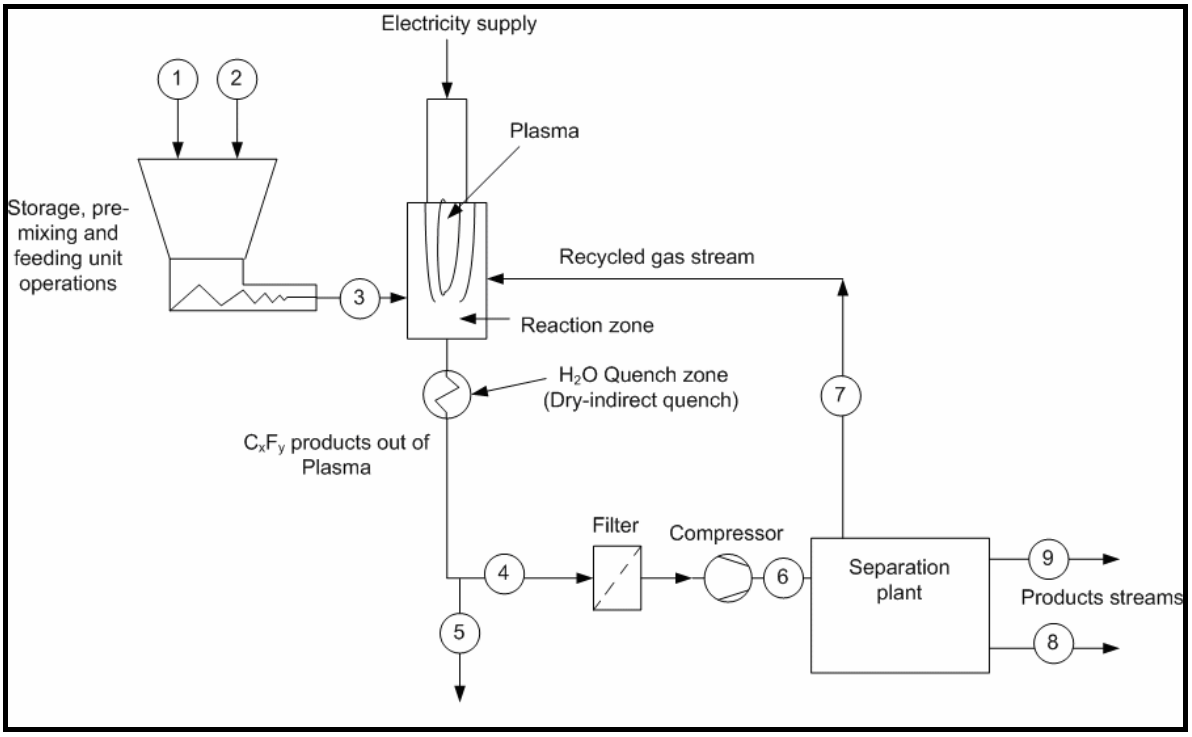
Table 2-4: Estimated transfer-arc plasma mixture composition (Moore, 1997)

Product molecule	% Yield (molar)
CF_4	40
C_2F_4	40
C_2F_6	10
C_3F_6	10

The basic reaction in the transfer-arc plasma and quench probe reaction is:

$$C\ (s) + CaF_2\ (s) = C_xF_y\ (g) + CaC_2\ (s)$$

A typical flow sheet and stream table of the transfer-arc plasma system is given in Figure 2-7. The mass balance is based on the same assumption as for the non-transfer-arc system.



Mass Flow	Molar mass	Streams	1	2	3	4	5	6	7		8	9
	kg/kmol	Units										
CaF_2 (s)	78	kg/h	1474.4		1474.36							
C (s)	12	kg/h		397.4	397.435							
C_2F_4	100	kg/h				355.56		355.6	3.5556	1.056	3.51	347.4
C_2F_6	138	kg/h				88.889		88.89	0.8889	87.12	0.01	0.871
C_3F_6	150	kg/h				88.889		88.89	0.8889	0.264	86.9	0.877
CF_4	88	kg/h				355.56		355.6	355.56			
CaC_2	52	kg/h				982.91	982.9					
C_6H_{14}	86	kg/h							0.043			
Total		kg/h	1474.4	397.4	1871.8	1871.8	894	888.9	360.89	88.44	90.4	349.2
Molar Flow	Molar mass	Streams	1	2	3	4	5	7	8	10	13	12
	kg/kmol	Units										
CaF_2 (s)	78	kmol/h	18.902		18.9021							
C (s)	12	kmol/h		33.12	33.1196							
C_2F_4	100	kmol/h				3.5556		3.556	0.0356	0.011	0.04	3.474
C_2F_6	138	kmol/h				0.6441		0.644	0.0064	0.631	0	0.006
C_3F_6	150	kmol/h				0.5926		0.593	0.0059	0.002	0.58	0.006
CF_4	88	kmol/h				4.0404		4.04	4.0404			
CaC_2	52	kmol/h				18.902	18.9					
C_6H_{14}	86	kmol/h							0.0005			
Total		kmol/h	18.902	33.12	52.0217	27.735	17.19	8.833	4.0883	0.644	0.61	3.487
Process parameters												
Temperature		oC	25	25	25	250	250	25	-75/25	25	25	-50
Pressure (a)		kPa	87	87	-40	-40	87	200	200/150	200	150	200

Figure 2-7: Transfer-arc plasma system, flow sheet and stream table

It clear from Figure 2-7 that this system is simpler and will use less energy than the two systems described above. The separation of these gases produced will be done at low pressures, making this a safe and cost-effective system.

2.4 Separation of fluorocarbon gases

2.4.1 Introduction

Distillation is traditionally used to separate C_xF_y gases and is a well-defined process, even if it is costly and dangerous. Separation of C_xF_y gases can at present only be achieved with distillation. Combining this with new technology such as membrane separation, adsorption and absorption processes is an alternative option. These last-mentioned processes still need to be proven and evaluated by industry to be feasible and safe. Understanding of the fundamentals of fluorocarbon gas/vapor separation processes is an essential part of the conceptual design.

2.4.2 Distillation

If we consider a counter current, binary distillation system as illustrated in Figure 2-8, a column will house an N amount of theoretical stages, a total or partial condenser and a partial re-boiler to vaporise the gas which is condensed from the partial condenser. By establishing multiple counter current contacts through the column and by manipulating the boil-up and reflux rates, high degrees of separation can be achieved.

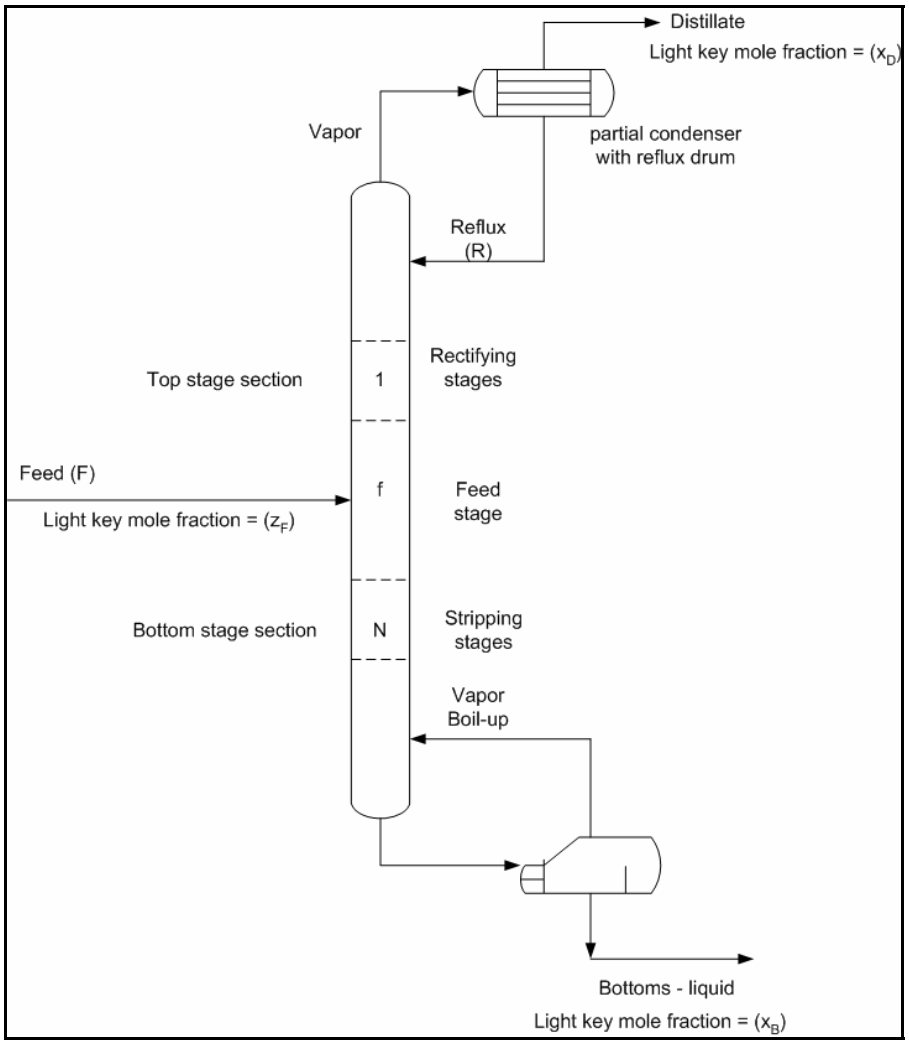


Figure 2-8: Distillation column with a partial condenser

Relative volatility is a way to measure how feasible it is to separate the components of a mixture from each other with distillation. For a binary AB-mixture it is the ratio of the two K-values, $K_i=y_i/x_i$:

$$\alpha_{AB} = \frac{K_A}{K_B} = \frac{y_A / y_B}{x_A / x_B} \qquad \text{Eq. 2-1}$$

As the temperature increases in a distillation column from top to bottom, the K-values also increase, but the relative volatility often remains more or less constant.

Although relative volatility in distillation seems to be the same as membrane selectivity there are two major differences: (i) the relative volatility is a true thermodynamic property, whereas membrane selectivity depends also on the

operating conditions; (ii) as distillation can easily be cascaded in a column, the required value of the relative volatility can be as low as 1.5, where the selectivity will preferably have to be higher than 5.

For a binary mixture equation 2-1 becomes:

$$y_A = \frac{(\alpha_{AB} x_A)}{1 + x_A(\alpha_{AB} - 1)} \qquad \text{Eq. 2-2}$$

Relative volatilities normally decrease when pressure is increased. Interesting to note is that the molar heats of evaporation of most organic chemicals usually differ only slightly, which means if 1 mol of A condenses, the heat released evaporates 1 mol of B. This means that molar flow rates in distillation columns are approximately constant. This is one of the major assumptions in the McCabe-Thiele graphical design method to determine the number of equilibrium stages in a binary distillation column, as will be discussed below.

Number of equilibrium stages

The graphical McCabe-Thiele method uses the xy-diagram to determine the number of equilibrium stages, see Figure 2-8.

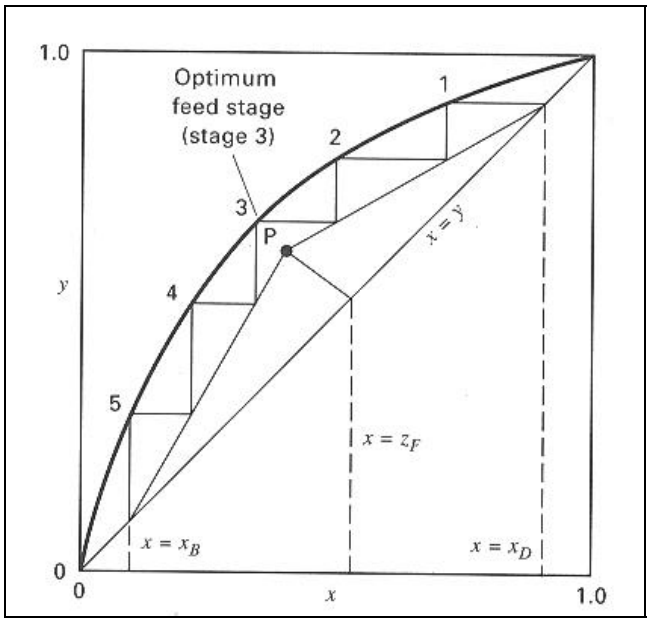


Figure 2-9: McCabe-Thiele xy-diagram (Seader & Henley, 2006)

The 1st step in the design is determination of the operating pressure. For volatile compounds this is selected as high as possible in order to avoid expensive cryogenic temperatures at the condenser. However, because of safety risks, as with C_2F_4, one may have to decide otherwise (see Chapter 5).
The molar balance for the enrichment section (Figure 2-9) gives the 1st operating line:

$$y_{n+1} = \frac{L}{V}x_n + \frac{D}{V}x_D = \frac{R}{R+1}x_n + \frac{1}{R+1}x_D \qquad \text{Eq. 2-3}$$

Where:
L=the liquid flow rate in the enrichment section (kmol/h)
V= the vapour flow rate in the enrichment section (kmol/h)
D=the distillate flow rate (kmol/h)
R=the reflux ratio (-), $\boldsymbol{R \equiv L/D}$

Similarly the molar balance for the stripping section below the feed tray gives the 2nd operating line:

$$y_{n+1} = \frac{V_B}{V_B + 1} x_n - \frac{1}{V_B} x_B \qquad \text{Eq. 2-4}$$

Equation 2-4 provides the equilibrium line.

Where
V_B=the boil up fraction (mole/mole)

The feed or q-line is given by the heat and mass balances over the feed stage:

$$y = \frac{q}{q - 1} x - \frac{z_A}{q - 1} \qquad \text{Eq. 2-5}$$

Where:
z_A=molar fraction of A in the feed (mole/mole)
q=change in relative molar liquid flow rate at the feed stage due to the condition of the feed, obtained through the heat balance over the feed stage; $q = \frac{L_{strip} - L_{enrich}}{F}$. E.g. for a bubble-point liquid feed; q=0.

The minimum reflux ratio, R_{min}, is determined by the slope of the operating line through the intersection of the q-line and the equilibrium curve. This slope is equal to $R_{min}/(R_{min}+1)$.
The real reflux ratio is obtained by minimizing the annualized cost (Peters, 2003). As a rule of thumb the optimum reflux ratio is:

$$R = 1.2 R_{\min} \qquad \text{Eq. 2-6}$$

The feed is entered at that stage, where its composition is closest to the composition of the equilibrium stage

The number of stages is determined graphically as shown in figure 2-6.

The real number of trays required depends on the overall efficiency, E, and the theoretical number of stages, N:

$$N_{real} = \frac{N}{E} \qquad \text{Eq. 2-7}$$

The overall efficiency depends on the liquid viscosity and the relative volatility; empirical relations are available to determine E (Seader & Henley, 2006).

Molar flow rates as well as internal column traffic can be determined by solving the mass and energy balances.

Column height

The height of the column will mainly be determined by the number of plates required, the plate distance and the sump at the bottom. The optimum plate distance is a function of diameter and operating conditions and the type of plates to be used. The smaller the diameter of the column, the shorter the spacing value will be.

For columns of 1 meter and above, a plate distance of 0.3 to 0.6 meter is recommended, where 0.5 meter can be used as a first estimation (Sinnott, 1986).

Condenser and re-boiler duties

In order to calculate the duties of the condenser and the re-boiler it will be assumed that no heat is lost to the surroundings and that the feed is entering as a bubble-point liquid.
The duty for a total condenser is then equal to:

$$Q_C = D(R+1)\Delta H^{vap} \qquad \text{Eq. 2-8}$$

Where:

ΔH^{vap} =the averaged molar heat of evaporation (kJ/kmol)

For a partial condenser this becomes:

$$Q_C = DR\Delta H^{vap} \qquad \text{Eq. 2-9}$$

The duty for a partial re-boiler is:

$$Q_R = BV_B\Delta H^{vap} \qquad \text{Eq. 2-10}$$

Column diameter

Vapor flow rate is one of the main contributors in determining the column diameter. The velocity should be at a value where liquid entrainment or high pressure drop is acceptable. The Souders and Brown equation is a method to estimate the maximum superficial vapour velocity and also the diameter of the column (Sinnott, 1986).

$$u_v = \left(-0.171 l_t^2 + 0.27 l_t - 0.0047\right)\left(\frac{(\rho_L - \rho_v)}{\rho_v}\right)^{0.5} \qquad \text{Eq. 2-11}$$

Where:

u_v = maximum allowable vapour velocity (m/s)

l_t = plate spacing, (m)

Calculation of the column diameter (Dc):

$$Dc = \sqrt{\frac{4V_w}{\pi\rho_v u_v}} \qquad \text{Eq. 2-12}$$

Where:

V_w = vapor mass flow rate (kg/s)

Stage-to-stage calculations

The methods for distillation column design as described above will be used as a starting value for more accurate conceptual design in Chapter 5, based on stage-to-stage calculations using the Aspen 10 simulation package.

2.4.3 Absorption

Introduction

Gas absorption is a unit operation where the gas mixture comes in contact with a liquid (absorbent or solvent) with the purpose to absorb one or more of the gas components into the liquid phase by means of mass-transfer. The gas absorbed in the liquid phase is called the solute or absorbate.

Stripping is the opposite of absorption where a liquid mixture comes in contact with a gas removing one more components from the liquid by means of mass-transfer. Strippers or distillation columns are usually part of absorbers when regeneration of the absorbent is required.

Design procedures and methods are well known and most of the methods are modified to suit the specific industries. For example in the hydrocarbon or fluorocarbon industries certain methods will be used with safety factors which are a function of the experience gained through the years.

Absorption and stripping columns are mainly designed with trays or packing as internals. Different types of internals are available, and are used where experience, practicality (dangerous chemicals) and high efficiencies are needed (Seader & Henley, 2006).

Absorption process can be divided into two categories:

- Purely physical
- With enhanced mass transfer due to chemical reaction

C_2F_6, C_2F_4, C_3F_6, CF_4 using n-hexane as absorbent will be purely physical.

Most concepts and principles of absorption can be derived from distillation. The main difference between absorption and distillation is that in distillation vapor has to be produced in each stage by partial vaporization of the liquid which is at its boiling point, where in absorption the liquid is below the boiling point.

For dilute concentrations of most gases, and over a wide range for some other gases, the equilibrium is given by Henry's Law:

$$x_A = y_A \frac{P}{H_A} \qquad \text{Eq. 2-13}$$

Where:
H_A = Henry's constant of compound A (kPa)
P=operating pressure (kPa)

Number of equilibrium stages

Figure 2-10 is a schematic representation of the equilibrium stages and flows and compositions of an absorber and a stripper.

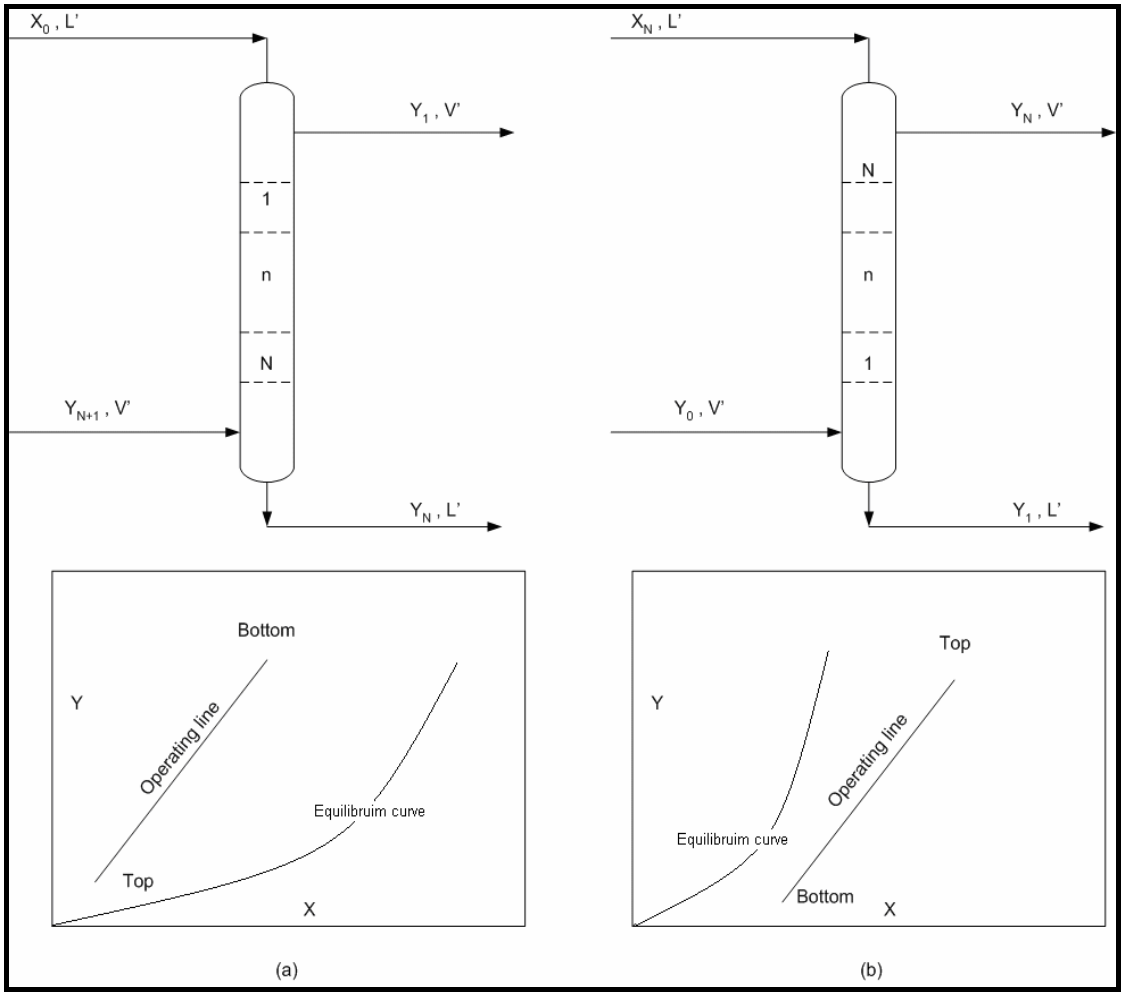


Figure 2-10: Continuous counter-current (a) absorber and (b) stripper

Where:
L' = molar flow rate of solute-free absorbent

V' = molar flow rate of solute-free gas

X = mole ratio of solute-free absorbent in the liquid

Y = mole ratio solute to solute-free gas in the vapor

If we assume that no vaporisation of the absorbent occurs, L' and V' will remain constant though the column. We can define the K-value (K_n) of the solute at any equilibrium stage n in terms of X and Y as:

$$K_n = \frac{y_n}{x_n} = \frac{\dfrac{Y_n}{1+Y_n}}{\dfrac{X_n}{1+X_n}} \qquad \text{Eq 2-14}$$

Where:

$$Y = \frac{y}{1-y} \qquad \text{Eq 2-15}$$

$$X = \frac{x}{1-x} \qquad \text{Eq 2-16}$$

From the above equations an equilibrium curve is calculated and plotted with Y as a function of X, as illustrated in Figure 2-10.
The operating lines are calculated and plotted from the mass balances:

Absorber

$$X_0 L' + Y_{n+1} = X_n L' + Y_1 V' \qquad \text{Eq 2-17}$$

or, solving Y_{n+1}

$$Y_{n+1} = X_n (L'/V') + Y_1 - X_o (L'/V') \qquad \text{Eq 2-18}$$

Stripper

$$X_{n+1} L' + Y_0 V' = X_1 L' + Y_n V' \qquad \text{Eq 2-19}$$

$$Y_n = X_{n+1} (L'/V') + Y_0 - X_1 (L'/V') \qquad \text{Eq 2-20}$$

The operating lines are straight lines in Figure 2-10 with a slope equal to L'/V' Using the graphical method the number of stages can be plotted to determine the amount of theoretical stages. The details to perform this method can be found in chapter 6 of Seader & Henley (2006).

The molar flow rate of absorbent, L', is determined in a way similar to the reflux ration of a distillation column. The minimum flow absorbent flow rate is given by:

$$L'_{min} = V' K_N (1 - \phi_A)$$ Eq 2-21

Where:

K_N=the geometric mean of the K-values over N stages

$(1-\phi_A)$=the fraction in the gas feed that is to be absorbed

The real absorbent flow rate, L', should be larger and is determined by optimizing the economy. The rule of thumb is:

$$L' = 1.2 L'_{min}$$ Eq 2-22

In case the K-value for the solute can be assumed to be more or less constant, the Kremser equation can be used conveniently to determine the number of equilibrium stages, N:

Absorber

$$\phi_A = \frac{A_e - 1}{A_e^{N+1} - 1}$$ Eq 2-23

Where:

$A_e \equiv \frac{L'}{K_N V'}$ =the average effective absorption factor (-) Eq 2-24

Stripper

$$\phi_S = \frac{S_e - 1}{S_e^{N+1} - 1}$$ Eq 2-25

Where:

$S_e \equiv \frac{k_N V'}{L'}$ =the average effective stripping factor (-) Eq 2-26

ϕ_S=the fraction in the liquid feed NOT stripped (-)

Solvent selection

The purpose of an absorption unit is to produce a solution that has sufficiently removed a specific compound out of the gas stream as product or waste. A process to remove low-boiling compounds from a C_2F_4 stream has been patented by Sulzbach & Oberauer (1979), as illustrated in Figure 2-10. This study will be used as basis for a conceptual design for separating CF_4 (the light key) from C_2F_4 (the heavy key) gas by absorption.

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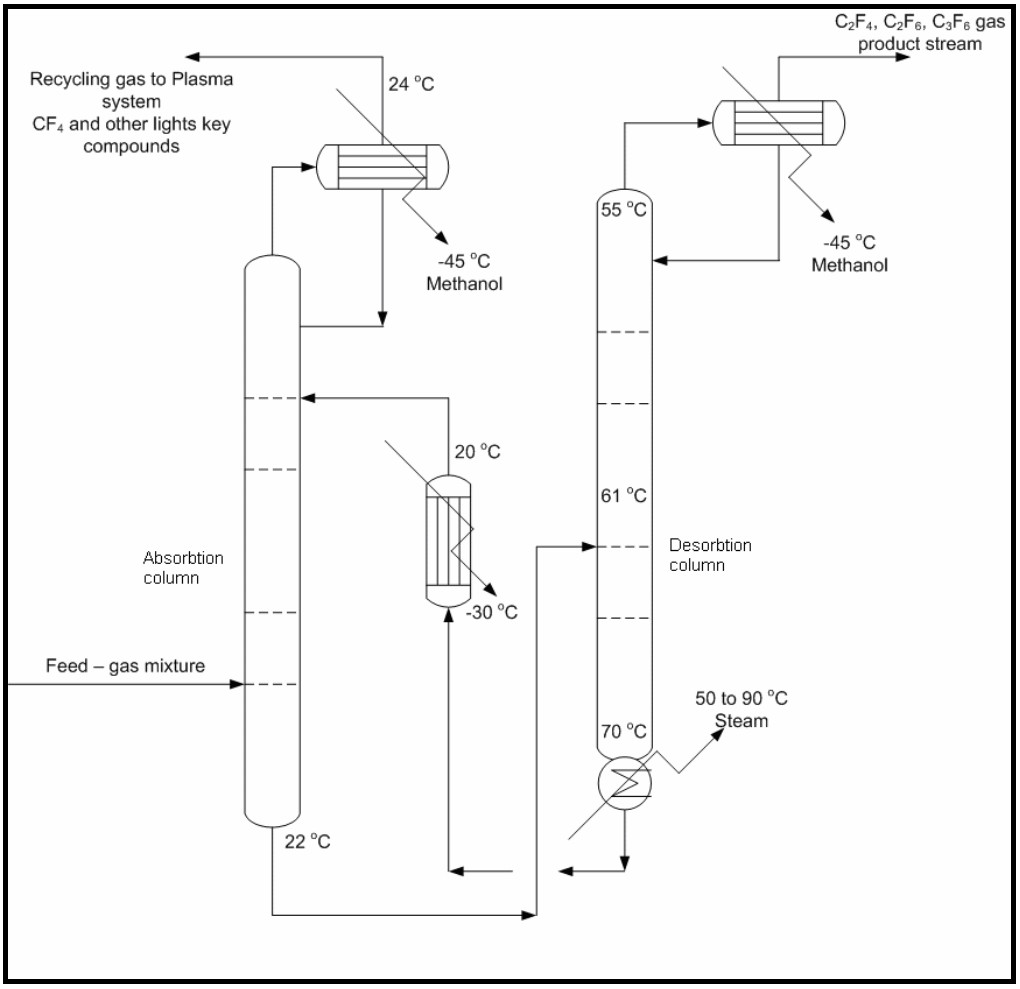


Figure 2-11: Absorption process patented by Sulzbach & Oberauer (1979).

The absorbent is introduced at the top of the column in counter flow with the C_xF_y stream. CF_4 has a low solubility in the absorbent and is withdrawn at the top of the absorber column in the gas phase. The absorbent with the absorbed heavy compounds C_2F_4, C_2F_6 and C_3F_8 is discharged from the bottom as liquid to the second column where the absorbent is recovered by distillation. C_2F_4 is

the light key in the design, whereas the absorbent is the heavy key. The amount of absorbent in the CF_4 stream, which is to be recycled to the plasma reactor, has to be set as low as necessary, in order not to disturb the plasma reactor.

Different absorbents have been investigated, as summarised in Table 2-5, showing that the selectivity of C_2F_4 relative to N_2 is acceptable.

Table 2-5: Absorbents used in C_2F_4 purification (Sulzbach)

Properties of absorbent in the process of absorption [United States Patent: 4137055:Jan. 30, 1997]			
Absorbent	Solubility ratio N_2 : C_2F_4 (20 °C and 98.66 kPa)	Boiling point (Bp) (°C)	Freezing point (°C)
Acetone	1:15.7	56.2	-95
Methylethylketone	1:20.5	79.6	-87
Methylisopropylketone	1:5	95	-92
Diethylketone	1:20.2	102.7	-42
Methylisobutylketone	1:11	116.8	-84
n-Hexane	1:12	68	-95
n-Octane	1:20.5	125	-56.5
Gasoline (Bp = 80 to 100 °C)	1:9.5	80 to 110	-
Iso-octane	1:13	99.2	-107

From the mass balance data in the patent a K-value for C_2F_4 in n-hexane is estimated as: K (C_2F_4, n-hexane) =128 (on mole basis)

In order to calculate the n-hexane fraction in the CF_4 at the top of the column, Antoine's equation is used to calculate the n-hexane partial pressure.

These data will be used in the absorption column design in Chapter 5 (Seader, 2006).

Column diameter and height

The same methodology will be followed as in the distillation section to determine the column diameter and height for cost estimation purposes.

2.4.4 Adsorption

Selective adsorption is a versatile method to separate gases. Ahn et all (2006) measured adsorption isotherms of CF_4 and C_2F_6 on zeolite, silica gel, and activated carbon. As these experiments were rather aimed at removing these two greenhouse gases, they do not provide the right information for the design of a selective adsorption process in order, for instance, to separate CF_4 from the heavier C_2F_4, C_2F_6 and C_3F_6. Bissett et al (2008) showed in a TGA study that a combination of the right temperature and the right zeolite gives promising results to selectively separate CF_4.

Adsorption using zeolites is a viable alternative to membrane separation as a future research technology. At this stage it is premature and seen beyond the scope of this study to consider adsorption as an alternative for absorption.

2.4.5 Membrane separation

Introduction

A short review on membrane principles is discussed in this section and basic concepts in designing membranes for gas separation are explained.

A membrane is a barrier that is semi-permeable and is made of natural or synthetic materials. Separation is achieved by restricting certain components, while allowing the transport of the others through the membrane (Vollbrecht, 1990)

Membranes can be macro-porous, micro-porous or non-porous. The micro-porous and non-porous membranes are permselective (Seader, 2006).

Separation in membranes occurs due to the membrane's ability to transport one of the upstream compounds more readily than the other due to physical and or chemical properties differences between the membrane and permeating components. The performance of a specific membrane is determined by its selectivity and the flux (Mulder, 2003).

Different membrane cascades can be designed in order to meet the separation task, usually defined by production capacity and purity of the products (Baker, 2004)

Different driving forces can be applied in membrane processes, as visualized in figure 2-12:

- Pressure difference (ΔP);
- Concentration difference (ΔC);
- Electrochemical potential difference (ΔE);
- Temperature difference (ΔT).

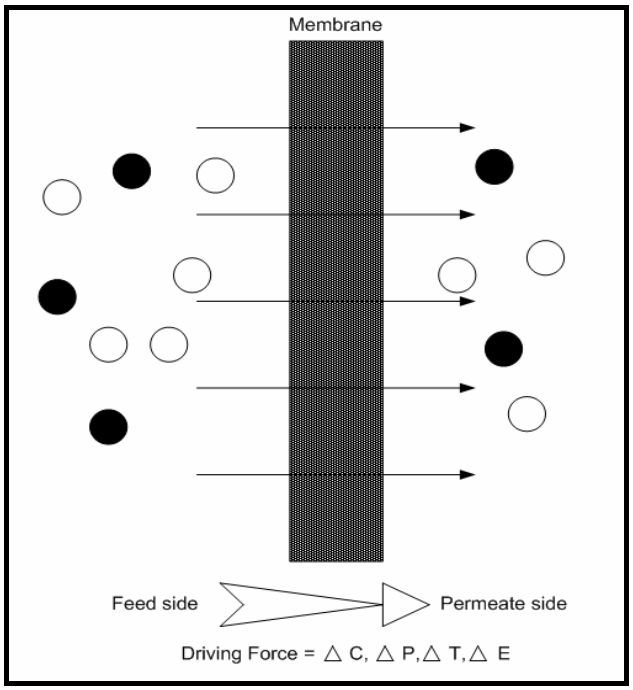


Figure 2-12: Membrane separation (Mulder, 2003)

The solution-diffusion model for dense membranes

Figure 2-13 shows a typical concentration and partial pressure profile of two gases transfusing through a dense membrane. This model includes the effect of the external boundary layers on mass transfer.

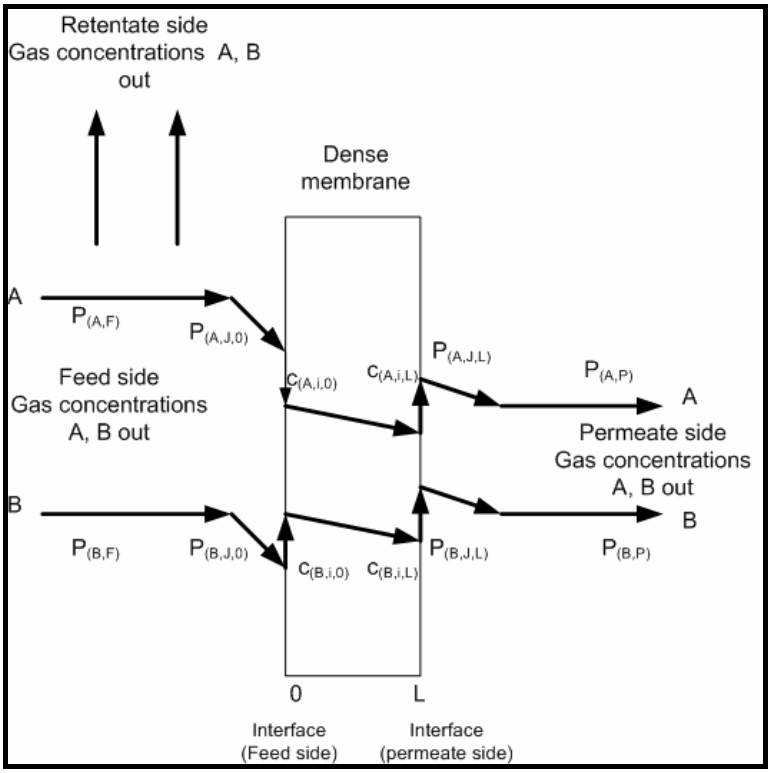


Figure 2-13: Partial pressure and concentration profiles - dense membrane

As seen in Figure 2-13 the diffusion from left to right in a binary mixture A and B can be described as follows:

- compounds A and B experience a drop in partial pressure in the laminar zone at the interface of the feed side of the membrane. If the feed flow rate is increased, the boundary layer thickness and resistance decrease due to increased turbulence;

- compounds A and B are adsorbed or absorbed at the feed interface. If we assume equilibrium conditions exist, Henry's law states that the concentration in the membrane is proportional to the partial pressure in the gas phase:

$$C_{A0} = H_A P_{A0} \qquad \text{Eq. 2-27}$$

$$C_{B0} = H_B P_{B0} \qquad \text{Eq. 2-28}$$

In Figure 2-13 $H_B > H_A$. An increase in concentration of compound B is observed due to absorption into the membrane. The solubilities, measured at different partial pressures, can be used to determine Henry coefficients;

- the concentrations of A and B in the membrane decrease, which is a function of the diffusion rate of each compound and which is often influenced by swelling of the membrane;

- both compounds A and B are desorbed at the permeate side of the membrane and can again be described by Henry's law, It is often assumed that the Henry coefficients at the feed and the permeate side are equal;

- finally, the partial pressures at the permeate side drop in the boundary layer, depending on the turbulence, the same as at the feed side.

As explained above, compound B is enriched at the permeate side if compared to the feed side.

Concentration gradients of both compounds are the driving force of diffusion through the dense membrane which is defined as the **flux**, which is:

$$N_A = \frac{D_A}{\lambda_M}\left(c_{A0} - c_{A\lambda}\right) \qquad \text{Eq. 2-29}$$

$$N_B = \frac{D_B}{\lambda_M}\left(c_{B0} - c_{B\lambda}\right) \qquad \text{Eq. 2-30}$$

Where:

N = molar flux (mol/m^2.s)

D = diffusion coefficient in the membrane (m^2/s)

ℓ_M = thickness of the membrane (m)

c = concentration at different interfaces (mol/m^3).

Ignoring boundary layer mass transfer resistance and using Henry's law and Dalton's law, this reduces to:

$$N_A = \frac{H_A D_A}{\lambda_M}\left(P_{AF} - P_{AP}\right) = \frac{H_A D_A}{\lambda_M}\left(x_A P_F - y_A P_P\right) \qquad \text{Eq. 2-31}$$

$$N_B = \frac{H_B D_B}{\lambda_M}\left(P_{BF} - P_{BP}\right) = \frac{H_B D_B}{\lambda_M}\left(x_B P_F - y_B P_P\right) \qquad \text{Eq. 2-32}$$

Where the subscript denotes:

P= permeate side

F = feed side

For a binary mixture the membrane performance is obtained by the ratio of both fluxes:

$$\frac{N_A}{N_B} = \frac{y_A}{y_B} = \frac{H_A D_A}{H_B D_B}\frac{x_A P_F - y_A P_P}{x_B P_F - y_B P_P} \qquad \text{Eq. 2-33}$$

The **selectivity** for a binary gas mixture A and B is defined as:

$$\alpha_{AB} = \frac{y_A / y_B}{x_A / x_B} \qquad \text{Eq. 2-34}$$

Where:

y = mole fraction at the permeate side

x = mole fraction at the feed side

When the permeate pressure is much lower than the feed pressure, equations 2-33 and 2-34 can be combined to give the ideal selectivity:

$$\alpha^{*}_{AB} = \frac{H_A D_A}{H_B D_B} = \frac{P_{M_A}}{P_{M_B}} \qquad \text{Eq. 2-35}$$

Where the permeability $\mathbf{P_{M_A}}$ is defined as the product of the Henry coefficient and the diffusion coefficient of A in the membrane.

In case the permeate pressure cannot be ignored the real selectivity for a binary system is given by:

$$\alpha_{AB} = \alpha^{*}_{AB}\left[\frac{x_A(\alpha_{AB}-1)+1-r\alpha_{AB}}{x_A(\alpha_{AB}-1)+1-r}\right] \qquad \text{Eq. 2-36}$$

Where r is the pressure ratio: $r = P_F / P_R$. Usually the ideal selectivity is reported in literature.

To achieve good separation, the solubility and diffusivity ratios should be high, even better if both are high. Real separation is different from the ideal separation values due to the fact that components, solubility and diffusivity interact with each other and cause swelling of the membrane.

The **percentage cut** or split factor is defined as the molar flow of the permeate stream divided by the molar flow of the feed stream:

$$\theta = \frac{n_p}{n_F} \qquad \text{Eq. 2-37}$$

The cut can vary between 0 and 1. Thus for a cut of 1 all the feed is permeated and no separation occurs.

Module flow patterns

Flow patterns in the membrane module can play a significant role in membrane separation. Three common flow patterns are shown in Figure 2-14:

- Co-current flow;
- Counter current flow;
- Cross-flow.

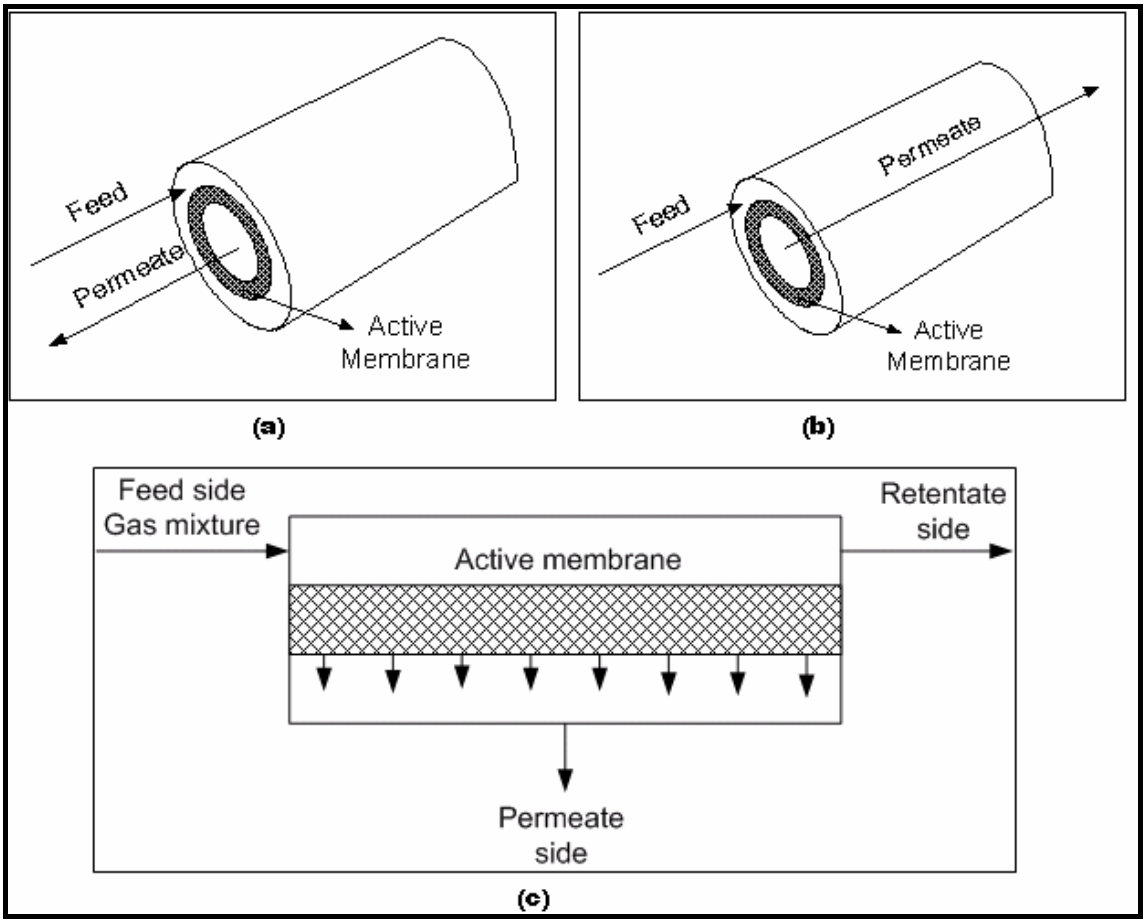


Figure 2-14: Flow patterns in the membrane module
(a) Co-current, (b) Counter current, (c) Cross-flow

It is not always clear which flow pattern is the best to assume in the calculation stage of design. As technology develops flow patterns become more complex and difficult to estimate without the supplier's input**.**

In order to improve performance, membrane cascades can be used. Various multistage membrane options have been considered, but only one will be

discussed here: the ideal recycle cascade. For other options, see Seader & Henley (2006), Baker (2004) and Benedict et al (1981).

The ideal recycle membrane cascade

In order to obtain higher separation yields as in single-stage units, counter-current cascade unit operations should be employed, similar to those of distillation, absorption, liquid-liquid extraction or hybrid process operations.

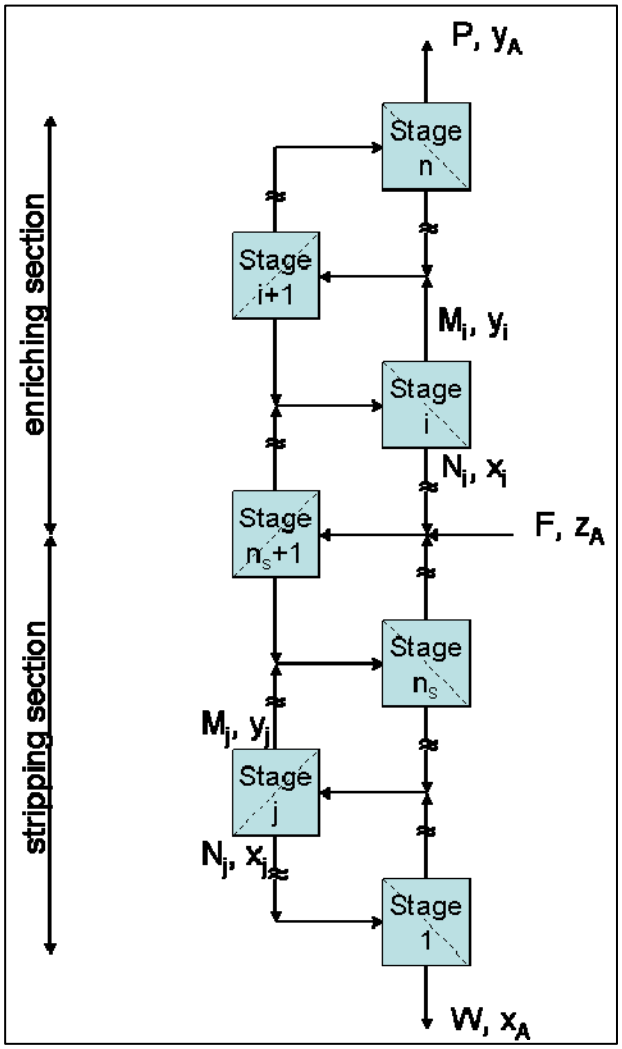


Figure 2-15: The ideal recycle membrane cascade

The cascade exists of an enriching and a stripping section. The feed F, with composition z_A, enters at stage n_{s+1} as illustrated in Figure 2-15, like in distillation, at the stage with the same composition. The permeate concentration is enriched with compounds of high permeability in the enrichment section, while on the other

hand the stripping section gets enriched with compounds of low permeability. The final permeate P is drawn off from stage n and the final retentate R from stage 1. The number of stages and recycle rate, like in distillation will affect the degree of separation. The recycle ratio is defined as the permeate recycle rate divided by the permeate rate. Hwang and Kammermeyer (Hwang, 1975), suggest in order to get the best results the cut and reflux to each stage should be manipulated separately to force the compositions of the streams entering the individual membrane stages to be equal; this is the **ideal** recycle membrane.

The composition of the retentate stream from stage 1 entering stage i+1 should be equal to the composition of permeate from stage i-1, both entering i. In order to design an ideal recycle cascade algebraic equations can be used, which were developed for nuclear enrichment processes, as will be discussed below. Binary systems can be calculated using the McCabe-Thiele diagrams to determine the mole fraction in the permeate (y_i) and retentate (x_i) sides of each stage. The equilibrium curve becomes the selectivity curve and is defined in terms of the separation factor for each stage.

The minimum number of stages is obtained using the Fenske equation and for the ideal recycle cascade it can be shown (Benedict et al, 1981), that the required number of stages is equal to two times the minimum number minus 1:

$$N = 2N_{min} - 1 = 2\left(\frac{\ln \frac{(1-x_A)y_A}{(1-y_A)x_A}}{\ln\alpha} \right) - 1 \qquad \text{Eq. 2-38}$$

The number of stripping stages is subsequently calculated as:

$$N_s = 2\left(\frac{\ln \frac{(1-x_A)z_A}{(1-z_A)x_A}}{\ln\alpha} \right) - 1 \qquad \text{Eq. 2-39}$$

Where:

α = Separation factor

z_A = concentration of A in the feed

The number of stages in the enriching section is then calculated:

$$\boldsymbol{N_e = N - N_s} \qquad \text{Eq. 2-40}$$

The composition of the permeate stage i in the enrichment section is then calculated as:

$$y_i = z_{i+1} = x_{i+2} = \frac{\beta^i y_a}{\beta^i y_A + \beta^n (1 - y_A)} \qquad \text{Eq. 2-41}$$

And in the stripping section:

$$x_j = z_{j-1} = y_{i-2} = \frac{\beta^{j-1} x_A}{\beta^{j-1} x_A + \beta^n (1 - x_A)} \qquad \text{Eq. 2-42}$$

Where:

x_A= the mole fraction of the key compound in the retentate

i=index for the enrichment section

j= index for the stripping section

n=total number of stages

y_P=the mole fraction of the key compound in the product

$$\beta = \sqrt{\alpha} \qquad \text{Eq. 2-43}$$

The molar flow rates of the permeate stage i, M_i, and the retentate stage i+1, N_{i+1}, in the enrichment section are given by:

$$\frac{M_i}{P} = \frac{N_{i+1}}{P} + 1 = 1 + \frac{1}{\beta - 1}\left[y_A\left(1 - \beta^{i-n}\right) + (1 - y_A)\beta\left(\beta^{n-i} - 1\right)\right] \qquad \text{Eq. 2-44}$$

For the stripping section, using index j, the molar flow rates are:

$$\frac{Mj}{R} = \frac{1}{\beta - 1}\left[x_R \beta\left(\beta^{j} - 1\right) + \left(1 - x_R\right)\beta\left(1 - \beta^{-j}\right)\right] \qquad \text{Eq. 2-45}$$

Where:

R = retentate molar flow rate from stage 1 (kmol/h)

The flow rates immediately provide the cut for stages i or j as:

$$\boldsymbol{cut}_{i,j} = \frac{\boldsymbol{M}_{i,j}}{\boldsymbol{M}_{i,j} + \boldsymbol{N}_{i,j}} \qquad \text{Eq. 2-46}$$

Finally these flow rates can be combined with the measured permeability to obtain the required membrane surface area per stage, which has a maximum at the feed stage and tapers off to the product and waste side (Benedict et al, 1981).

This procedure will be used for the conceptual design of the membrane cascade in Chapter 5, using experimental data regarding flux en selectivity described in Chapter 3 and the definition of the separation task (capacity, z_A, y_A and x_A) in Chapter 4.

2.5 Thermodynamic properties of fluorocarbon gases

2.5.1 Introduction

Physical Property Models for compounds as illustrated in Figure 2-16 can be used to model VLE data.

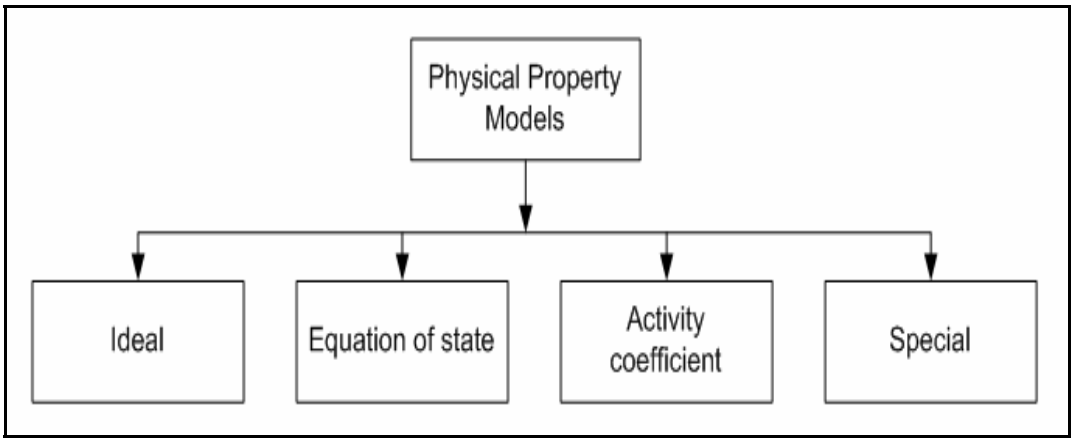


Figure 2-16: Physical Property Models (Aspen, 2004)

The choice of the model depends on the degree of non-ideal behaviour and the operating conditions.

Ideal behaviour is when non-polar compounds of similar size and shape follow ideal gas and Raoult's laws, as illustrated in Figure 2-17.

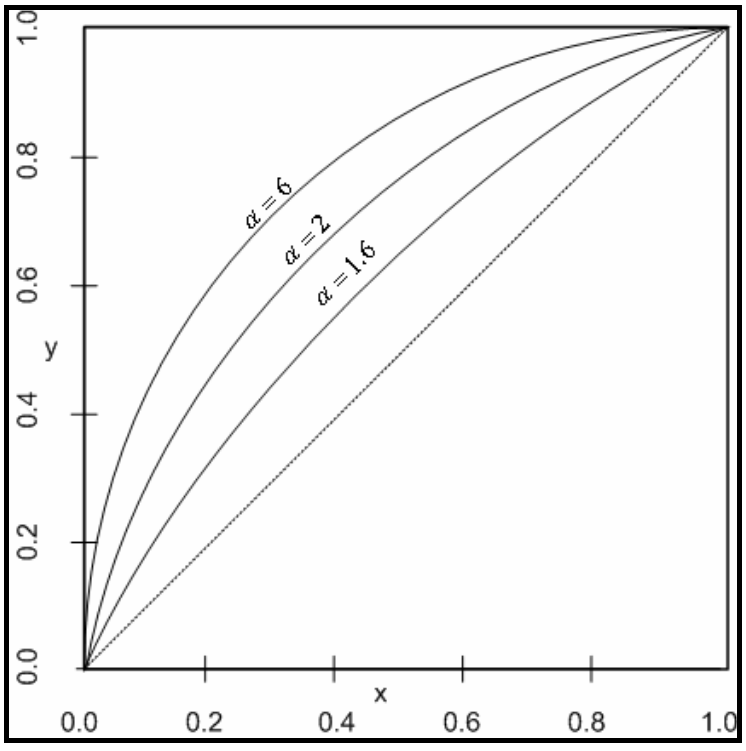


Figure 2-17: Ideal xy-diagrams for different α's

Non-ideal behaviour is controlled by molecule interactions e.g. polarity, size and shape of the molecules, resulting in xy-diagrams which are not symmetrical.

Common property methods used are:

- Equation of state property method (EOS):
    - PENG-ROB (non-polar);
    - RK-SOAVE (non-polar).

- Activity coefficient property methods:
    - NRTL (polar);
    - UNIFAC;
    - UNIQUAC;
    - WILSON (polar).

The procedure of selecting a property method is given in Figure 2-18:

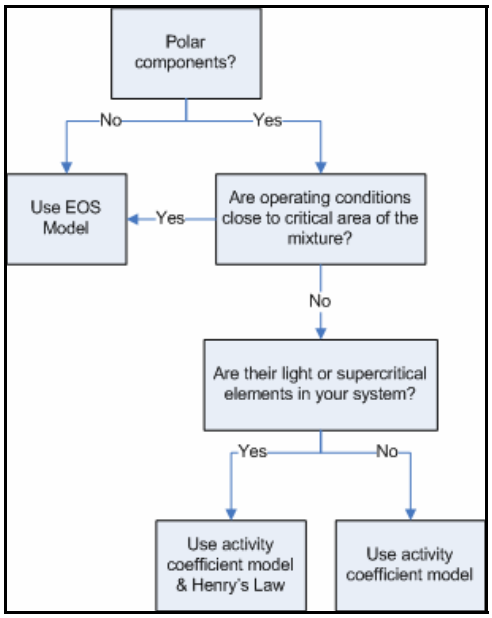


Figure 2-18: Property method selection (Aspen, 2004)

Due to the fact that most fluorocarbon compounds are non-polar or very little polar, the PENG-ROB EOS model (liquid/vapour phase) is the preferable option and was suggested through Aspen specialist and distillation design company Chemdes South Africa (A. Nell, 1999).

2.5.2 Binary VLE's

Because of the high purity and safety demand of the C_xF_y gases it is necessary to obtain binary data to fine-tune and to optimize the multi-component separation systems.

CF_4/C_2F_4

The T-xy data were calculated with Aspen, 2004 and are presented in Figure 2-19 at a pressure of 200 kPa, which is considered the safe operating pressure. It is observed that distillation can be done, but only at very low cryogenic temperatures.

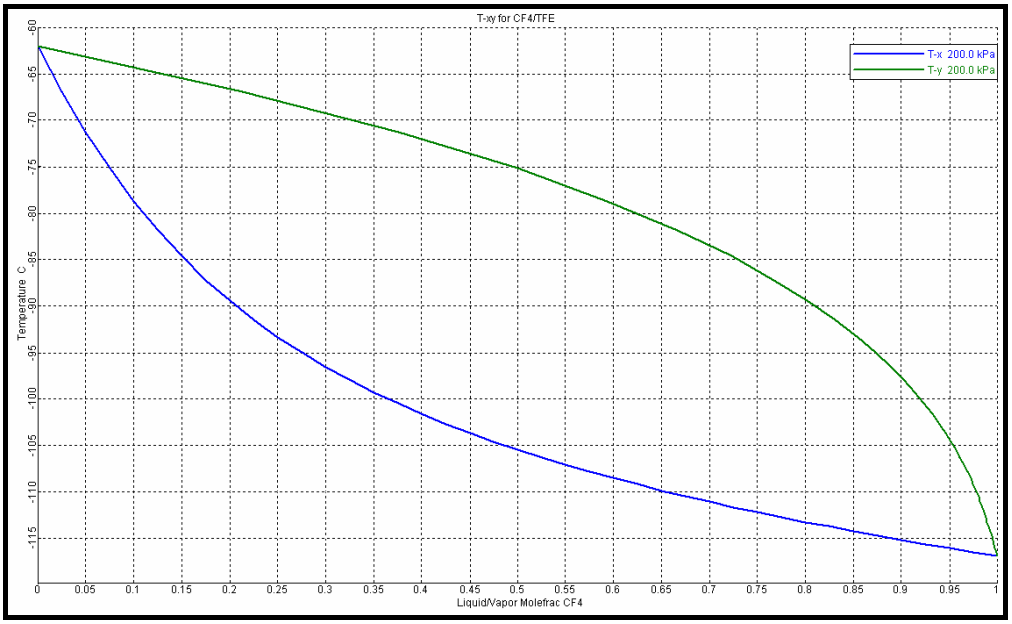


Figure 2-19: T-xy diagram CF_4/C_2F_4 (Aspen, 2004)

In view of the very low temperature, even at 200 kPa the removal of CF_4 gas from the other CF-compounds should rather NOT be done by distillation. Absorption and adsorption seems better choices.

C_2F_6/ C_2F_4

The T-xy diagram of C_2F_6/ C_2F_4 at 150 kPa shows that this is a difficult separation with relative volatilities below 1.1 for x>0.5 and a boiling point difference of only 2.3 ^oC, as illustrated in Figure 2-20 and 2-21. Pressures below 200 kPa are considered safe.

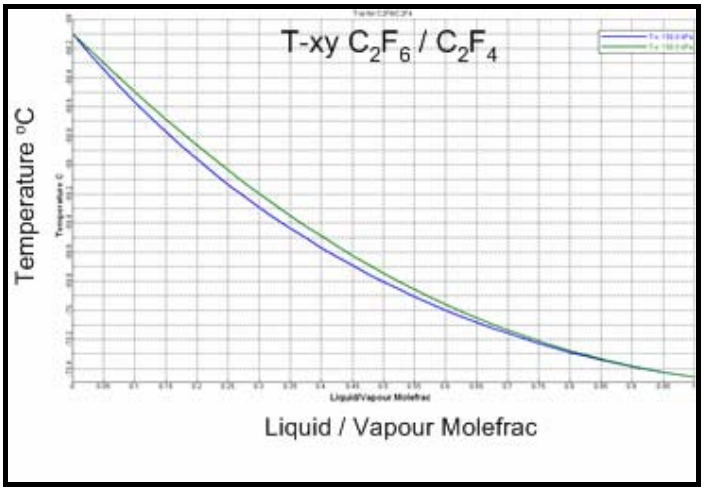


Figure 2-20: T-xy diagram C_2F_6/C_2F_4 (Aspen, 2004)

The low boiling point of this mixture and low pressure in the column makes it difficult to pump this mixture, especially if a split column is used. In this case membrane separation can be an option and will be investigated experimentally.

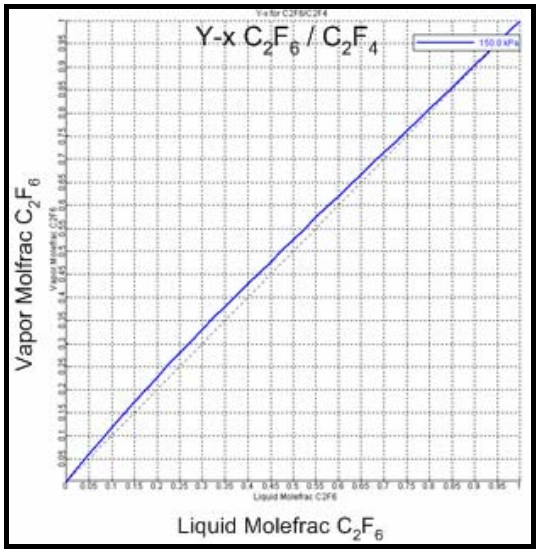


Figure 2-21: xy diagram for C_2F_6/C_2F_4 (Aspen, 2004)

The VLE data for C_2F_6/C_2F_4 are given in Figures 2-20 and 2-21.

C_2F_4/ C_3F_6

The T-xy data are given in Figures 2-22 and 2-23 with a pressure of 150 kPa, which is chosen for safety reasons. C_2F_4 is highly explosive even at very low energy inputs e.g. (self- polymerisation). Explosions can occur equal to 50% of TNT force. Due to this fact it was advised to keep liquid C_2F_4 below -50^oC and 220 kPa (a) (Du Pont, 1998).

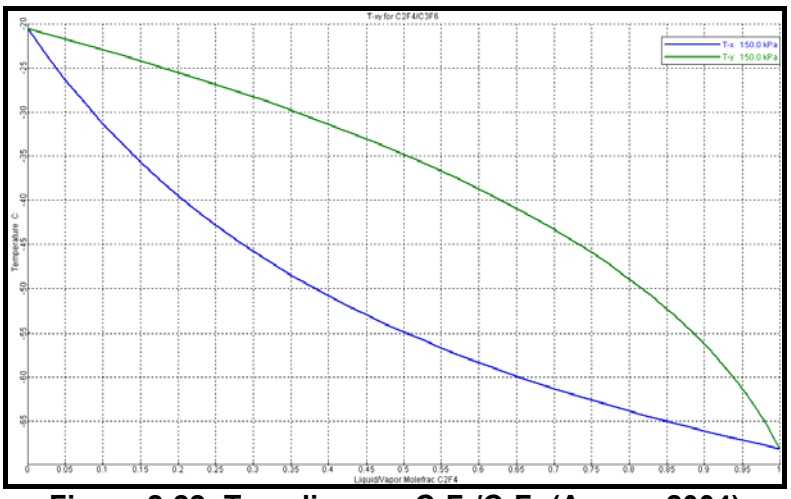


Figure 2-22: T-xy diagram C_2F_4/C_3F_6 (Aspen, 2004)

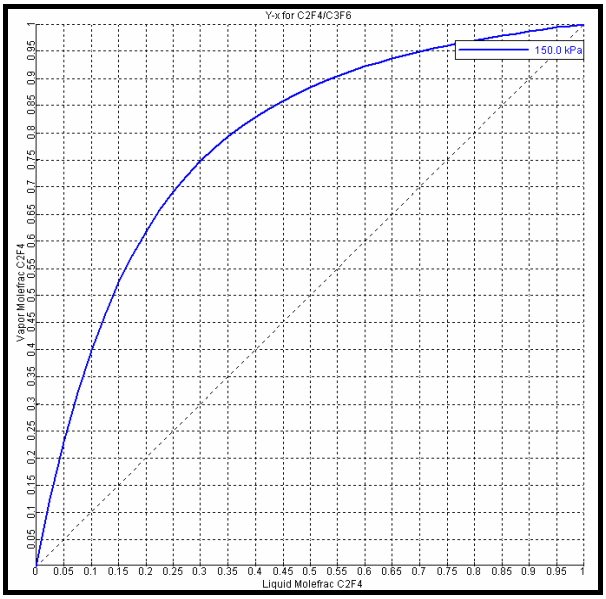


Figure 2-23: xy diagram C_2F_4/C_3F_6 (Aspen, 2004)

Although the relative volatility of the C_2F_4/C_3F_6 system facilitates cryogenic distillation, the low cryogenic temperature of -67^oC makes this an expensive although safe method of separation.

n-Hexane

n-Hexane is used at 25^oC at a ratio of 1 kg C_xF_y to 10kg n-hexane. A K-value of 128 is calculated from the Sulzbach & Oberauer (1979), patent.
Aspen 2004 Peng Robinson is used to calculate fractions of n-hexane which is 0.1% that will be present in the CF_4 stream recycled back to the plasma system.
The following assumption is made:

- No CF_4 is absorbed;
- Absorption takes place at 25 ^oC, 160 kPa;
- A ratio of 1:10 is used to calculate the amount of absorbent, n-hexane.

Physical data

All physical data are retrieved from Aspen 2001, which used the well-known dipper international data base (Aspen, 2001).
Other data of the gases are also retrieved from the Matheson unabridged gas data book (Matheson, 1980).

Summary of the separation challenge

- Clearly there are reasons for deviating from the traditional cryogenic distillation, in particular:

Separate CF_4 from the heavier CF-compounds by absorption, using the data in the Sulzbach & Oberauer (1979) patent and n-hexane as absorbent. C_2F_4 and n-hexane are the key compounds. The absorbent n-hexane will then be recovered by distillation;

- Develop a membrane process for the most difficult separation: C_2F_4/C_2F_6. This requires an experimental study to identify a good

membrane and to optimize operating conditions with respect to selectivity and flux. This is the subject of Chapter 3;

- The C_2F_6 influence in the C_2F_4 stream to the PTFE plant is relatively low, as C_2F_6 does not participate in the polymerization process, and can easily be recycled using the PTE plant as a reactive separation stage;
- Separate C_2F_4 and C_3F_6 in a conventional cryogenic distillation process.
- Recycle the waste products, the CF_4 and C_2F_6, to the plasma reactor in order to avoid loss of "F-values".

2.6 Costing method

Cost estimation will be done using a proven and suggested method used by Necsa management to calculate the IRR, NPV and payback times of C_xF_y gas manufacturing plants (WESTON, 1982). The basis of this method is to estimate capital equipment cost by using cost examples (Previous or similar plants built), multiplying them with cost indexes which are available in engineering magazines using 2008 costs prices (CHE, 2008).

$$\text{Present cost} = \text{original cost}\left(\frac{\text{Present time index value}}{\text{original cost obtained index value}}\right) \qquad \text{Eq. 2-48}$$

$$\text{Cost equip.a} = \text{cost equip.b}\left(\frac{\text{capacity equip.a}}{\text{capacity equip.b}}\right)^{n} \qquad \text{Eq. 2-49}$$

Where:

n = exponential cost factor (Peters, 2003).

b= historical cost as indicated in appendix D

2.7 Chapter summary

The market analysis provides the production capacity and the product specifications: 2500 t/a C_2F_4 and 625 t/a C_3F_6, both at 96% purity. Mass and energy balances will provide the key to selecting the best plasma reactor option.

The transfer-arc plasma is preferred to the N_2/CF_4 non-transfer-arc plasma system due to the fact that the technology of the transfer-arc plasma at high energies is proven up to 40MW (Bateman,2008) whereas the non-transfer-arc plasma is only proven up to 0.45 MW, which is a pilot PTFE pilot facility at Necsa. Furthermore, the heat losses in the non-transfer-arc plasma are high due to the necessity to recycle unreacted CaF_2 and C, 4 to 5 times through the plasma. The use of recycled CF_4 and N_2 gas as carrier gas will use a lot of energy due to the fact that must be separated from the other C_xF_y gases with cryogenic distillation methods, which consumes a lot of energy.

Aspen simulations together with McCabe-Thiele methods will be used to conceptually design the distillation unit.

Absorption data from the Sulzbach patent will be used to conceptually design a n-hexane absorption unit and a C_2F_4, C_3F_6 / n-hexane distillation column.

Membrane units will be designed in conjunction with experimental data (chapter 3) and with calculation methods developed by Benedict et al and others.

Finally, the cost index calculations will be based on the Marshall and Swift Index method in combination with scale-up procedures.

3. The separation of C_xF_y gases with polymer membranes

*The separation of a C_2F_4 -C_2F_6 -C_3F_6 mixture was investigated using a number of polymer membranes at 25^oC and trans-membrane pressures of 60 to 260 kPa. The AF 2400 Teflon-coated membrane was the only one successful one with an optimized selectivity of 2.5 and a flux of 0.002 mole/m^2.s at 160 kPa. The unsaturated CF gases, C_2F_4-C_3F_6, permeated, whereas the C_2F_6 remained in the retentate. The selectivity of C_2F_4/C_2F_6 is close to one. This presents an excellent opportunity to remove the impurity C_2F_6 from the valuable products C_2F_4 and C_3F_6, which can easily be separated from each other by means of cryogenic distillation. Increasing the transmembrane pressure leads to an increase in the permeance at 160 kPa from 25*10^{-6} to 100*10^{-6} mol/m^2.s.kPa.*

3.1 Introduction

The plasma essentially produces a mixture of CF_4, C_2F_6, C_2F_4 and C_3F_6. After absorption the last three still have to be separated, where C_2F_6 is difficult to separate from C_2F_4 as explained in chapter 2. Membrane separation of the waste C_2F_6 from the products C_2F_4 and C_3F_6 is the ultimate goal.
Traditionally, cryogenic distillation separation of C_xF_y composition streams is difficult, costly and unsafe due to the fact that columns are high and pumping of cryogenic liquids, especially liquid C_2F_4, is a engineering nightmare on its own.

The aim will be to test various proposed membranes and use pre-mixed C_xF_y gases that will represent a real plasma process stream to be separated.

The membranes tested were selected initially as CF-polymer: AF2400 Teflon, and Nafion.

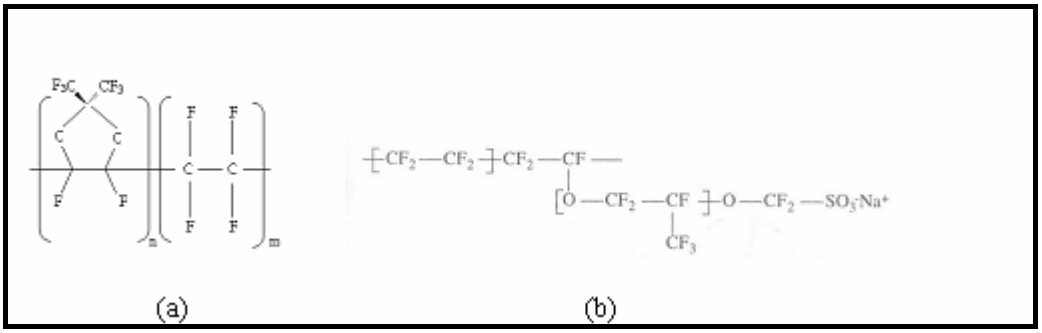


Figure 3-1: Molecular structures of (a) AF2400 Teflon and (b) Nafion

Furthermore, one other commercial polymer membrane was included; POMS (polyoctylmethylsiloxane, a silicon rubber which has been applied successfully for the separation of aromatic compounds (Sampranpiboon, 2000)).

The objectives of this experimental study are:

- To select a number of commercial membranes in order to identify one or more candidates for the separation of C_2F_6 from C_2F_4, and C_3F_6;
- To optimize the operating conditions;
- To quantify selectivity and flux at optimum conditions.

3.2 Experimental

3.2.1 The experimental system

The experimental system is shown in Figure 3-2. Due to the explosive and poisonous nature of C_2F_4 and of some of the compounds produced by the plasma process, the total pressure of the mixtures was kept below 400 kPa (a) and at a temperature of 25 ±1 ^{o}C. The permeate pressure was kept constant at 87 kPa while the feed pressure was varied with a fixed flow rate of approximately 140 ml/min from 87 kPa to 300 kPa. Pre-testing and calibrations were done to ensure that accurate readings were obtained. Prepressure testing of the membrane was done with SF_6 gas with each new membrane to ensure membrane integrity and system leak-tightness.

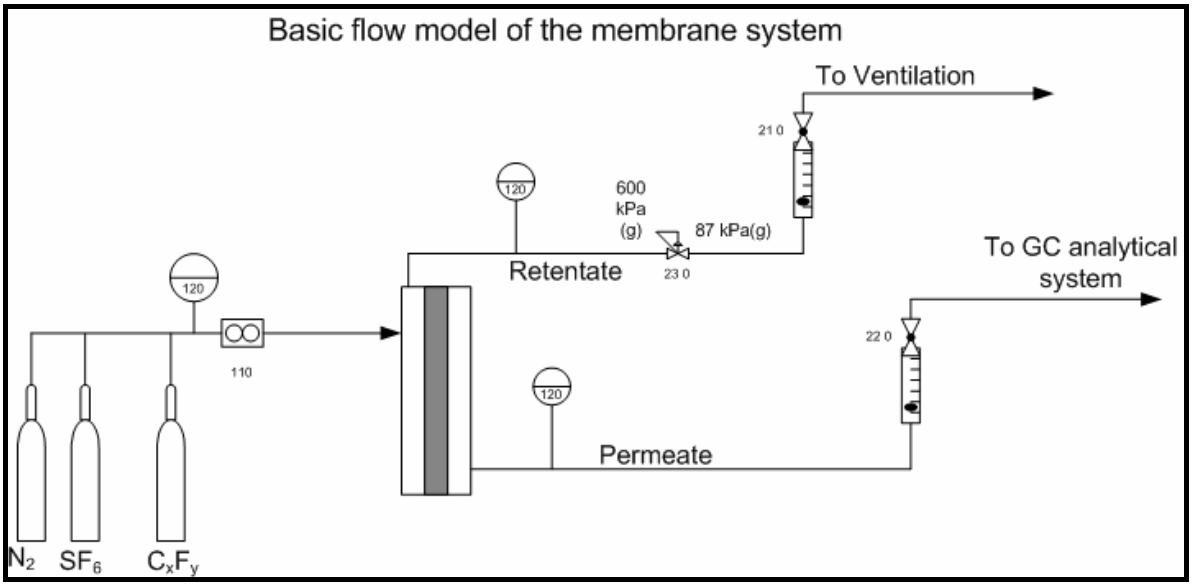


Figure 3-2: Experimental system

A detail process and instrumentation sheet is available in Appendix A.

Gas supply and feed

10L and 200L C_xF_y purpose-built gas cylinders were used except for the N_2 purge which is supplied through the main supply ring at 400 kPa.

Table 3-1: C_xF_y Cylinder mass concentration ranges

Compound	Mass %
C_2F_4	50 to 60
C_2F_6	8 to 12
C_3F_6	20 to 40

The cylinders as illustrated in Figure 3-3 were coupled with high-density PVA piping with high-integrity “Swagelok” fittings to the membrane system. Illustrated in Figure 3-2, the total system was encased in a polycarbonate enclosure which was ventilated (10 to 15 air changes per hour) and at a controlled temperature of 300K.

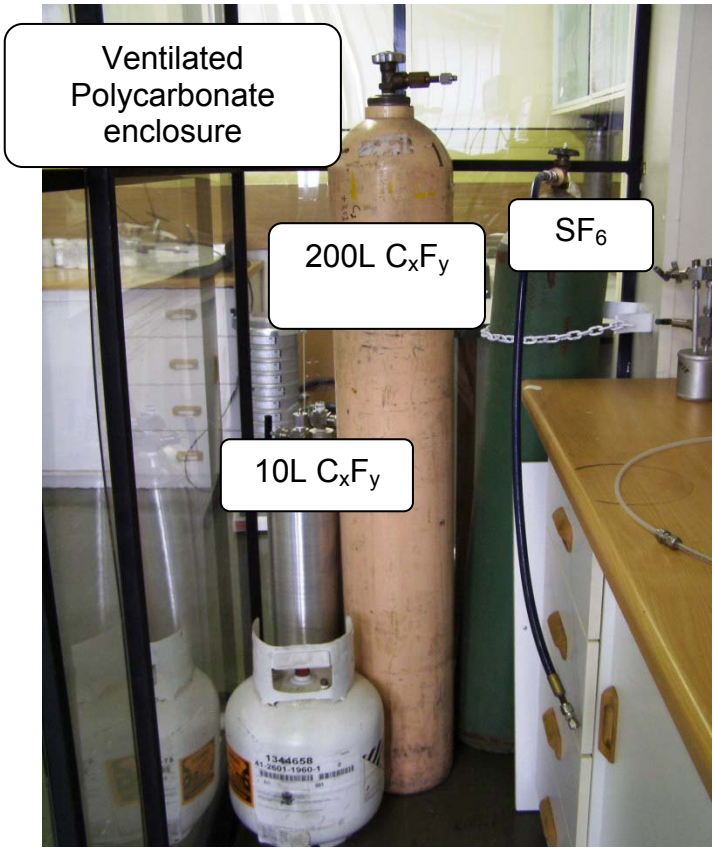


Figure 3-3: Gas supply

The gas mixtures (as indicated in Table 3-1) were produced in a lab scale PTFE depolymerisation reactor (Van der Walt, 2007). The gases were compressed into cylinders to 400 kPa.

Membranes

Membrane sheets, 95mm in diameter, as shown in Figure 3-4, were fitted into a membrane cell as shown in Figure 3-5 which shows a typical experimental membrane system, and is tabled in Figure 3-5.

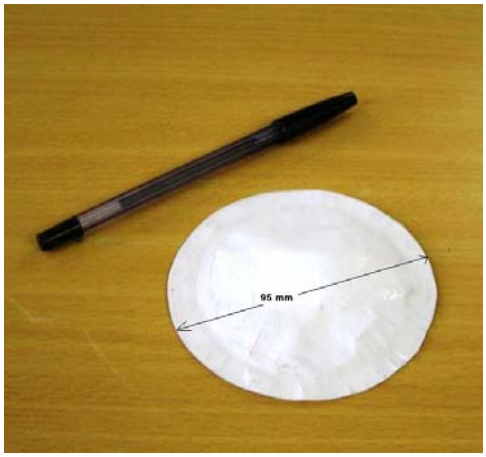


Figure 3-4: Photo of membrane taken from the top

The cylinders were coupled to feed pressure regulators which are indicated in Figure 3-5, number 1. N_2 is supplied from a main ring supply at 600 kPa pressure and was coupled downstream of regulator 1 to be used for purging and leak testing. The gas passed the mass flow controller 2 through to the membrane unit as feed gas and was split in the retentate, which flowed through rotameter 7, and the permeate through rotameter 8 to manifold 6. The manifold consisted of outlets to a grab sample holder, a vacuum pump, ventilation to off-gas and to a gas-chromatograph (GC).

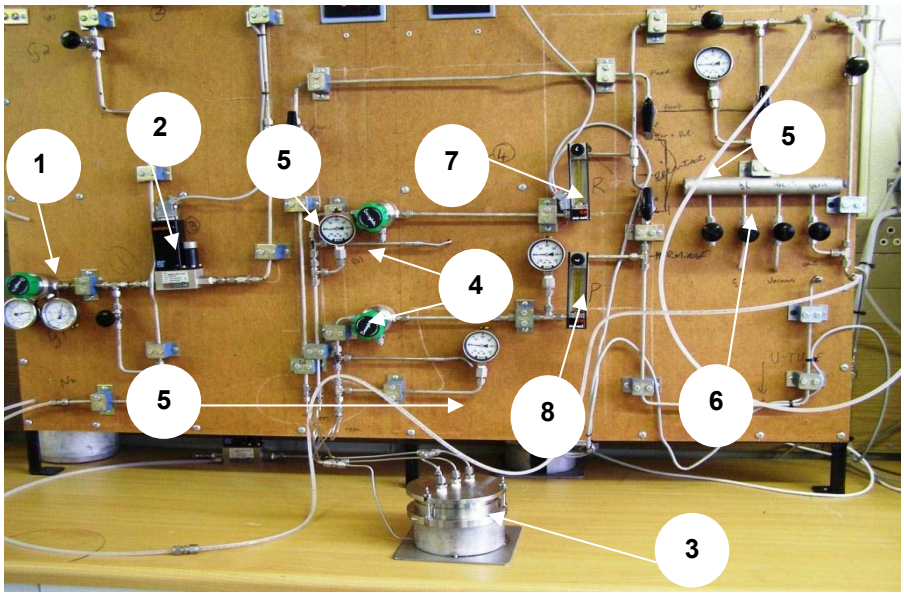


Figure 3-5: Experimental membrane system

1) Feed regulator (gas feed) 2) Mass flow controller 3) Membrane cell unit 4) Back-pressure regulators 5) Pressure gauges 6) Manifold 7) Retentate rotameter 8) Permeate rotameter.

A soap bubble flow meter as illustrated in Figure 3-6, Calibrator 2, was used to calibrate the flow meters for each new C_xF_y cylinder used.

Figure 3-6: Soap bubble flow meter – Calibrator 2

The sampling holder illustrated in Figure 3.5 which was used to grab a sample from the process, was designed with high-integrity fittings and valves and was tested and maintained regularly.

Figure 3-7: High-integrity gas sample holder

A gas chromatograph (Varian 3600) was used which was equipped with a Haysep N, 2 meter packed column from Scientific Supply Services cc. The GC was equipped with a thermal conductivity detector (TCD) and He (g) was used as the mobile phase. The signal from the detector was analysed by means of Chrompack commercial software (from Scientific Supply Services cc) and a chromatogram was produced for each analysis. The integrated peak area for each peak was used for quantification purposes.

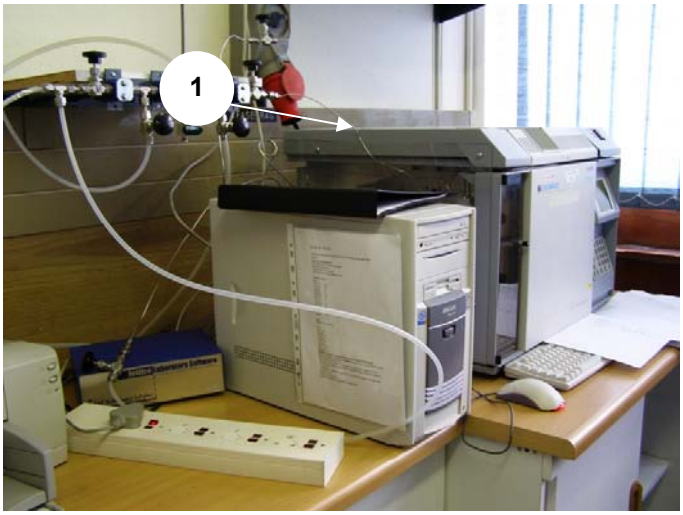


Figure 3-8: Gas chromatograph (Varian 3600)

The products to be analysed for in this study were gaseous fluorocarbon compounds including CF_4, C_2F_6, C_2F_4, and C_3F_6 A typical gas chromatogram of a gas mixture containing this variety of perfluorinated mixtures that were analysed during this study is shown in Figure 3.8. The retention times and calibrated identities for each of the compounds are indicated on top of each peak. In this study the response factors of the detector were not calculated and the area under the peak was used as the measurement of concentration.

The sample was continuously flushed through a six-port valve, which was connected inline to the process, and a sample was pneumatically injected into the injection port of the GC. The temperature of the injection port was controlled at 120 °C. The GC was programmed with a temperature program where the temperature was increased from 80 to 140 °C within the first two

minutes and then the temperature was regulated at 140 °C for 8 more minutes. All of the depolymerisation products eluted within 12 minutes.

The GC was calibrated using a standard, especially prepared by Pelindaba Analytical Labs, which is an accredited analytical laboratory. Peak identification was conducted and confirmed with a mass spectrometer.

These values were not corrected, but the analyses during experimentation were corrected for air which could leak into the system because it does not participate in the reactions.

3.2.2 Experimental procedures

Prior to all experimental procedures the following safety precautions, integrity checks and calibrations were undertaken:

- Ventilation was switched on, as most C_xF_y gases are considered dangerous and can cause suffocation at high concentrations;
- Leak-tightness of the system was verified by soap leak test with 400 kPa N_2 pressure;
- Temperature was controlled at 25 ± 1 ^oC;
- Membrane integrity pressure test with SF_6 gas;
- General inspection of integrity of system, which includes correct valves, fittings etc.;
- Calibration was done before start-up of the experiment, the mass flow controller together with the rotameters needed to be recalibrated to ensure high-accuracy readings.

.

After safety precautions, calibration and integrity checks were completed, the pre-calibrated mass flow controller 2 was used to regulate the flow of gas into the system at a predetermined mass flow rate.

The back-pressure regulator 4 was used to control the feed-side pressure. These pressures can be read from the pressure gauge 5. Rotameters 7 and 8

which are pre-calibrated with the soap bubble flow meter, gives the volume flow rate results for the retentate and permeate sides.

After the system stabilised at a controlled pressure (approximately 1min) a sample was taken by letting the gas flow through the sample holder for approximately one minute and was then blocked in by closing the outlet and then the inlet valves of the sampling cylinder. This sample was then analysed with the GC analytical instrument.
Mole balances were established by taking samples of both the retentate and permeate sides.

In summary the following measurements were taken:

- Cylinder composition;
- Controlled temperature (K);
- Feed pressure (kPa);
- Permeate pressure (kPa);
- Permeate flow rate (ml/min);
- Retentate flow rate (ml/min);
- Permeate composition;
- Retentate composition.

With the above data the flux through the membrane, the selectivity and the percentage cut could be calculated and the mole balance verified.

3.2.3 Data handling

All the above data were used to calculate:

- The flux;
- Selectivity;
- Percentage cut;
- Mass balance.

The method used to calculate these parameters is as follows:

The Molar flow rates are calculated using the ideal gas law:

$$\dot{M} = \frac{P_{atm}\dot{V}}{RT} \qquad \text{Eq 3-1}$$

The Flux is defined as the molar flow per unit membrane area, A:

$$\text{Flux} = \frac{\dot{M}}{A} \qquad \text{Eq 3-2}$$

The selectivity (α_{AB}) is the ratio of concentrations of components A, B and C in the permeate side divided by the ratio of concentrations of components A B and C in feed side.

$$\alpha = \frac{(y_A/x_B)}{(y_A/x_B)} \qquad \text{Eq 3-3}$$

The average selectivity of components A, B and C (α_{ave}) is then defined:

$$\alpha = \frac{\left[\left(\frac{(y_A/x_B)}{(y_A/x_B)}\right)+\left(\frac{(y_C/x_B)}{(y_C/x_B)}\right)\right]}{2} \qquad \text{Eq 3-4}$$

The **cut (**θ), is the ratio of molar feed rate to the molar permeate flow rate.

$$\theta = \frac{n_P}{n_F} \qquad \text{Eq 3-5}$$

3.3 Results and discussion

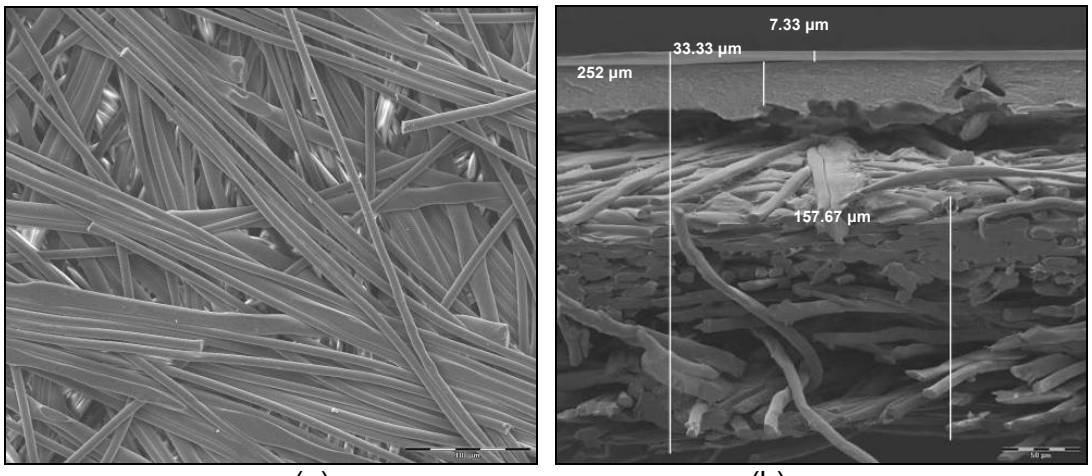
3.3.1 Membrane screening

Table 3-2 shows the only successful membrane is the AF2400 Teflon-coated membrane. The Nafion and the POMS membranes showed no detectable gas permeation up to 260 kPa transmembrane pressure and were therefore discarded for future testing.

Table 3-2: Membrane screening for $C_2F_4/C_2F_6/C_3F_6$ gas mixtures

Membrane	Supplier	Outcome
AF 2400 Teflon	GKSS	Successful
POMS	Borsig	Unsuccessful
Nafion 117	ElectroChem Inc.	Unsuccessful
Nafion 1135	ElectroChem Inc.	Unsuccessful
Nafion NRE 212	ElectroChem Inc.	Unsuccessful

Figure 3-9 (a) and (b) shows scanning electron microscopy (SEM) pictures of the successful AF2400 Teflon membrane. Figure 3.9 (a) shows the texture of the PAN support and Figure 3-9(b) shows the active Teflon layer of 7.33 µm is attached to the 158 µm support by means of 33 µm intermediate layer.



(a) (b)

Figure 3-9: SEM photos of the AF2400 Teflon membrane

Detailed experimental results are given in Appendix B

3.3.2 Optimization of the AF 2400 Teflon membrane separation

For the AF2400 Teflon membrane a more detailed study was made in order to optimize and quantify its performance in the separation of $C_2F_4/C_2F_6/C_3F_6$.

Flux

The influence of the transmembrane pressure on the total flux was measured and presented in figure 3-10.

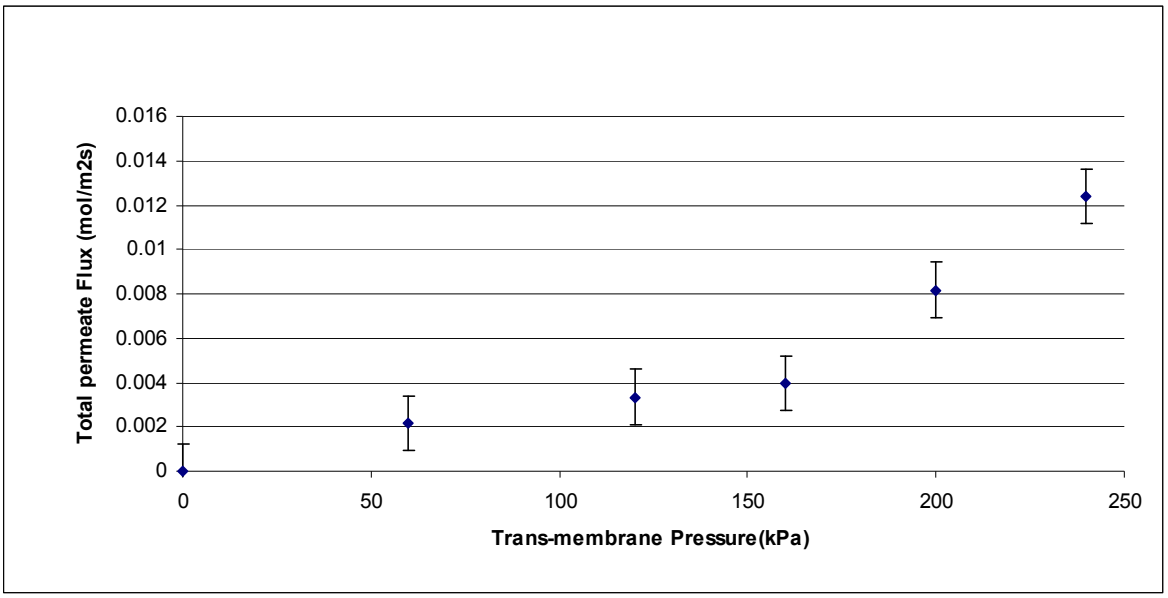


Figure 3-10: The influence of the transmembrane pressure on total flux

For transmembrane pressures of 0 to 160 kPa the permeance is constant and is equal to $25*10^{-6}$ mol/m^2.s.kPa. At higher pressures a constant permeance is again observed ($100*10^{-6}$ mol/m^2.s.kPa) which is an indication that the unsaturated fluorocarbons start to dissolved in the polymer membrane as predicted by the solution diffusion model.

Individual compound flux rates were measured and analyzed at differential transmembrane pressures and the results are summarized in Figure 3-10.

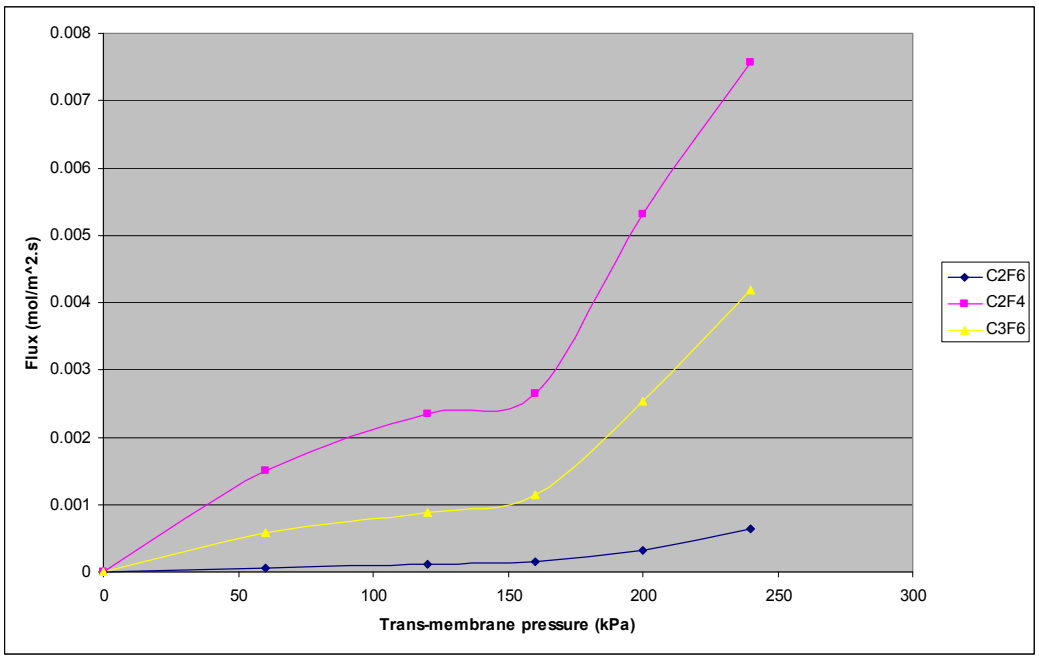


Figure 3-11: The influence of the transmembrane pressure on the C_2F_6, C_2F_4 and C_3F_6 fluxes

Selectivities

The influence of transmembrane differential pressure on the selectivity of C_2F_4/C_2F_6, C_2F_4/C_3F_6 and C_3F_6/C_2F_6 mixtures were determined and the results are plotted in Figure 3-12.

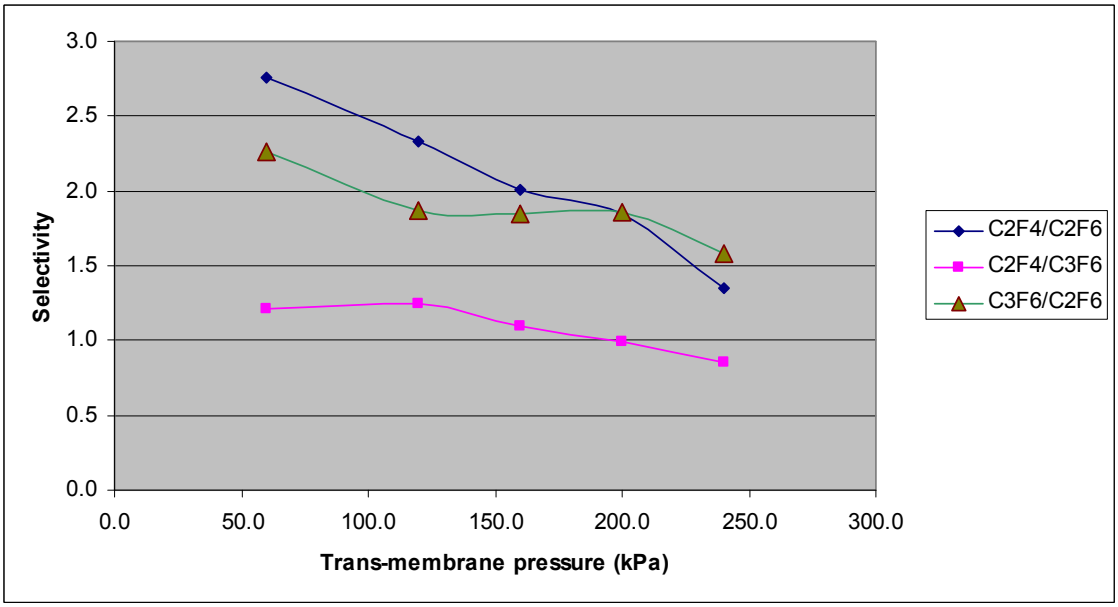


Figure 3-12: The influence of the transmembrane pressure on the selectivities

C_2F_4 and C_3F_6 are enriched in the permeate side and C_2F_6 in the retentate side.

The selectivities of C_2F_4 / C_3F_6 relative to C_2F_6 are about equal, which corresponds with a C_2F_4 / C_3F_6 selectivity of close to one.

The average selectivity C_2F_4, C_3F_6/C_2F_6 is plotted in Figure 3-13, giving the selectivity to be used in conceptual design purposes.

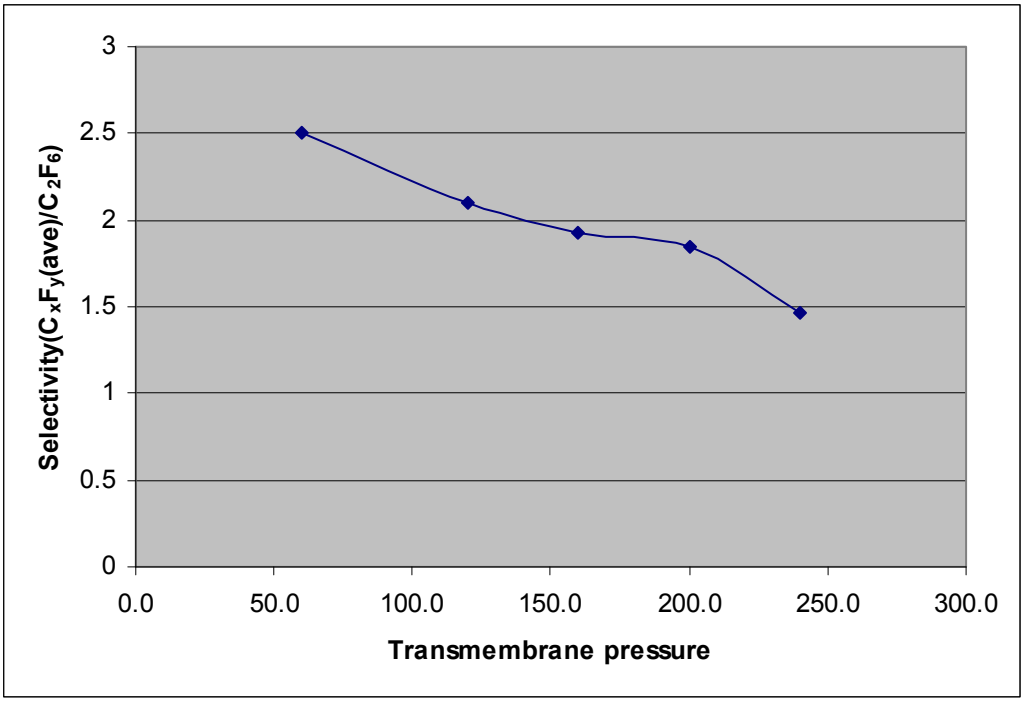


Figure 3-13: The influence of the transmembrane pressure on the selectivities

The cut was plotted against the selectivity in Figure 3-14 in order to determine the design parameters and to see if the membrane follows a predicted hyperbolic curve, as it does below.

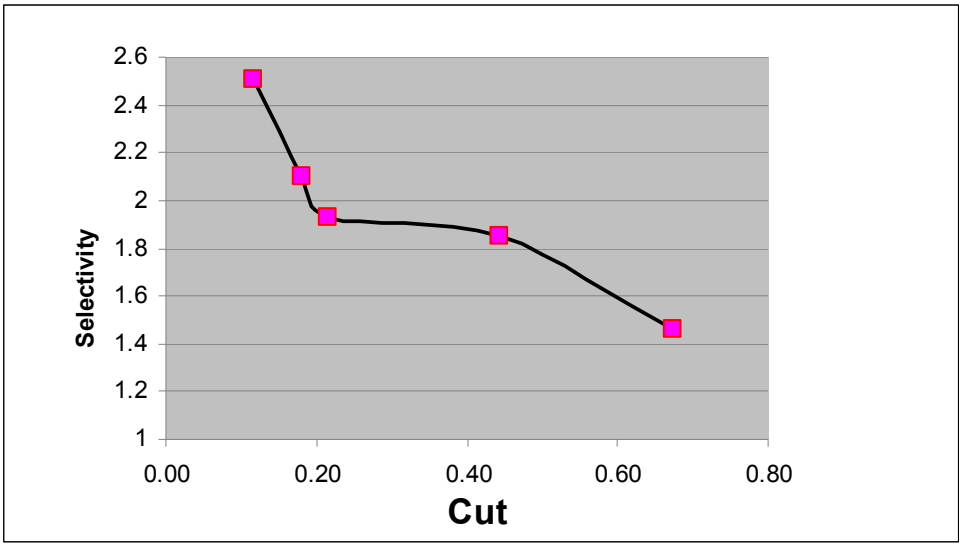


Figure 3-14: The cut versus average selectivity

3.3.3 Repeatability and consistency check

The system integrity and repeatability of the experimental data was checked by means of a mass balance over the process at a selected pressure of 200 kPa. A pressure of 200 kPa was chosen to ensure that all flow meters were within range and instrument measuring error was at minimum. The tests were repeated three times as indicated in Table 3-3, with averages used.

Table 3-3: Selectivity and flux results.

	Exp. 1	Exp. 1	Exp. 1	Ave Selectivity
Selectivity	2.37	1.73	1.63	1.91
Flux	0.00779	0.00315	0.00877	0.00657

Due to the small flows and robustness of the rotameter used, a 10 to 15 % error can be expected as shown in Table 3-4, which is in line with the equipment used.

Table 3-4: Percentage error.

	Feed	Retentate	Permeate		
	ml/min	ml/min	ml/min	R+P	%
Test1	712	637.68	59.22	696.90	0.104
Test2	710	637.68	66.62	704.30	0.102
Test3	709	637.68	66.62	704.30	0.101
					10.228

3.4 Experimental results and discussion

The ideal selectivity at P_R = 247kPa and P_P = 87 kPa was calculated with the selectivity of α =2 with:

$x_R C_x F_y$ = 0.92 (Retentate concentration of C_2F_4 + C_3F_6 calculated from measured values):

$$r = \frac{P_P}{P_R} = 0.35$$

$$\alpha^* = \frac{\alpha}{\left[\frac{x_R C_x F_y(\alpha - 1) + 1 - r\alpha}{x_R C_x F_y(\alpha - 1) + 1 - r}\right]} = 2.5$$

The selectivity/percentage cut curve is a good indication at which percentage cut the design should be done. As illustrated in Figure 3-14, at a 20 to 40 percentage cut the selectivity is in the region of 2 to 2.5. At a selectivity of 2.5 the average molar flux was calculated to be equal to 0.002 mol/m^2.s at 160 kPa transmembrane pressure and can be used in the conceptual design to separate C_2F_6 from C_2F_4 and C_3F_6.

3.5 Conclusions

Of the 5 tested polymer membranes only the AF2400 Teflon membrane showed an acceptable flux. The consistency and repeatability of the experiments shows that the AF2400 membrane can be used to develop a membrane system to be proposed in the conceptual design. C_2F_6 is enriched in the retentate side, whereas C_2F_4 and C_3F_6 are partially permeated.

The conclusions are that C_2F_6 can be separated with a PAN coated Teflon AF2400 membrane with real selectivity (α) of 2.5 at a 21 % cut, which can be

practically implemented. The area per stage will be large but is manageable with new technology available.

A proposed unit will be conceptually designed based on the above data, and will be part of the hybrid separation system to separate C_2F_6 from C_xF_y gases.

4 Process synthesis and conceptual design

4.1 Introduction

Evaluation of the three processes as explained in chapter 2 is conclusive and based on the energy requirements it is evident that the transfer-arc plasma should be used to produce C_xF_y gases from CaF_2 and carbon as feedstock.

This chapter will propose a separation process that will be interlinked with the transfer-arc plasma system to separate the C_xF_y gases produced. The process proposed will be a conceptual design to provide information to do a cost evaluation.

The basis of the conceptual design is to provide for the production of 2500 t/a C_2F_4 and 625 t/a C_3F_6, both of purity, 96 %, in a transfer-arc plasma.

Design assumptions

The following assumptions were made to perform the conceptual design:

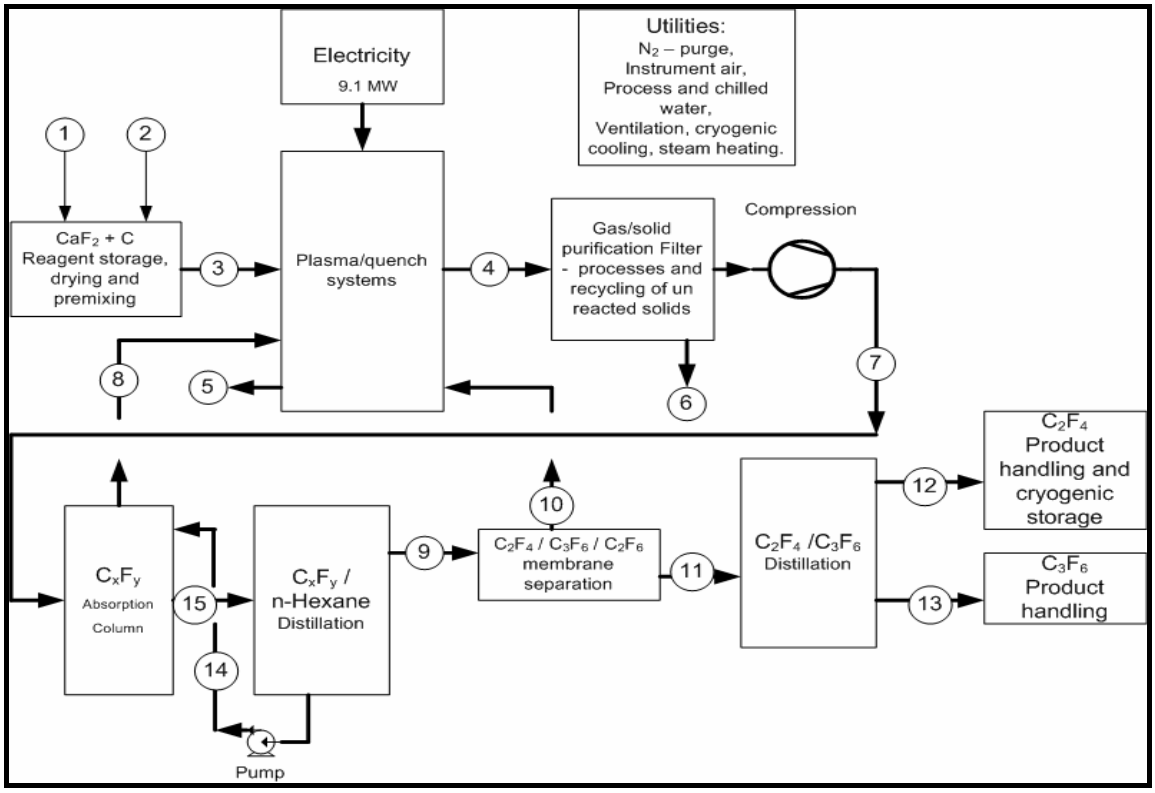
- In the plasma-arc system, four C_xF_y products will be produced, namely CF_4, C_2F_6, C_2F_4, and C_3F_6;
- No provision is made for waste products formed in the reactor or distilled to be diverted to a waste destruction section. This will be considered as future work in detail design;
- The organic impurities that are removed in the feed preparation section can be ignored in the mass balance as they do not significantly contribute to the products;
- The distillation and absorption columns give 99% separation in mass balance;
- The heat exchangers are based on a heat transfer coefficient of 500 $W/m^2.C$ and a $\Delta T_{lm} = 10^oC$ (Sinnott, 1986).

4.2 Basic process

The basic process description as shown in Figure 4-1 embodies a 9.3 MW transfer-arc plasma reactor with a quench system and a filter to remove entrained solids, a compressor section, multi-step separation section and product storage and handling facility.

The first separation stage is to separate CF_4 from the C_xF_y gas mixture, which will be recycled back to the plasma system (8). Small amounts of n-hexane will be present in the stream and may be of concern due to hydrogen-carbon compounds that may form which will then form hydrofluoric acid, causing extreme corrosion at very high temperatures. CF_4 separation will be done by means of the Reinhard A. Sulzbach method, using n-hexane to absorb C_2F_4, and the heavy key C_2F_6 and C_3F_6 gases from the gas stream. The enriched n-hexane mixture will be distilled in a distillation column from the C_xF_y gases. The n-hexane will be cooled and recycled (14) to the absorber as absorbent.

The gases (9) from the n-hexane distillation go through a multi-stage membrane cascade separating the C_2F_6 (10) from the C_xF_y gas stream (11). The C_2F_4 (12) and C_3F_6 (13) are cryogenically distilled to 96 % purity.



Mass Flow	Molar mass	Streams	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	kg/kmol	Units															
CaF_2 (s)	78.00	kg/h	1474.36		1474.36												
C (s)	12.00	kg/h		397.44	397.44												
C_2F_4	100.00	kg/h				355.56			355.56	3.56	352.00	1.06	350.94	347.43	3.51		352.00
C_2F_6	138.00	kg/h				88.89			88.89	0.89	88.00	87.12	0.88	0.87	0.01		88.00
C_3F_6	150.00	kg/h				88.89			88.89	0.89	88.00	0.26	87.74	0.88	86.86		88.00
CF_4	88.00	kg/h				355.56			355.56	355.56							
CaC_2	52.00	kg/h				982.91	894.02	88.89									
C_6H_{14}	86	kg/h								0.043						59080	59080
Total		kg/h	1474.36	397.44	1871.80	1871.80	894.02	88.89	888.89	360.89	528.00	88.44	439.56	349.18	90.38	59080	59608

Molar Flow	Molar mass	Streams	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	kg/kmol	Units															
CaF_2 (s)	78.00	kmol/h	18.90		18.90												
C (s)	12.00	kmol/h		33.12	33.12												
C_2F_4	100.00	kmol/h				3.56			3.56	0.04	3.52	0.01	3.51	3.47	0.04		3.52
C_2F_6	138.00	kmol/h				0.64			0.64	0.01	0.64	0.63	0.01	0.01	0.00		0.64
C_3F_6	150.00	kmol/h				0.59			0.59	0.01	0.59	0.002	0.58	0.01	0.58		0.59
CF_4	88.00	kmol/h				4.04			4.04	4.04							
CaC_2	52.00	kmol/h				18.90	17.19	1.71									
C_6H_{14}	86	kmol/h								0.0005						686.98	686.98
Total		kmol/h	18.90	33.12	52.02	27.73	17.19	1.71	8.83	4.09	4.74	0.64	4.10	3.49	0.61	686.98	691.72
Process parameters																	
Temperature		°C	25	25	25	250	250	25	25	-75/25	25	25	25	-50	25	25	25
Pressure (a)		kPa	87	87	-40	-40	87	87	200	200/150	200	200	200	200	150	200	200

Figure 4-1: Transfer-arc plasma system basic process flow sheet

The subsequent sections will be discussed in more detail:

- The plasma system;
- The compressor system;
- The separation plant;
- The product storage and handling.

4.3 Reactor plasma system

The plasma reactor illustrated in Figure 4-2 will produce C_xF_y (3) gases from a pre-mixed CaF_2 (1) and C (2) mixture. CaF_2 (s) and C (s) powder are pre-mixed and preheated to remove any moisture and then fed into a chamber of the plasma system. A carbon/graphite rod which is a consumable electrode is continuously fed into the reagent mixture. An electric arc will be generated between the cathode (reagent s) and carbon anode.

Heat will be generated up to 6000K (9.1 MW splitting to various electrodes in the plasma system), causing evaporation of the mixture and subsequent chemical reactions.

The unit will use demineralised water to cool and quench at a rate of approximately 10^6K/sec in an indirect dry quench system to produce various compositions of C_xF_y gases. Demineralised water is used to prevent electrical discharge to the surrounding structures.

The gases produced (7) will be cleaned from entrained unreacted solids (6) with PTFE filters < 150 um. CaC_2 and unreacted CaF_2 will be extracted (5) via a screw-sieve mechanism as waste from the reactor plasma system. The fact that the plasma process takes place at low pressures ranging from 20 kPa requires compression to drive the process to the separation stage pressure (200 kPa (a)).

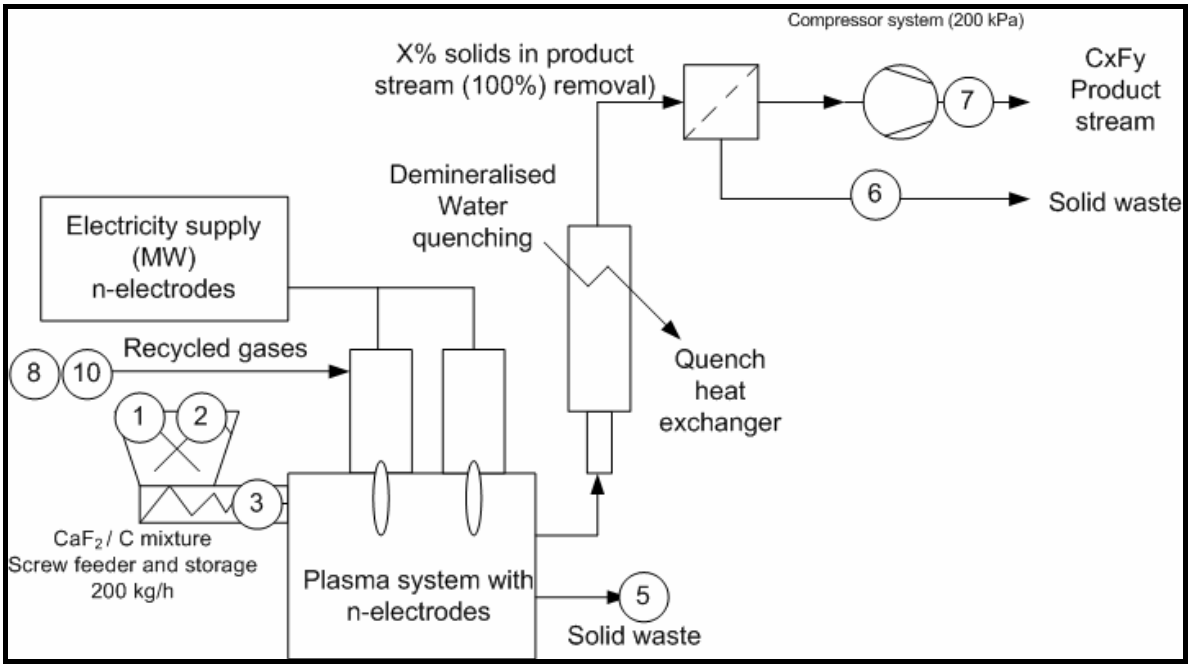


Figure 4-2: The plasma-arc system

4.4 Compressor system

The compressor plant will have diaphragm compressors compressing the gas from the plasma (7) to the separation system from 20 kPa to 200 kPa. These high integrity compressors will be part of a parallel system feeding gas from the plasma units to the separation plant. Each separate unit operation includes cooling and buffer vessels for smooth control to the separation plant. A typical compressor system is illustrated in Figure 4-3.

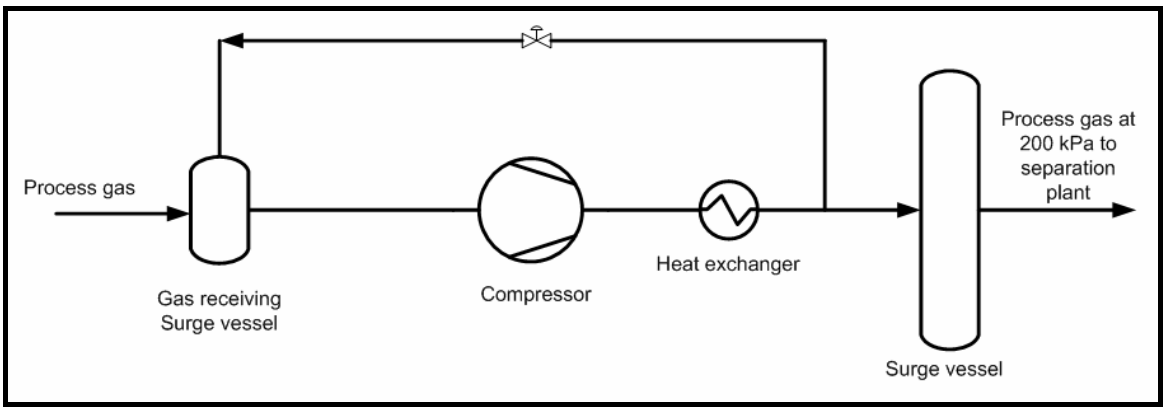


Figure 4-3: The compressor system

Table 4-1 shows the design specification of the compressor system that will be used to feed the separation plant from the plasma system.

Table 4-1: The compressor system specifications

Specification description	Size
Gas flow	261 (STP) m^3/h
Pressure	20 to 200 kPa
Temperature	25 ^oC gas outlet temperature
Material	Stainless steel
Type	Diaphragm or blower
Support equipment • Cooler • Surge vessels • Control system	Total vendor package

4.5 Separation plant

4.5.1 Absorption column

The absorption section will consist of an absorber column using n-hexane as absorbent (14) to purify CF_4 from the gas feed (7), at 261 (STP) m^3/h. The unit will recover 99% C_xF_y gases from the process gas stream produced by the plasma units, purifying the stream of CF_4 gas which is recycled to the plasma at 102 (STP) m^3/h, with less than 0.01% absorbent.

The unit will be fitted with a cooler condensing n-hexane from the CF_4 stream. The K-value (K=128, C_2F_4) is calculated from analytical data from the Sulzbach patent assuming that the feed is at equilibrium. The absorbent detail calculation is attached in Appendix C.
A general configuration of a C_xF_y gas absorption column and n-hexane distillation column is illustrated in Figure 4-4.

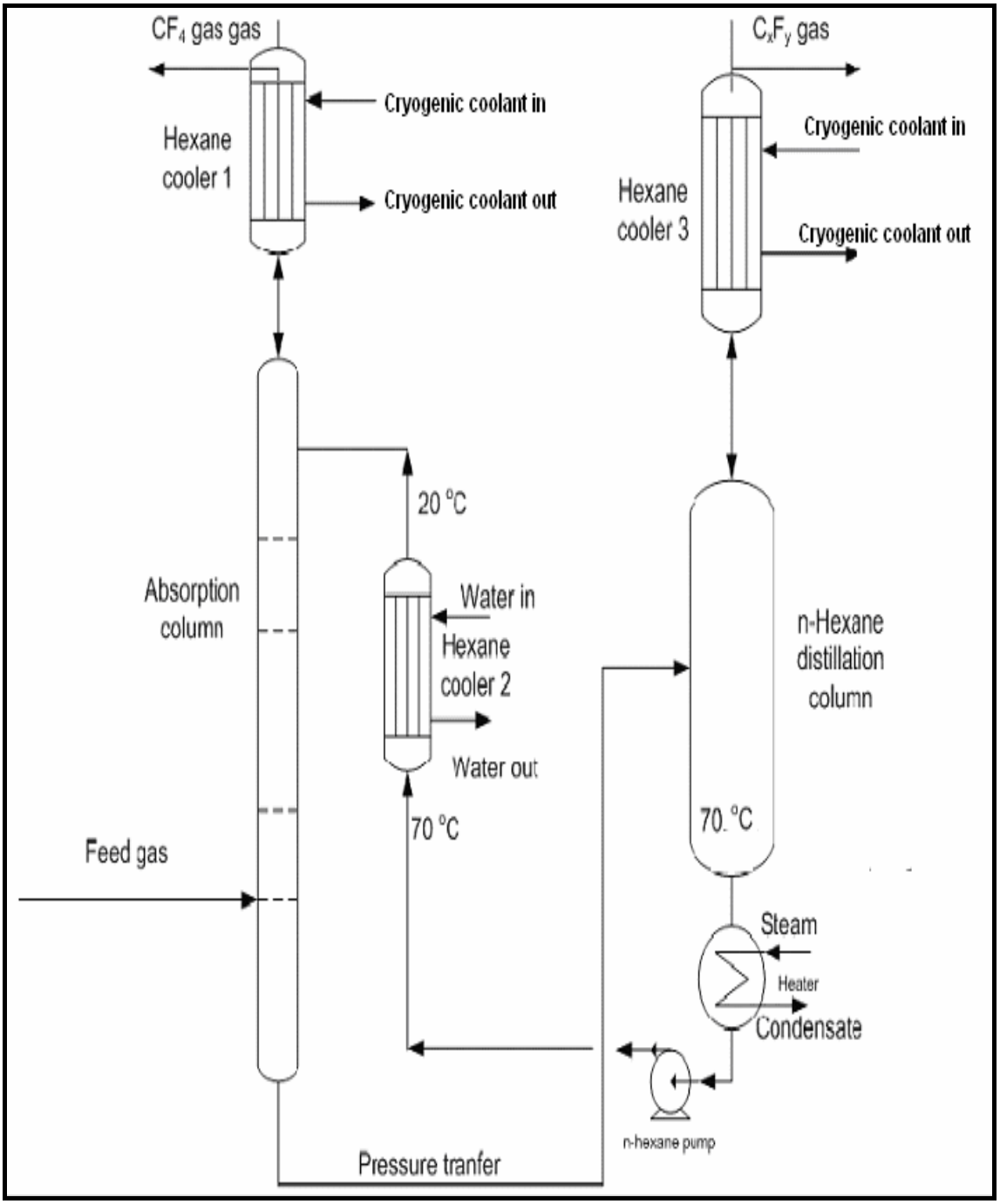


Figure 4-4: The absorption and recovery system

The column dimensions and absorber flow rate have been calculated as described in chapter 2.

With equation $Dc = \sqrt{\frac{4Vw}{\pi\rho_v u_v}}$ (Eq.2-6) the diameter was estimated with detail calculations shown in Appendix C.

Overall absorber column specifications:

The conceptual design specification is tabled in Table 4-2 from conceptual calculations.

Table 4-2: Absorber column specifications

Specification description	Size
Gas flow	261 (STP) m^3/h
Liquid flow	104 m^3/h
Height	8m
Stages	13
Diameter	0.3m
Pressure	200 kPa
Temperature	25 ^oC
Material	Stainless steel
Support equipment • Cooler 1 [Aspen B-JAC 2004] • Cooler 2 [Aspen B-JAC 2004] • Pump	 28 kW Heat area = 5.6 m^2 2831 kW Heat area = 566 m^2 30 kW (estimated)

4.5.2 n-Hexane distillation column

The design of the n-hexane distillation column illustrated in Figure 4.4 is based on separating C_xF_y gases from the n-hexane liquid mixture (15). This separation is via a two-stage action as illustrated in the VLE data in Chapter 2. From VLE data illustrated in Figure 2-20 and 2-21, this separation is via a two-stage column with detail simulation shown in Appendix C.

n-Hexane distillation column specifications:

The conceptual design specification is tabled in Table 4-3 from conceptual calculations.

Table 4-3: n-hexane Distillation column specifications

Specification description	Size
Height	2m
Stages	2
Diameter	0.3m
Pressure	200 kPa
Temperature	70 ^{o}C
Material	Stainless steel
Internals	Packing or trays
Support equipment • Condenser (cooler 3) • Heater	 66 kW Heat area = 13.2 m^2 55 kW Heat area = 11 m^2

4.5.3 Membrane unit

The design specifications of the ideal recycle membrane cascade are to recover 96% of C_2F_6 from the C_xF_y stream (9) whereby the C_2F_6 will be in the retentate stream (10) and the C_xF_y gases (11) in the permeate stream. Based on the experimental data from chapter 3, the $\alpha_{C3F6,C2F4} = 1$; $\alpha_{CxFy,C2F6} = 2.5$; flux $2*10^{-3}$ mol/m^2.s is used, which gives less stages but larger total area, with smaller mass flows, which in turn gives smaller compressor cost, a factor of 2 lower.

Stages required are calculated as 11 with the detail calculations shown in Appendix C.

The **area per stage** requirements is shown in Figure 4-5 with the detail calculation can be seen in Appendix C.

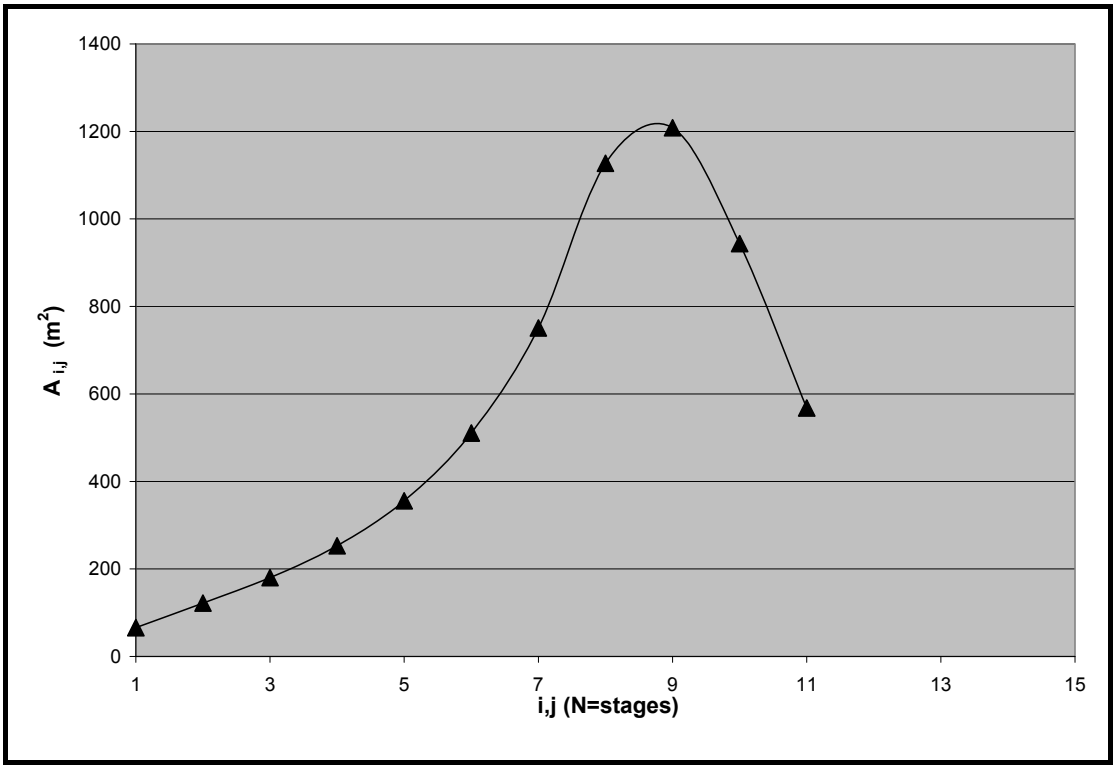


Figure 4-5: Membrane cascade stage and area requirements

The feed stream is fed between the stripping and enriching stage which is shown at stage 9 and is illustrated in Figure 4-6:

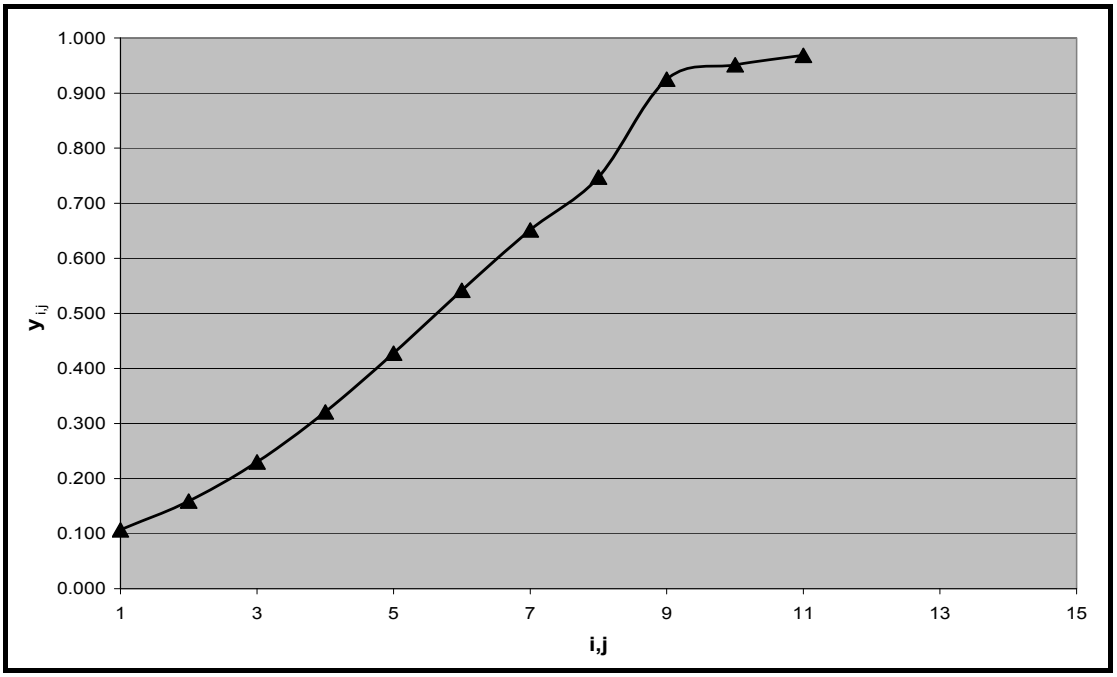


Figure 4-6: Membrane cascade feed stage

A cascade system is proposed to achieve the required separation of 96 % of C_2F_6 gas from the C_xF_y gas stream. Compressor requirements per stage are shown in Figure 4-6.

Cascade systems are very complex and vary depending on technology used. Due to recycling permeate-streams to the first stage, the permeate becomes the feed to the second and so on through the process.

C_2F_6 is the retentate and C_2F_4/C_3F_6 is the permeate streams where the permeate C_2F_4/C_3F_6 could have a higher pressure than the rest of the membranes in the cascade, discharging C_2F_4/C_3F_6 to the C_2F_4/C_3F_6 distillation column via pressure difference, avoiding unnecessary compression of enriched C_2F_4.
Conceptual design specifications for the ideal recycle membrane cascade system are shown in Table 4-4:

Table 4-4: Ideal recycle membrane cascade

Specification description	**Size**
Area (total)	6084 m^2
Stages	11
Diameter	Technology dependent
Pressure	200 kPa inlet maximum
Temperature	298 K
Material	PAN coated with Teflon AF2400
Type	Ideal recycle cascade, using area change gas-pressure boosters per stage.

Membrane compressors

This system is a pressure-driven system and is dependant on the membrane technology chosen, with the compression requirements illustrated in Figure 4-7. For conceptual purposes counter air – area change booster compressors are proposed.

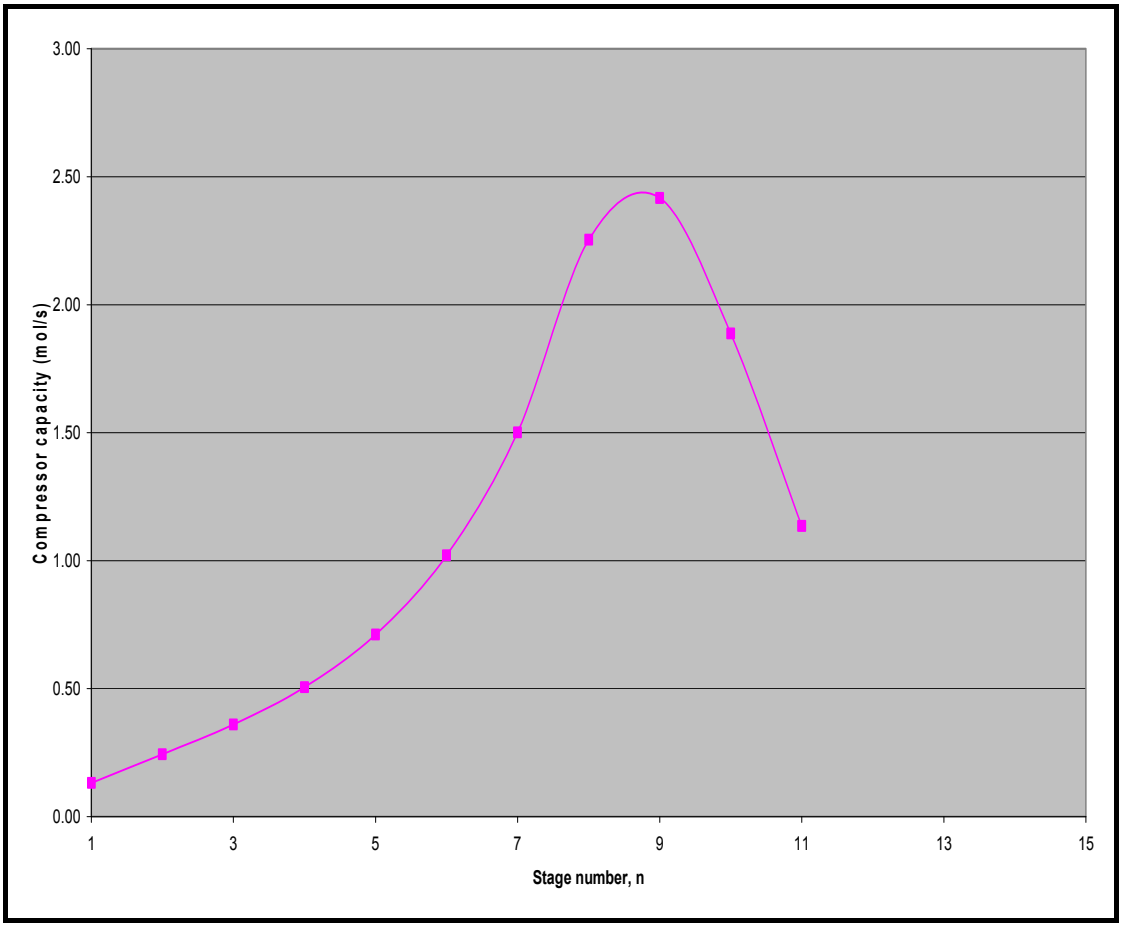


Figure 4-7: Membrane compression requirements per stage

4.5.4 C_2F_4/C_3F_6 Distillation

The C_2F_4/C_3F_6 distillation column as illustrated in Figure 4-8 will be a cryogenic column separating (11) C_2F_4 from C_3F_6 which are both products, at a rate of 350 kg/h C_2F_4 at 96% and 88 kg/h C_3F_6 at 96% purity. The C_2F_4 (12) will be fed to a cryogenic storage unit and the C_3F_6 (13) will be compressed into loading cylinders for dispatch.

The C_2F_6 which is a light key compound will be part of the gas stream and can be vented from the polymer reactor head space as is usually done.

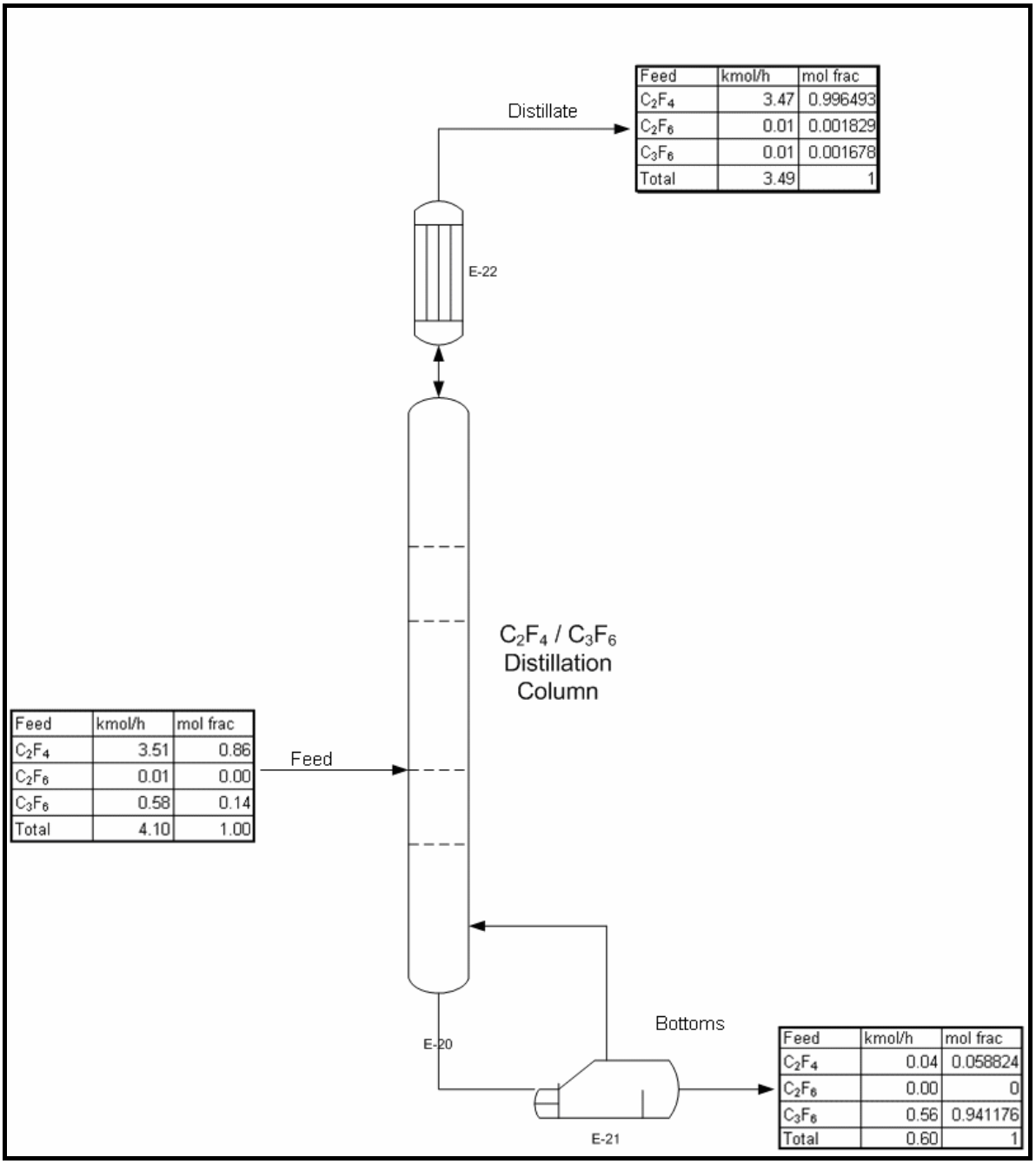


Figure 4-8: C_2F_4/C_3F_6 Distillation mole balance.

Detail of the conceptual design calculations are shown in Appendix C

The design specifications:

The conceptual design specification is tabled in Table 4-5 from conceptual calculations.

Table 4-5: C_2F_4/C_3F_6 Distillation column specifications

Specification description	Size
Height	6m
Stages	10
Diameter	0.3m
Pressure	200 kPa
Temperature	-70 to 30 ^oC
Material	Stainless steel
Internals	Packing or Trays
Support equipment • Condenser (Partial) • Re-boiler	 66 kW, Heat area = 13.2m^2 55 kW Heat area = 11m^2

4.5.5 C_2F_4 Storage vessels

The storage system is an essential part of the distillation system. The storage system is situated in a bunker due to the explosive nature of pure C_2F_4 (0.5 TNT equivalents). C_2F_4 is stored as a liquid at cryogenic temperatures and pressure: -50^oC, 220 kPa (a).

The system as illustrated in Figure 4-9 is equipped with condensers matching the distillation column and a cooling jacket ensuring that the C_2F_4 stays liquid. A vaporiser is used to vaporise the C_2F_4 which is fed to the polymerization plant at a feed pressure of 220 kPa and a predetermined feed rate.

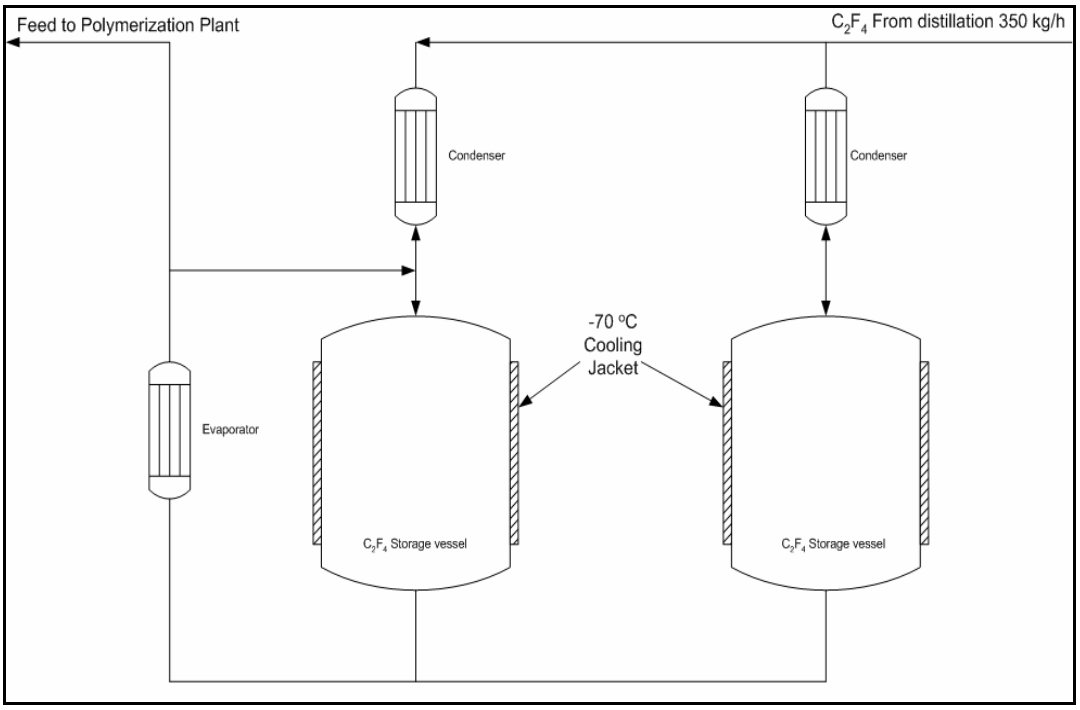


Figure 4-9: C_2F_4 storage

The energy requirement of the cooling jacket and condensers matching the distillation column as a safety back-up is to ensure that losses to the environment (50 W/m^2, rule of thumb) are kept to a minimum. The vessel is sized to store 8400 kg of C_2F_4 per vessel ensuring storing one day's production.

Table 4-6: C_2F_4 Storage vessels specifications

Specification description	**Size**
Dimensions	2*10 m^3 vessels
Pressure	Maximum 220 kPa (a)
Temperature	-75 ^{o}C minimum
Material	Stainless steal
Type	Pressure vessel
Duty tanks + condensers	68 kW
Support equipment • Condenser (Partial) • Evaporator (d-limonene)	 66 kW Heat area = 13.2 m^2 66 kW Heat area = 13.2 m^2

4.5.6 C_3F_6 Storage

The C_3F_6 is stored in 200 litre cylinders at a maximum pressure of 2000 kPa (30^{o}C) Details of the storage facility are given in table 4-7.

Table 4-7: C_3F_6 Storage conceptual specifications

Specification description	**Size**
Dimensions	200 litre gas storage vessels
Pressure	Maximum 2000 kPa (a)
Temperature	30 ^{o}C minimum
Material	Standard mass storage cylinders (Carbon steel)
Type	Pressure vessel
Utilities	Compressor 2000 kPa/ cylinder

4.6 Summary

The plasma units are of 9.3 MW power, fed with CaF_2 and C, with a consumable graphite electrode, operating at 20 kPa and 6000K, equipped with a quench system, producing C_xF_y gases and CaC_2 as waste.

The compression increases the feed pressure to the separation plant.

The separation plant consists of an absorption column and n-hexane distillation column separating CF_4 from the rest of the C_xF_y mixture.

The membrane system will be a compact turnkey system with variable-area type pressure boosters driving the process and recycle streams to separate C_2F_6 from C_2F_4 and C_3F_6.

The separation of C_2F_4 and C_3F_6 will be via a cryogenic distillation column. The column will be designed to cater for the explosive nature of C_2F_4, and will be a Zone 2 (spark-proof) classified area.

C_2F_4 liquid storage is dangerous and the system will be situated in a bunker. The storage system will continuously be cooled down to -70 ^oC. The C_2F_4 liquid will be evaporated to a pre-determined pressure and feed rate required by the polymerisation plant (batch process).

C_3F_6 will be compressed and stored directly in bulk storage vessels for external transport as the preferred and tested method.

The conceptual design proposed will be used as information in the next chapter to perform a techno-economic study.

5 The techno-economical study

5.1 Introduction

In this techno-economic study, a full-scale plant of 2500 t/a C_2F_4 and 625 t/a C_3F_6 will be considered. Economically it makes sense that one plant produces both products due to the fact that C_3F_6 is produced by the transfer-arc plasma as a fraction of a main stream which consists of various C_xF_y gases.

A 300 day continuous process is considered, with 30 days non-production for maintenance purposes. A high theoretical yield is the result of the recycle streams, where it is also assumed that the recycle streams are 100 % converted to products given in Table 5-1.

Table 5-1: Product spectrum from the plasma-arc system (Moore, 1997)

Compound	Weight fraction	Mole fraction
CF_4	0.40	0.45
C_2F_6	0.10	0.08
C_2F_4	0.40	0.40
C_3F_6	0.10	0.07

Figure 5-2 explains the plant requirements excluding indirect utilities like instrument air, water, nitrogen etc. The conceptual design doesn't cater for plant area selection and excludes environmental constraints which will be handled by more accurate feasibility studies at the detailed design stage. Figure 5-1 shows the inter-phases acting on the plant in total and will be described in more detail in the detail design stage.

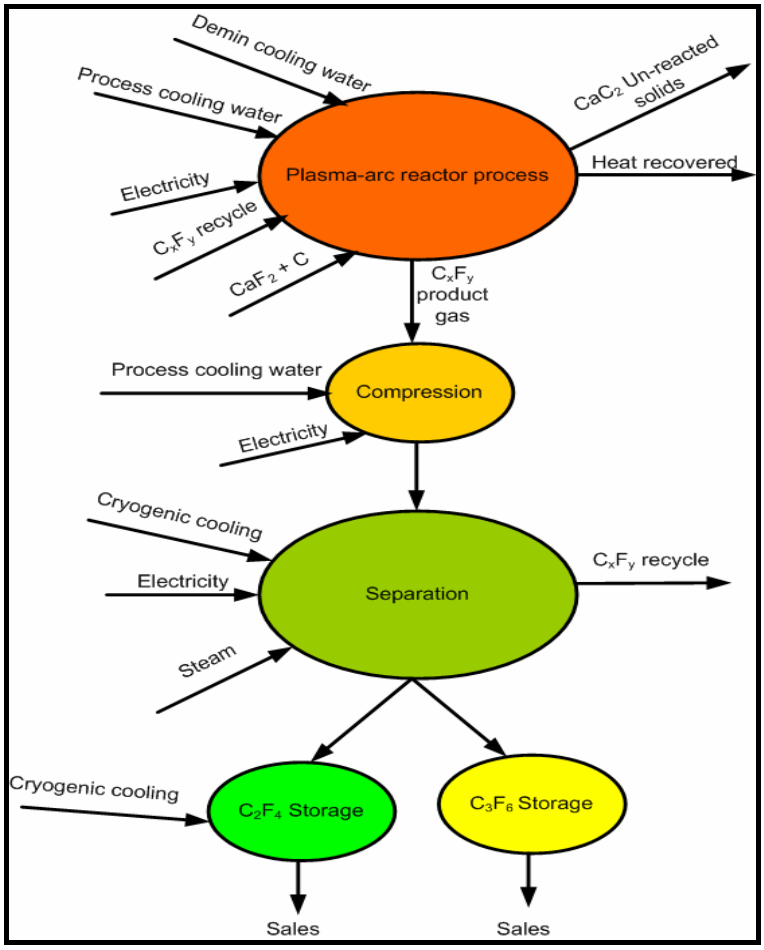


Figure 5-1: Basic C_2F_4/C_3F_6 plant.

5.2 Costing

The costing method is based on methods developed by Necsa for fluorochemicals through experience gained nationally and internationally. Cost estimation is based on experience and real plant unit operations for plants built at Necsa during the last two years. Table 5-2 is used as basis and was used in the Necsa cost estimation program.

Costing assumptions made:

- Plasma power supply is assumed as R3/W used;
- Membrane system is assumed to be \$400 / m^2 total installed, which includes compressors etc.

Table 5-2: Capex and start-up costs

2500 t/a C2F4 & 625 t/a C3F6 PLANT				Total Cost Estimate
UNIT OPERATION 1 : REACTOR PLASMA SYSTEM		**Notes**		
1.1	Plasma reactors	10 * 1MW /Plasma		R 2,900,000
1.2	Filters	100 m2		R 2,900,000
1.3	Cooling water supply	10 MW		R 2,000,000
1.4	Other equipment	Analytical, vessels etc		R 2,000,000
	Subtotal Main Equipment (ME)			R 9,800,000
1.16	Home Office	41%	of ME	R 3,969,000
1.16.1	*Eng Design*	*20%*	*of ME*	*R 1,960,000*
1.16.2	*Risk Management*	*3%*	*of ME*	*R 294,000*
1.16.3	*Project Management*	*10%*	*of ME*	*R 980,000*
1.16.4	*Documentation*	*2.5%*	*of ME*	*R 245,000*
1.16.5	*Process Commissioning*	*5.0%*	*of ME*	*R 490,000*
1.17	Valves	65%	of ME	R 6,370,000
1.18	Instrumentation	75%	of ME	R 7,350,000
1.19	Installation Cost	25%	of ME	R 2,450,000
				R 29,939,000
UNIT OPERATION 2 : COMPRESSERS SYSTEM				
2.1	Compressers	2 diaphragm units		R 5,000,000
	Subtotal Main Equipment (ME)			R 5,000,000
2.5	Home Office	41%	*of ME*	R 2,025,000
2.5.1	*Eng Design*	*20%*	*of ME*	*R 1,000,000*
2.5.2	*Risk Management*	*3%*	*of ME*	*R 150,000*
2.5.3	*Project Management*	*10%*	*of ME*	*R 500,000*
2.5.4	*Documentation*	*2.5%*	*of ME*	*R 125,000*
2.5.5	*Process Commissioning*	*5.0%*	*of ME*	*R 250,000*
2.6	Valves	65%	*of ME*	R 3,250,000
2.7	Instrumentation	65%	*of ME*	R 3,250,000
2.8	Installation Cost	25%	*of ME*	R 1,250,000
				R 14,775,000
UNIT OPERATION 3 : SEPARATION PLANT				
3.1	Absorber column	H=6m, D= 0.3m		R 920,000
3.2	n-Hexane distillation	H=2m, D= 0.3m		R 2,730,000
3.3	Membrane system	6084 m2 11 stages		R 18,250,000
3.4	C_2F_4/C_3F_6 distillation	Cryogenic distillation		R 2,890,000
3.5	Storage vessels	2 * 10 m3 Pressure vessels cryogenic cooled and bunkered		R 19,000,000
3.6	C_3F_6 Product handling			R 1,000,000
3.7	Other equipment	Analytical		R 1,000,000
	Subtotal Main Equipment (ME)			R 45,790,000
3.8	Home Office	43%	*of ME*	R 19,689,700
3.6.1	*Eng Design*	*20%*	*of ME*	*R 9,158,000*
3.6.2	*Risk Management*	*5%*	*of ME*	*R 2,289,500*
3.6.3	*Project Management*	*10%*	*of ME*	*R 4,579,000*
3.6.4	*Documentation*	*3%*	*of ME*	*R 1,373,700*
3.6.5	*Process Commissioning*	*5%*	*of ME*	*R 2,289,500*
3.7	Valves	24%	*of ME*	R 10,989,600
3.8	Instrumentation	43%	*of ME*	R 19,689,700
3.9	Installation Cost	25%	*of ME*	R 11,447,500
				R 107,606,500

Table 5-2: First order capex costs estimation (continued)

OTHER COSTS				
6	Safety equipment			R 3,500,000
7	Flow meters			R 1,000,000
8	Control system			R 3,000,000
9	Ventilation - installed			R 4,000,000
10	Power supply	Power supply units R3/W		R 30,000,000
11	Spares			R 1,000,000
12	Contingency			R 15,000,000
	Subtotal others			**R 57,500,000**
TOTAL PLANT FACILITY COST				**R 209,820,500**
			% involve	Total
OPERATORING PERSONNEL				
Senior Process Controller			100%	R 273,420
Junior Process Controller			100%	R 219,695
Senior Process Engineer - Chemical			50%	R 291,699
Process Engineer - Chemical			100%	R 654,783
Senior Scientist			50%	R 291,699
Senior Chemical Technologist			100%	R 674,472
Chemical Techician X1			100%	R 510,755
Chemical Techician X2			100%	R 461,851
Process Engineering - Mechanical (Support)			50%	R 280,031
Senior Artisans (Maintenance Support)			25%	R 131,033
Electrical Artisan (Support)			15%	R 50,168
Instrumentation Technician (Support)			25%	R 141,383
Analytical Technician (Support)			30%	R 135,728
TOTAL OPERATING PERSONNEL				**R 4,116,716**
VARIABLE COST		**Start-up**		
Raw materials and reagents		1 Months		R 2,000,000
Effluents				R 30,000
External contractors				R 500,000
Packaging				R 1,000,000
Utilities				R 300,000
TOTAL VARIABLE COST				**R 3,830,000**
TOTAL PROJECT COST				**R 217,767,216**

Details on this costing are shown in Appendix D. The Capex for the plant to be erected is estimated to be MR217; MR209 for the facility and MR8 for start-up. The difference between the major plant units is seen in Figure 6-2 where the highest cost is that of the separation plant of which the storage unit contributes 45 % of the costs due to the fact that this system is made of more than one type of unit and each unit is custom-fitted.

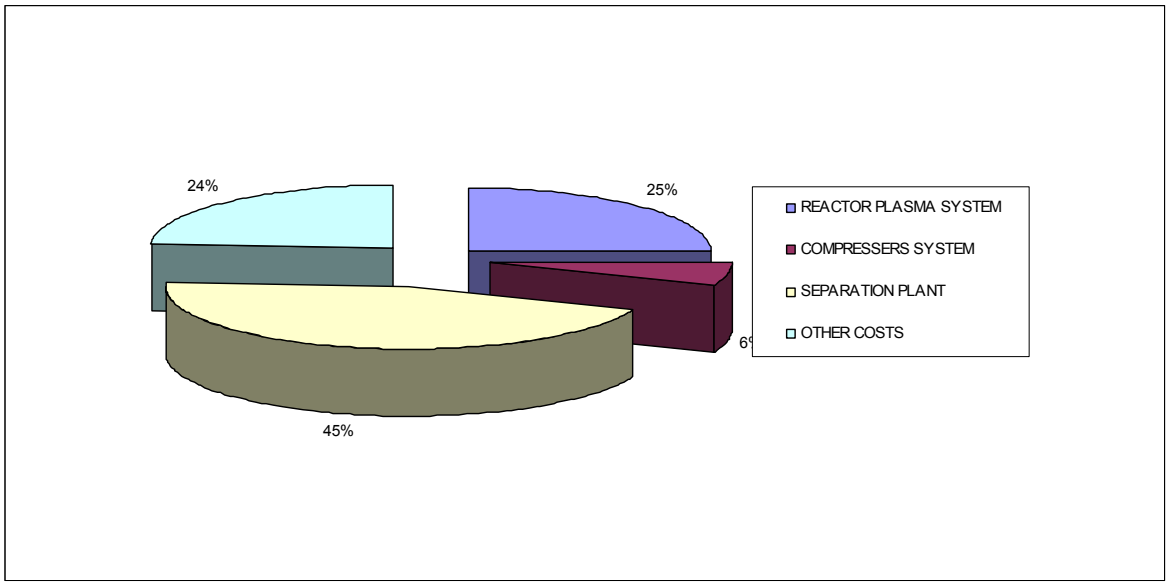


Figure 5-2: Percentage Capex costs summary

The costing of this C_2F_4/ C_3F_6 plant is summarised in Table 5-3. In the costing exercise was included nine industrial scale plasma units with power supply, a compression system, a separation system consisting of a cryogenics plant, an absorption column, two distillation columns, a membrane section, a C_2F_4 storage facility and 625 t/a C_3F_6 loading system.

Table 5-3: Economic indicators associated with the 2500 t/a C_2F_4 and 625 t/a C_3F_6 kg/h production plant

Cost category	Units	Value
Capital and start-up cost	R Million	217
Fixed cost	$R{\cdot}kg^{-1}$	5.54
Variable cost	$R{\cdot}kg^{-1}$	50.38
Overheads	$R{\cdot}kg^{-1}$	0.49
Total production cost	$R{\cdot}kg^{-1}$	56.41
Sales price	$R{\cdot}kg^{-1}$	80
Profit	$R{\cdot}kg^{-1}$	23.59

Necsa developed a budgeting model for speciality fluorochemicals such as C_3F_6 and C_2F_4. According to this model a variable cost of R50.38 per kg was calculated and is illustrated per product in Figure 5-3 and 5-4.

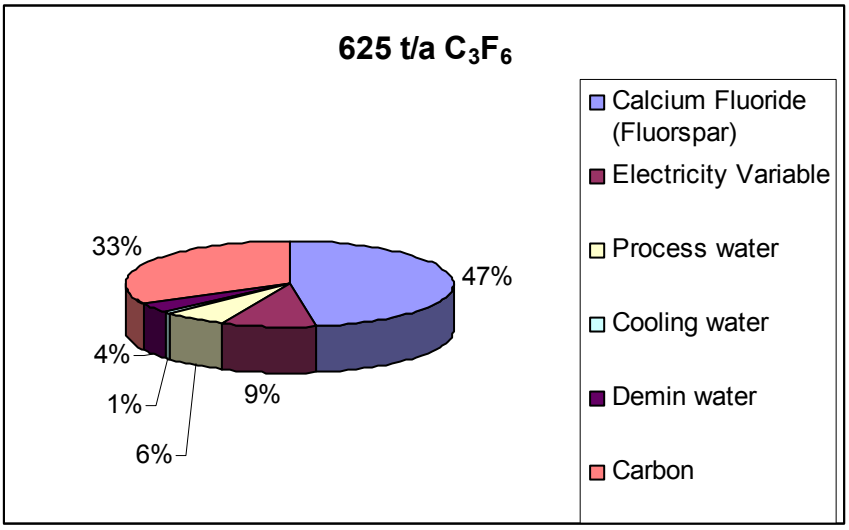


Figure 5-3: Variable costs summary for C_3F_6

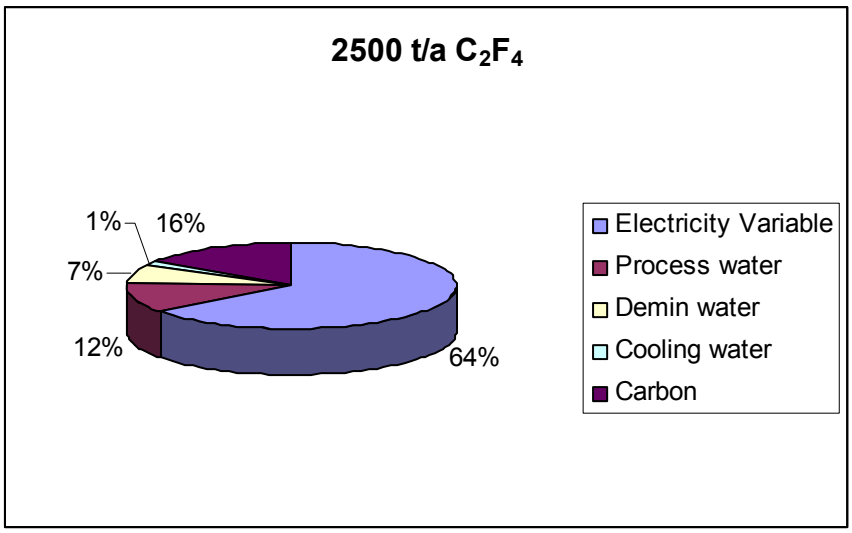


Figure 5-4: Variable costs summary for C_3F_6

Business overheads (R0.49 per kg), fixed costs of R5.54per kg, and variable costs add up to the total production cost per kilogram of C_2F_4/C_3F_6 of R56.41 A profit of R23.59 per kg/h C_2F_4/C_3F_6 is expected based on a selling price of C_2F_4/C_3F_6 of R80 per kg.

Necsa marketing intelligence supported this selling price by estimating that the product could be priced between R70 to R100 per kg on the open market for C_3F_6 and also for C_2F_4.

This is also indicated in the following sensitivity analysis graphs for the IRR (Figure 5-5) and NPV (Figure 5-6). The sales price seems to be the most sensitive of the indicators.

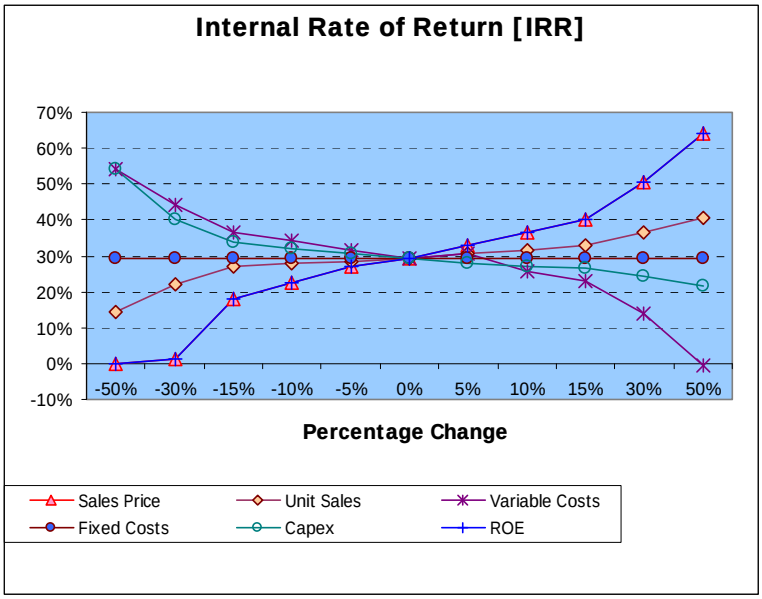


Figure 5-5: Sensitivity analysis for the IRR

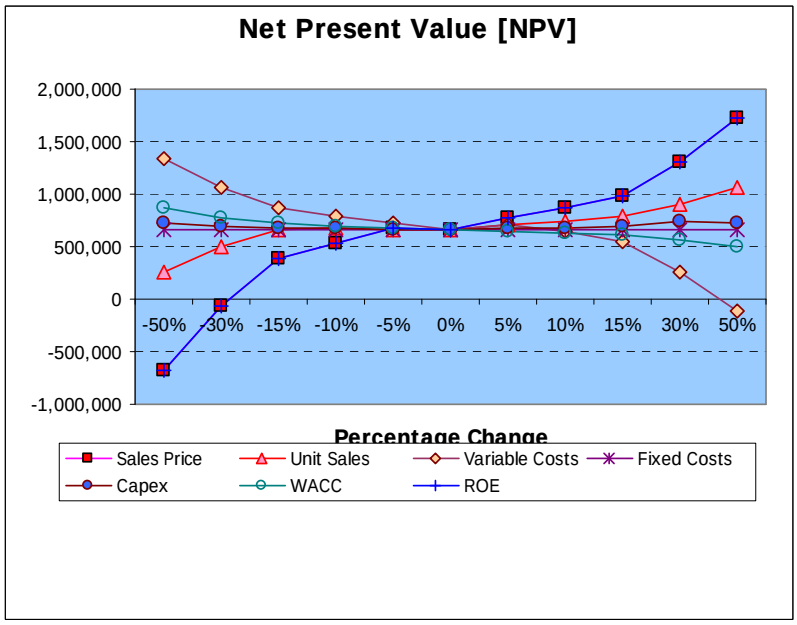


Figure 5-6: Sensitivity analysis for the NPV after a 5 year period.

A summary of the techno-economic indicators are presented in Table 5-4 and is an indication of a good investment.

Table 5-4: Techno-economic indicators for the C_2F_4/C_3F_6 production plant

CAPITAL BUDGET DECISION TOOLS:		
Net Present Value [NPV]	Thousands	661,870
Internal Rate of Return [IRR]	%	29.17%
Modified IRR [MIRR]	%	17.16%
Payback Period	Years	3.73 yrs
Profitability Index	Times	3.67
Gross Profit %	%	33%
Earnings Before Interest & Tax	Thousands	80,318

5.3 Summary

A NPV of R662 million after 5 years can be achieved with an attractive IRR of 29.17 %. The payback period for this plant of 3.73 years, is relatively short.

An ± 5 % analysis on the sales price shows this will change the IRR ± 3 % and the NPV after 5 years with -MR9 and +MR133, respectively, which is shown in Table 5-5.

Table 5-5: Sensitivity analysis on the sales price of C_2F_4/C_3F_6

Sales price (R kg^{-1})	IRR (%)	NPV (MR, 5 years)
75	26.17	653
80	29.17	662
85	33.85	795

A sensitivity analysis on the electrical power variable cost was done and indicates that the IRR and NPV do change aggressively as indicated in Table 5-6).

Table 5-6: Sensitivity analysis on the electricity costs

Electrical cost (R kWh)	IRR (%)	NPV (MR, 5 years)
0.22	29.17	653
0.33 (+50%)	18.39	425
0.35 (+60%)	16.55	349

If the electrical power price is increased by 50% or 60 % the IRR drops from 29.7 to 18.39 to 16.55 % respectively, and the NPV, after 5 years from MR653 to MR425 and MR 349 respectively, which is concerning high?

6 Conclusions, recommendations and outlook

6.1 Conclusions

Product specifications and production capacity

A market analysis and the product spectrum of a plasma reactor system form the basis to select a production capacity of 2,500 t/a C_2F_4 and 625 t/a C_3F_6, both with a purity of 96 wt%.

Plasma reactor

A transfer-arc plasma reactor of 9.3 MW, operating at 20 kPa and 6,000 K together with a quenching probe capable of a typical cooling rate of 10^6 K/s and a filter to produce a solids-free C_xF_y-gas containing 40 wt% CF_4, 40 wt% C_2F_4, 10 wt% C_2F_6 and 10 wt% C_3F_6. The two low-value by-products, CF_4 and C_2F_6 are recycled from the separation plant into the plasma reactor, in order to avoid losses of F-values.

Compressor system

The compressor system will provide the driving force to feed the separation plant from 20 kPa to 200 kPa. This compressor will be a diaphragm type compressor or a blower.

Separation plant

The separation section consists of:

- A 8 m/0.3 m packed column using 59080 kg/h n-hexane as absorbent. The CF_4 that is not absorbed is recycled to the plasma reactor;
- A 2 m/0.3 m packed distillation column with a partial condenser to regenerate the n-hexane as bottom product. The distillate is fed to the membrane unit;
- A 11 stage ideal recycle membrane cascade with a total surface area of 6084 m^2 and AF2400 Teflon as active separation polymer with a selectivity of 2.5 and a flux of 2^{-3} mol/m^2.s. The C_2F_6 rich retentate is recycled to the

plasma reactor and the C_2F_4/C_3F_6 permeate is the feed to the cryogenic distillation column;

- A 6 m/0.3 m cryogenic distillation column operated at 200 kPa and a partial condenser at – 70 ^{0}C.

Product storage

The 96 % C_2F_4 is stored as a liquid in two 10 m^3 tanks at – 50 ^{0}C and 200 kPa, equipped with a condenser system. Via an evaporator the C_2F_4 is fed to the PTFE plant, which is not part of the design. The C_2F_6, which is the main impurity in the C_2F_4 that is released from the PTFE plant, is recycled to the plasma reactor.

The 96 % C_3F_6 is stored for sale in 200 litre gas bottles with a maximum pressure of 2,000 kPa

Economic analysis

The variable cost of 6.72$/kg is the main cost driver. It was estimated that the capital cost of such a system will be R217 million. The system can be optimized if the evaporation of CaF_2 +C is done below 10kW / kg C_xF_y gas. Reducing the energy will reduce the amount of power supply units, which is becoming a scarce commodity in South Africa.

Using new innovative separation methods as opposed to the old unsafe cryogenic separation systems, the techno-economic study shows positive results. The following techno-economic indicators for the commercial plant are based on a conservative selling price of R80 per kg and sales volume of 2500 t/a C_2F_4 and 625 t/a C_3F_6, and shows an IRR = 29.17% and a NPV of R662 million, with a payback period of 3.7 years. Plants with a total turn-over of MR200 and above with an IRR of 15% and higher is considering viable by Pelchem board.

6.2 Recommendations

Process synthesis and techno-economic evaluation

The plasma arc needs to be refined to optimize energy usage to ensure that an energy-efficient plant can be built. The 10 kWh / kg C_xF_y gas formed at 6000 K is high and the optimum must be found at whichever level, still producing high yields of C_xF_y gases. At present the design is done with C mixed with the CaF_2; present and future experimental work must be done to conclusively prove that only the graphite rod alone will be sufficient as C reactant.

CF_4 is very stable and considered an uncondensable gas, therefore the CF_4 concentrations need to be reduced if possible by changing plasma and quench conditions so that a minimum is formed with a maximum of C_2F_4/C_3F_6 gases produced. Transforming CF_4 directly to C_2F_6 was done at lab scale and needs to be pursued at pilot level and can be a valuable technology to be added to this process.

Absorption is a solution to economically get rid of unwanted light gases from usable C_xF_y gases economically, if we consider the alternatives which are high-pressure unsafe cryogenic distillation. Little is known about absorbents which absorbed C_xF_y gases efficiently and in this respect more experimental work in the future is required, especially on C_2F_6/C_2F_4 separation.

Instead of using expensive cryogenic liquid storage, low-pressure gas storage should be investigated as a more feasible and safe method, even if the size of such a unit is physically huge.

Membrane separation

Due to high compressor costs, especially with high-purity gases, variable area type boosters should be considered.

Teflon AF2400 was found to be suitable for separating C_2F_6 from C_2F_4 and C_3F_6 experimentally but needs to be tested on the long term before a final decision can be made for building a plant. Other polymer membranes should be investigated to find separation factors higher than for AF2400 Teflon. The cost will be reduced if higher separation factors with high fluxes are found, decreasing area requirements.

Flow conditions with commercial membrane units need to be tested on a pilot scale, to optimize stage requirements which will have an end-result of reducing the number of costly compressors.

6.3 Outlook

The next step will be to design and build a pilot facility of approximately 1 to 10 kg/h of C_xF_y gas. If a successful pilot plant is erected and the problem areas pointed out in the recommendations can be solved, there is no reason why a plant to produce 2500 t/a C_2F_4 and 625 t/a C_3F_6, both with 96 % purity cannot be built.

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APPENDIX A: FLOW SHEETS

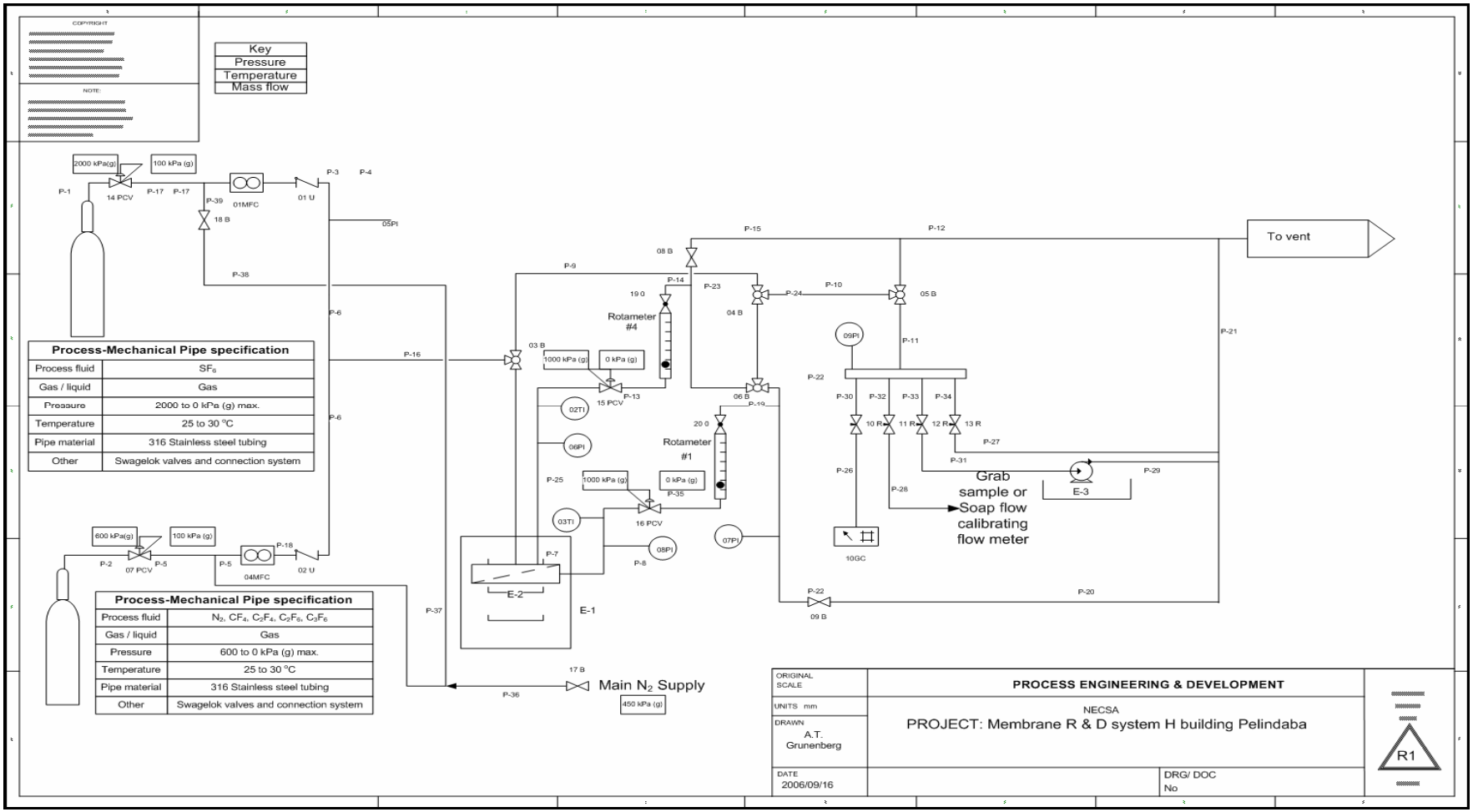

Figure A-1 Experimental flow sheet of membrane unit operation [Necsa]

APPENDIX B: EXPERIMENTAL DATA & CALCULATIONS

Firstly the tables with all the raw experimental data are given for the different experimental runs for the different gases.

Table B-1: Input values of Polymer (POMS) Membrane test C_2F_4/C_3F_6 gas mixture.

	Yellow = inputs				
	Flow valve =25%	Feed composition			
	Flow rate 231 ml/min (87kPa)	Mol mass		Mol Frac	
	C2F4	100.000	8	0.5	
	C3F6	150.000	8	0.5	
			16	1	
Gas: C_3F_6,TFE		The feed pressure is varied from 500 kPa(g) and the permeate pressure was kept constand at 87 kPa or 0 kPa(g)			
Feed temperature: K 300					
Feed pressure: 500 to 40 kPa (g)					
			A(m2)		stdev
delta P	Retentate	Permeate Volume Flow	Mol flow	0.004417865	0
(kPa)	ml/s	ml/s	mol/s	mol/m2s	interval
40.000	3.85	0.00	0	0	0
80.000	3.85	0.00	0	0	
120.000	3.85	0.00	0	0	
200.000	3.85	0.00	0	0	
300.000	3.85	0.00	0	0	
400.000	3.85	0.00	0	0	
500.000	3.85	0.00	0	0	

Table B-2: Input values of Nafion membrane test: CF_4/C_2F_4 gas mixture.

	Yellow = inputs				
	Flow valve =25%	Feed composition			
	Flow rate 231 ml/min (87kPa)	GC area	Mol Frac	Mol Frac	alpha
	CF4	245149.000	0.528	0.528247285	0.893
	C2F4	218931.000	0.472	0.471752715	
		464080.000	1.000	1	
Gas = CF4/C2F4		The feed pressure is varied from 500 kPa(g) and the permeate pressure was kept constand at 87 kPa or 0 kPa(g)			
Feed temperature: K 300					
Feed pressure: 500 to 40 kPa (g)					
			A(m2)		stdev
delta P	Retentate	Permeate Volume Flow	Mol flow	0.004417865	0
(kPa)	ml/s	ml/s	mol/s	mol/m2s	interval
40.000	3.85	0.00	0	0	0
80.000	3.85	0.00	0	0	
120.000	3.85	0.00	0	0	
200.000	3.85	0.00	0	0	
300.000	3.85	0.00	0	0	
400.000	3.85	0.00	0	0	
500.000	3.85	0.00	0	0	

Table B-3: Input values of Polymer (Poms) Membrane test CF_4/C_2F_4 gas mixture.

	Yellow = inputs				
	Flow valve =25%	Feed composition			
	Flow rate 231 ml/min (87kPa)	Mol mass		Mol Frac	
	CF4	88	8	0.5	
	TFE	100	8	0.5	
			16	1	
Gas: CF_4,TFE		The feed pressure is varied from 500 kPa(g) and the permeate pressure was kept constand at 87 kPa or 0 kPa(g)			
Feed temperature: K 300					
Feed pressure: 500 to 40 kPa (g)					
			A(m2)		stdev
delta P	Retentate	Permeate Volume Flow	Mol flow	0.004417865	0
(kPa)	ml/s	ml/s	mol/s	mol/m2s	interval
40.000	3.85	0.00	0	0	0
80.000	3.85	0.00	0	0	
120.000	3.85	0.00	0	0	
200.000	3.85	0.00	0	0	
300.000	3.85	0.00	0	0	
400.000	3.85	0.00	0	0	
500.000	3.85	0.00	0	0	

Table B-4: Input values of AF 2400 (PAN) Membrane test $C_2F_6/C_2F_4/C_3F_6$ gas mixture.

	Yellow = inputs					
	Flow valve =25%	Feed composition				
	Flow rate 140 ml/min (87kPa)	Mol mass	GC area	Mol Frac	Mol%	
	C2F6	138	5.6	0.07	7.11	
	TFE	100	49.7	0.63	63.07	
	C3F6	150	23.5	0.30	29.82	
			78.8	1		
Gas:C2F6,TFE/ C3F6		The feed pressure is varied from 240 kPa(g) and the permeate pressure was kept constand at 87 kPa or 0 kPa(g)				
Feed temperature: K 300						
Feed pressure: 240 to 60 kPa (g)						
			A(m2)	stdev	interval	
delta P	Permeate Volume Flow	Mol flow	0.004417865	0.004016722	0.001760406	
(kPa)	ml/sec	mol/s	mol/m2s			
240	1.6	5.47787E-05	0.012399365			
200	1.0	3.61148E-05	0.008174727			
160	0.5	1.7451E-05	0.003950088			
120	0.4	1.47847E-05	0.003346568			
100	0.3	1.21184E-05	0.002743049			
60	0.3	9.45748E-06	0.002140736			
0	0	0	0			

Table B-5: Permeate and Selectivity results of AF 2400 Teflon Membrane test: $C_2F_6/C_2F_4/C_3F_6$ gas mixture.

Total Permeate mol flow/s	**Permeate at 240 kPa(g)**				Flux
5.47787E-05	Mol mass	Area GC	Mol Frac	mol/s	mol/m2s
C2F6	138	4.156	0.051084124	2.79832E-06	0.000633411
C2F4	100	49.7	0.610895324	3.34641E-05	0.007574714
C3F6	150	27.5	0.338020552	1.85163E-05	0.00419124
		81.356	1		
Selectivity's (C2F4/C3F6)P/(C2F4/C3F6)F	0.854545455				
Selectivity's (C2F4/C2F6)P/(C2F4/C2F6)F	1.347449471	Average Selectivity C2F4/C3F6		1.462126021	
Selectivity's (C3F6/C2F6)P/(C3F6/C2F6)F	1.576802572				
Total Permeate mol flow/s	**Permeate at 200 kPa(g)**				Flux
3.61148E-05	Mol mass	Area GC	Mol Frac	mol/s	mol/m2s
C2F6	138	3.5	0.039727582	1.43476E-06	0.000324762
C2F4	100	57.3	0.650397276	2.3489E-05	0.00531682
C3F6	150	27.3	0.309875142	1.11911E-05	0.002533145
		88.1	1		
Selectivity's (C2F4/C3F6)P/(C2F4/C3F6)F	0.992438145				
Selectivity's (C2F4/C2F6)P/(C2F4/C2F6)F	1.844668008	Average Selectivity C2F4/C3F6		1.851695706	
Selectivity's (C3F6/C2F6)P/(C3F6/C2F6)F	1.858723404				
Total Permeate mol flow/s	**Permeate at 160 kPa(g)**				Flux
1.7451E-05	Mol mass	Area GC	Mol Frac	mol/s	mol/m2s
C2F6	138	3.4	0.037610619	6.56341E-07	0.000148565
C2F4	100	60.7	0.671460177	1.17176E-05	0.002652327
C3F6	150	26.3	0.290929204	5.07699E-06	0.001149196
		90.4	1		
Selectivity's (C2F4/C3F6)P/(C2F4/C3F6)F	1.091300656				
Selectivity's (C2F4/C2F6)P/(C2F4/C2F6)F	2.011599006	Average Selectivity C2F4/C3F6		1.927451568	
Selectivity's (C3F6/C2F6)P/(C3F6/C2F6)F	1.84330413				
Total Permeate mol flow/s	**Permeate at 120 kPa(g)**				Flux
1.47847E-05	Mol mass	Area GC	Mol Frac	mol/s	mol/m2s
C2F6	138	3.2	0.033862434	5.00645E-07	0.000113323
C2F4	100	66.2	0.700529101	1.03571E-05	0.002344369
C3F6	150	25.1	0.265608466	3.92694E-06	0.000888877
		94.5	1		
Selectivity's (C2F4/C3F6)P/(C2F4/C3F6)F	1.247084098				
Selectivity's (C2F4/C2F6)P/(C2F4/C2F6)F	2.330985915	Average Selectivity C2F4/C3F6		2.100067426	
Selectivity's (C3F6/C2F6)P/(C3F6/C2F6)F	1.869148936				
Total Permeate mol flow/s	**Permeate at 60 kPa(g)**				Flux
9.45748E-06	Mol mass	Area GC	Mol Frac	mol/s	mol/m2s
C2F6	138	2.55	0.028635598	2.70821E-07	6.13013E-05
C2F4	100	62.3	0.699606962	6.61652E-06	0.001497674
C3F6	150	24.2	0.27175744	2.57014E-06	0.000581761
		89.05	1		
Selectivity's (C2F4/C3F6)P/(C2F4/C3F6)F	1.217262251				
Selectivity's (C2F4/C2F6)P/(C2F4/C2F6)F	2.75283071	Average Selectivity C2F4/C3F6		2.507162122	
Selectivity's (C3F6/C2F6)P/(C3F6/C2F6)F	2.261493534				

Table B-6: Selectivity/ %Cut results of AF 2400 Teflon Membrane test: $C_2F_6/C_2F_4/C_3F_6$ gas mixture.

delta P (kPa)	Permeate Mol flow mol/s	Cut molf)p/mol)f	Selectivity (TFE/C2F6)P/(TFE/C2F6)F
240	5.47787E-05	0.67	1.35
200	3.61148E-05	0.44	1.84
160	1.7451E-05	0.21	2.01
120	1.47847E-05	0.18	2.33
100	1.21184E-05	0.15	3.52
60	9.45748E-06	0.12	2.75

Table B-7: Results of AF 2400 Teflon molar balance test of C_2F_6/C_2F_4 gas mixture

	Area membrane (m^2)	0.004417865					
	Temperature	300	K				
	Pressure	300	kPa				
		ml/min	ml/sec	Concentrations mol frac.			
At Pressure difference 300 kPa	Feed	504	8.4	C2F6	C2F4		Cut = mols)p /mols)f
						mol/sec	%cut
	Permeate	256.1	4.268333333	0.1	0.9	0.000148883	0.489674952
	Retentate	267.72	4.462	0.27	0.73	0.000155639	
		523.82	8.730333333			0.000304522	
	Temperature	300	K				
	Pressure	260	kPa				
		ml/min	ml/sec	Concentrations mol frac.			
At Pressure difference 260 kPa	Feed	504	8.4	C2F6	C2F4		Cut = mols)p /mols)f
						mol/sec	%cut
	Permeate	223.3	3.721666667	0.08	0.92	0.000129815	0.426959847
	Retentate	296.8	4.946666667	0.25	0.75	0.000172544	
		520.1	8.668333333			0.000302359	
Selectiviy calcs.							
Yellow = inputs							
Flow valve =80%			**Feed composition**				
Flow rate 504 ml/min (87kPa)	Mol mass	GC area	Mol Frac			Mol%	
C2F6	138	19.5	0.20			19.50	
C2F4	100	80.5	0.81			80.50	
		100	1				
					Feed N mol/s	**0.000304045**	
Total Permeate mol flow/s	**Permeate at 260 kPa(g)**						
3.721666667	Mol mass	Area GC	Mol Frac			mol/s	
C2F6	138	8.2	0.08			0.31	
C2F4	100	91.8	0.92			3.42	
		100	1				
Selectivity's (TFE/C2F6)P/(TFE/C2F6)F	2.711861839						
Total Permeate mol flow/s	**Permeate at 300 kPa(g)**						
4.268333333	Mol mass	Area GC	Mol Frac			mol/s	
C2F6	138	10.3	0.10			0.44	
C2F4	100	89.7	0.90			3.83	
		100	1				
Selectivity's (TFE/C2F6)P/(TFE/C2F6)F	2.109570042						

Table B-8: Results of AF 2400Teflon membrane molar balance test of $C_2F_6/C_2F_4/C_3F_6$ gas mixture

		Feed	Retentate	Permeate									
Total Flow		ml/min	ml/min	ml/min	R+P	%							
	Test1	712	637.68	59.22	696.90	0.104							
	Test2	710	637.68	66.62	704.30	0.102							
	Test3	709	637.68	66.62	704.30	0.101							
						10.228							
Test													
1		F	frac	mol/min	mol/s	P	frac	mol/min	mol/s	R	frac	mol/min	mol/s
	C2F4	75	0.681818182	0.016933103	0.00028222	46.4	0.573548	0.001185	1.97E-05	35	0.510949	0.011365	0.000189416
	C2F6	5	0.045454545	0.001128874	1.8815E-05	1.8	0.02225	4.6E-05	7.66E-07	6.5	0.094891	0.002111	3.51773E-05
	C3F6	30	0.272727273	0.006773241	0.00011289	32.7	0.404203	0.000835	1.39E-05	27	0.394161	0.008767	0.000146121
		110	1	0.024835218	0.00041392	80.9	1	0.002065	3.44E-05	68.5	1	0.022243	
				%Difference									
				2.121270306									
	Ave Selectivity	2.373148											
Test													
2		F	frac			P	frac	mol/min	mol/s	R	frac	mol/min	mol/s
	C2F4	75	0.681818182	0.016933103	0.00028222	48.2	0.577938	0.001194	1.99E-05	35	0.510949	0.011365	0.000189416
	C2F6	5	0.045454545	0.001128874	1.8815E-05	2.5	0.029976	6.19E-05	1.03E-06	6.7	0.09781	0.002176	3.62597E-05
	C3F6	30	0.272727273	0.006773241	0.00011289	32.7	0.392086	0.00081	1.35E-05	28.4	0.414599	0.009222	0.000153698
		110	1	0.024765456	0.00041276	83.4	1	0.002324	1.35E-05	70.1	1.023358	0.022243	
				%Difference									
				0.803030997									
	Ave Selectivity	1.732667											
Test		F	frac	mol/min	mol/s	P	frac	mol/min	mol/s	R	frac	mol/min	mol/s
3	C2F4	75	0.681818182	0.016933103	0.00028222	44.6	0.571063	0.00118	1.97E-05	35.4	0.516788	0.011495	0.000191581
	C2F6	5	0.045454545	0.001128874	1.8815E-05	2.5	0.03201	6.61E-05	1.1E-06	6.47	0.094453	0.002101	3.5015E-05
	C3F6	30	0.272727273	0.006773241	0.00011289	31	0.396927	0.00082	1.37E-05	26	0.379562	0.008443	0.000140709
		110	1	0.024730575	0.00041218	78.1	1	0.002324	3.87E-05	67.87	0.990803	0.022243	
				%Difference									
				0.663119898									

APPENDIX C: CALCULATIONS

C-1: Membrane area calculation

Membranes

The exposed area of the membrane can be calculated by taking the exposed diameter of the membrane, and calculating the area.

$d = 7.5cm$

$A = \pi * \frac{d^2}{4}$

$A = 4.42 \times 10^{-3} m^2$

C-2: Standard deviation calculation formula used

The standard deviation the data can be calculated by the following equation, obtained from Excel:

$$STDEV = \sqrt{\frac{\Sigma(x - \bar{x})^2}{(n-1)}}$$

A 95% confidence interval was chosen and calculated as:

$$95\% = average \pm 1.96 \frac{STDEV}{\sqrt{n}}$$

C-3: n-Hexane Absorption Conceptual design

n-Hexane Absorbtion Column Calculations

Mass balance

kmol/h	F	L	G_top	L_bot
CF4	4.062	0.000	4.062	0.000
CxFy	4.768	0.000	0.048	4.721
n-hexane	0.000	675.884	0.000	675.884
	8.830	675.884	4.109	680.604
mol/mol				
CF4	0.4600	0.0000	0.9884	0.0000
CxFy	0.5400	0.0000	0.0116	0.0069
n-hexane	0.0000	1.0000	0.0000	0.9931
	1.0000	1.0000	1.0000	1.0000

Stage requierments (N)

$y_{Top} := \frac{0.01}{1 + 0.01}$ $k := 1000$

$y_{CxFy} := 0.$ $y_2 := 1 - y_{CxFy}$ $X_2 := 0$ $K_{factor} := 128$ $x_0 := 0.$

$Mr_{CF4} := 88 \frac{kg}{kmol}$ $Mr_{CxFy} := 108 \frac{kg}{kmol}$ $n_{hexane} := 86 \frac{kg}{kmol}$

$Mr_{gas} := y_2 \cdot Mr_{CF4} + Mr_{CxFy} \cdot y_{CxFy}$ $Mr_{gas} = 100 \frac{kg}{kmol}$

$G_{Top} := 4.11 \frac{kmol}{h}$ $F_{gas} := 8.8 \frac{kmol}{h}$

$L\_Lmin := 1.2$ $Lmin := 0.99 \cdot G_{Top} \cdot K_{factor}$ $Lmin = 520.819 \frac{kmol}{hr}$

$L := Lmin \cdot 1.2$ $L = 624.983 \frac{kmol}{hr}$ $L_{mass} := L \cdot 86$ $L_{mass} = 5.375 \times 10^4 \frac{kg}{hr}$

$A := \frac{L}{K_{factor} \cdot G_{Top}}$ $A = 1.188$

$$N := \left[\frac{\log\left[\frac{(y_{CxFy})}{(y_{Top})} \cdot \left(1 - \frac{1}{A}\right) + \frac{1}{A} \right]}{\log(A)} \right] \qquad N = 13.611$$

Kremser-Brown Souders

Column Diameter calculation

$\rho_v := 7$ $\rho_L := 660 \frac{kg}{m^3}$

$$u_w := \left(-0.171 \cdot 0.6^2 + 0.27 \cdot 0.6 - 0.047\right) \cdot \left[\frac{(\rho_L - \rho_v)}{\rho_v} \right]^{0.5} \cdot \frac{m}{sec}$$

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$u_w = 0.516 \frac{m}{s}$

$Gasflow := \frac{925}{3600} \frac{kg}{sec}$ $\rho_v := 7 \frac{kg}{m^3}$

$$D_{column} := \sqrt{4 \cdot \frac{Gasflow}{\pi \cdot \rho_v \cdot u_w}} \qquad D_{column} = 0.301\,m$$

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C-3: n-Hexane Absorption Conceptual design (continued)

Cooler 1 Calculation

Assume 20% n-hexane entrainment

$$m_{total} := \left(4.09 \cdot Mr_{gas}\right) \cdot \frac{1}{3600} \frac{kg}{s}$$

$$\lambda hexane := 410 \frac{k \cdot J}{kg} \quad \Delta T := 50K \quad m_{hexane} := \left(4.09 \cdot Mr_{gas}\right) \cdot \frac{0.2}{3600} \quad cp := 3.45k \cdot \frac{J}{kg \cdot K}$$

$$Qcooling1 := m_{total} \cdot cp \cdot \Delta T + m_{hexane} \cdot \lambda hexane$$

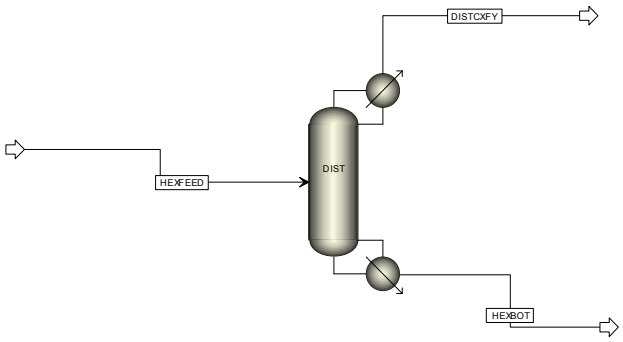
$$Qcooling1 = 28.914k \cdot W$$

Cooler 2 Calculation

$$\Delta T := 50K \quad m_{hexane} := 59080 \frac{kg}{hr}$$

$$Qcooling2 := m_{hexane} \cdot cp \cdot \Delta T \qquad Qcooling2 = 2.831 \times 10^{3} k \cdot W$$

C-4: n-Hexane/C_xF_y Distillation column conceptual design (continued)



Summary | Balance | Split Fraction | Reboiler | Utilities

View: Condenser / Top stage Basis: Mole

Condenser / Top stage performance

Temperature:	211.80746	K
Heat duty:	-66.099449	kW
Subcooled duty:		
Distillate rate:	3.7	kmol/hr
Reflux rate:	14.5873456	kmol/hr
Reflux ratio:	3.94252583	
Free water distillate rate:		
Free water reflux ratio:		

Summary | Balance | Split Fraction | Reboiler | Utilities

View: Reboiler / Bottom stage Basis: Mole

Reboiler / Bottom stage performance

Temperature:	260.085957	K
Heat duty:	55.4037094	kW
Bottoms rate:	0.6	kmol/hr
Boilup rate:	10.7962802	kmol/hr
Boilup ratio:	17.9938003	

Heat and Material Balance Table

Stream ID		HEXFEED	HEXBOT	DISTCXFY
From			B5	B5
To		B5		
Phase		LIQUID	LIQUID	VAPOR
Substream: MIXED				
Mole Flow	kmol/hr			
TFE		3.699423	1.64239E-3	3.697780
HFP		.6065720	.0553795	.5511925
C2F6		.6738525	1.25614E-4	.6737269
CF4		.0420432	1.23677E-7	.0420431
N-HEXANE		107.3370	107.3279	9.16505E-3
Mole Frac				
TFE		.0329250	1.52944E-5	.7434356
HFP		5.39852E-3	5.15710E-4	.1108168
C2F6		5.99732E-3	1.16975E-6	.1354522
CF4		3.74187E-4	1.15172E-9	8.45274E-3
N-HEXANE		.9553049	.9994678	1.84263E-3
Mass Flow	kg/hr			
TFE		370.0000	.1642649	369.8357
HFP		91.00000	8.308220	82.69178
C2F6		93.00000	.0173362	92.98266
CF4		3.700000	1.08842E-5	3.699989
N-HEXANE		9250.000	9249.210	.7898180
Mass Frac				
TFE		.0377254	1.77436E-5	.6724286
HFP		9.27842E-3	8.97439E-4	.1503487
C2F6		9.48235E-3	1.87263E-6	.1690594
CF4		3.77255E-4	1.17569E-9	6.72725E-3
N-HEXANE		.9431365	.9990829	1.43603E-3
Total Flow	kmol/hr	112.3589	107.3850	4.973908
Total Flow	kg/hr	9807.700	9257.700	550.0000
Total Flow	cum/hr	14.27266	15.17591	57.91427
Temperature	K	300.0000	357.1313	233.2927
Pressure	kPa	160.0000	160.0000	160.0000
Vapor Frac		0.0	0.0	1.000000
Liquid Frac		1.000000	1.000000	0.0
Solid Frac		0.0	0.0	0.0
Enthalpy	kJ/kmol	-2.2559E+5	-1.8687E+5	-8.0519E+5
Enthalpy	kJ/kg	-2584.399	-2167.639	-7281.677
Enthalpy	kW	-7040.837	-5574.265	-1112.478
Entropy	J/kmol-K	-6.2891E+5	-6.1488E+5	-1.6266E+5
Entropy	J/kg-K	-7204.968	-7132.372	-1471.052
Density	kmol/cum	7.872318	7.076019	.0858839
Density	kg/cum	687.1669	610.0261	9.496796
Average MW		87.28902	86.21036	110.5770
Liq Vol 60F	cum/hr	14.33172	13.97294	.3587804
*** LIQUID PHASE ***				
MUMX	Pa-sec	2.94669E-4	1.99049E-4	

C-5: Membrane unit conceptual design

alpha	2.5	beta	1.58							
yP	**n**	**loss prod fract**								
0.99	**21.43**	**0.002**	11.1235	0.016773						
0.90	**14.51**	**0.020**								
0.80	**12.17**	**0.039**								
F	kg/h	wt fract	mol/h	mol fract						
C2F4	352.176	0.664	3521.760	0.740						
C2F6	88.915	0.166	644.313	0.135						
C3F6	88.968	0.170	593.120	0.125						
	528.000	1.000	4759.193	1.000						
MW's	kg/kmol		**zA**	**0.865**						
C2F4	100									
C2F6	138	**Flow rates from fig 5.6**								
C3F6	150									
Prod loss	1.68	%								
zA	0.865									
xA	0.107	(for n=15)								
yA	0.969									
n	11									
nstrip	7.681442	8								
nenrich	3.318558	3								
iFeed		8	**counting from the bottom**							
beta	1.58									
F	4759.193	mol/h								
P	4088.436	mol/h								
R	645.868	mol/h								
Flux	**0.002**	mol/m2.s	assuming fixed ΔP=160 kPa							
Blue=stripping, red=enrichment, feed enters at 10										
j	Mj/R	Mj (mol/s)	Aj (m2)	yj	Nj (mol/s)	Cutj				
1	0.73	0.13	66	0.107	0.179	0.552	strip section (index=j)			
2	1.36	0.24	122	0.159	0.311	0.605				
3	2.01	0.36	180	0.230	0.423	0.610				
4	2.82	0.51	253	0.321	0.539	0.612				
5	3.96	0.71	356	0.428	0.685	0.624				
6	5.69	1.02	510	0.542	0.891	0.653				
7	8.37	1.50	751	0.652	1.200	0.697	**Note: changed molar flow rate from mol/h to mol/s**			
8	12.56	2.25	1127	0.747	1.681	0.751	0.865	zF		
9	2.13	2.42	1208	0.925	2.440	0.723				
10	1.66	1.89	944	0.951	1.281	0.665	enrich section			
11	1.00	1.14	568	0.969	0.752	0.540				
i	Mi/P	Mi (mol/s)	Ai (m2)	yi	Ni(mol/s)	Cuti				
		Mitot: compressor capacity			**12.17**	**mol/s**				
Cost calculation			3.E-01	5.E+04						
$/m2	400	**Atotal**	**6084**	**m2**						
$/R	7.5	**Cost**	**2.43**	**M$**						
			18.25	**MR**						

stage 15										
	P	kg/h	wt fract	mol/h	mol fract					
	C2F4	339.456	0.768	3394.56	0.830					
	C2F6	17.680	0.040	128.12	0.031					
	C3F6	84.864	0.192	565.76	0.138					
		442.000	1.000	4088.44	1.000					
			1.000							
		0.969	**=yA**							
		Fraction desired comp=C2F4+C3F6								
α=2										
n=15										
i_{Feed}=10	W	kg/h	wt fract	mol/h	mol fract					
	C2F4	5.916	0.068	59.160	0.092					
	C2F6	79.605	0.915	576.848	0.893					
	C3F6	1.479	0.017	9.860	0.015					
		87.000	1.000	645.868	1.000					
		0.107	**=zA**							
		Fraction desired comp=C2F4+C3F6								

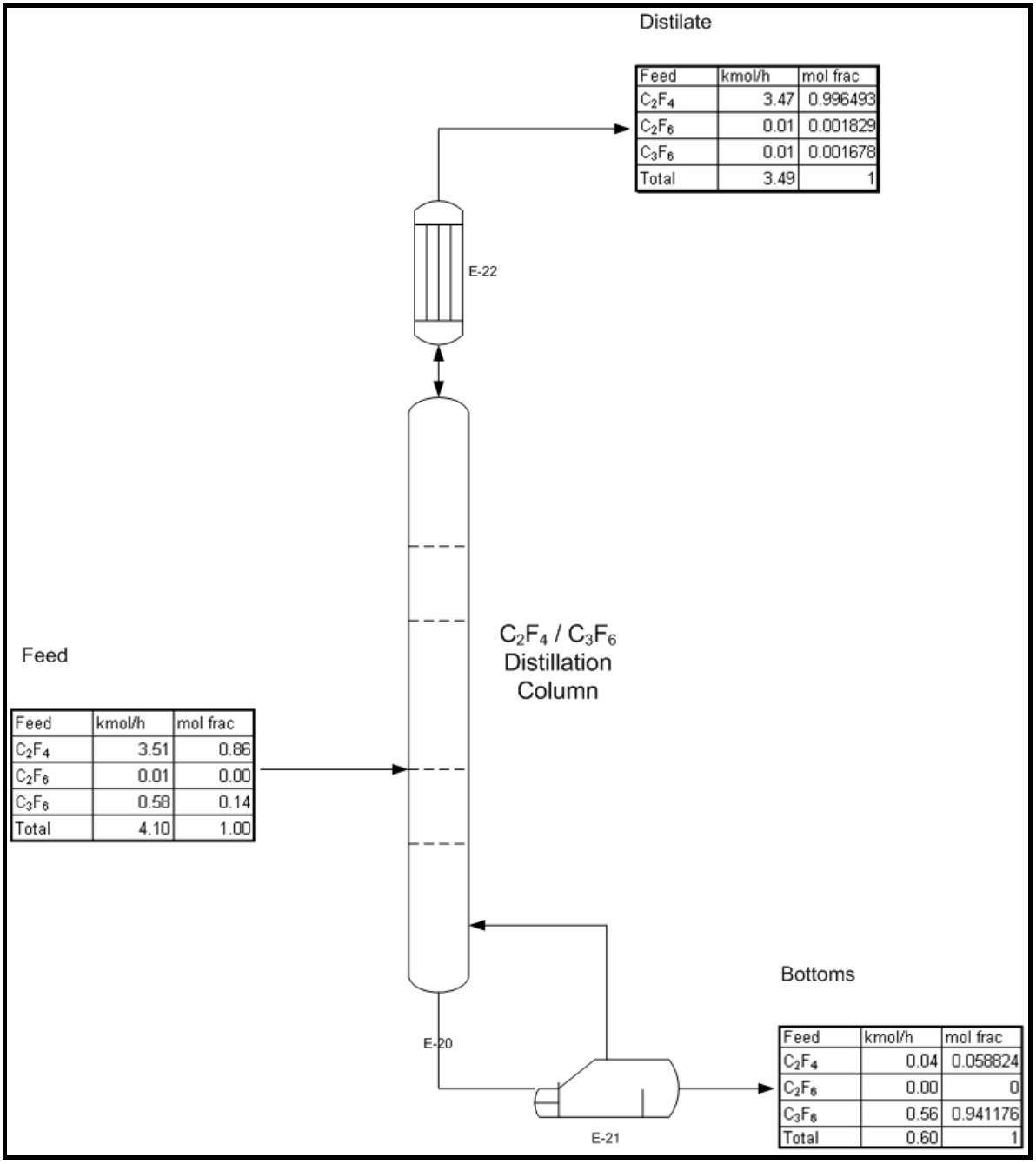
$$n = 2\frac{\ln\left[y_P(1-x_W)/(1-y_P)x_W\right]}{\ln\alpha} - 1$$

$$n_s = 2\frac{\ln\left[z_F(1-x_W)/(1-z_F)x_W\right]}{\ln\alpha} - 1$$

$$\frac{M_j}{R} = \frac{N_{j+1}}{R} - 1 = \frac{1}{\beta - 1}\left[x_A\beta(\beta^j - 1) + (1 - x_A)(1 - \beta^{-j})\right]$$

$$\frac{M_i}{P} = \frac{N_{i+1}}{P} + 1 = 1 + \frac{1}{\beta - 1}\left[y_A(1 - \beta^{i-n}) + (1 - y_A)\beta(\beta^{n-i} - 1)\right]$$

C-6: C_2F_4/C_3F_6 Distillation conceptual design



C-6: C_2F_4/C_3F_6 Distillation conceptual design (continued)

C_2F_4/C_3F_6 Distillation conceptual design

$C \equiv 1000$ $K \equiv 1$ $kmol := k \cdot mol$

Mass feed input

$Total\_feed := 439 \frac{kg}{hr}$ $Mass\%\_feed\_C2F4 := 80\%$ $Mass\%\_feed\_C3F6 := 20\%\%$

$Mass\%\_distilate\_C2F4 := 96\%$ $Mass\%\_bottoms\_C3F6 := 96\%$

$Mass\%\_bottoms\_C2F4 := 4\%$ $Mass\%\_distilate\_C3F6 := 4\%$

$xf := Mass\%\_feed\_C2F4$ $x_w := Mass\%\_bottoms\_C2F4$ $x_d := Mass\%\_distilate\_C2F4$

$F := Total\_feed$

Feed properties

$C2F4_{molmass} := 100 \frac{kg}{k \cdot mol}$ $C3F6_{molmass} := 150 \frac{kg}{k \cdot mol}$

$Mr_{ave\_feed} := (0.85 \cdot C2F4_{molmass}) + (0.15 \cdot C3F6_{molmass})$ $Mr_{ave\_feed} = 107.5 \frac{kg}{k \cdot mol}$

$Mol\_feed := \frac{Total\_feed}{Mr_{ave\_feed}}$ $Mol\_feed = 4.084 \frac{kmol}{hr}$

Calculations

F=Feed kg/h W=Bottoms feed rate kg/h D=Distillate feed rate kg/h

$F = W + D$ $W = F - D$ $V_W = (R + 1) \cdot D$

Mass balance

$F \cdot xf = x_W + x_d \cdot D$

Thus: Replace with W=F-D

$F \cdot x_W = (F - D) + x_d \cdot D$ $D := 347 \frac{kg}{hr}$

$W := F - D$ $W = 92 \frac{kg}{hr}$

$R := 1.2$ Assumption

$V_w := D \cdot (R + 1)$ $V_w = 763.4 \frac{kg}{hr}$

C-6: C_2F_4/C_3F_6 Distillation conceptual design (continued)

Molar Balance

$$xD := \left[\frac{\left(\frac{Mass\%\_distilate\_C2F4}{C2F4_{molmass}} \right)}{\left(\frac{Mass\%\_distilate\_C2F4}{C2F4_{molmass}} \right) + \left(\frac{Mass\%\_distilate\_C3F6}{C3F6_{molmass}} \right)} \right] \qquad xD = 0.973$$

$$xB := \left[\frac{\left(\frac{Mass\%\_bottoms\_C2F4}{C2F4_{molmass}} \right)}{\left(\frac{Mass\%\_bottoms\_C2F4}{C2F4_{molmass}} \right) + \left(\frac{Mass\%\_bottoms\_C3F6}{C3F6_{molmass}} \right)} \right] \qquad xB = 0.059$$

$$xF := \left[\frac{\left(\frac{Mass\%\_feed\_C2F4}{C2F4_{molmass}} \right)}{\left(\frac{Mass\%\_feed\_C2F4}{C2F4_{molmass}} \right) + \left(\frac{Mass\%\_feed\_C3F6}{C3F6_{molmass}} \right)} \right] \qquad xF = 0.998$$

q Line calculation

Input

Taking datum T_{ref} =273K

Assum feed at bloiling point

$q := 1$ $\quad q_{helling} := 1$ $\quad y_{operating} := \frac{xD}{R+1}$ $\quad y_{operating} = 0.442$

Mass feed input

$u_w := V_w \quad u_w = 763.4 \frac{kg}{hr}$

Column Diameter

$\rho_V := 7 \frac{kg}{m^3}$ Ideal gas law $\quad \rho_L := 1400 \frac{kg}{m^3}$

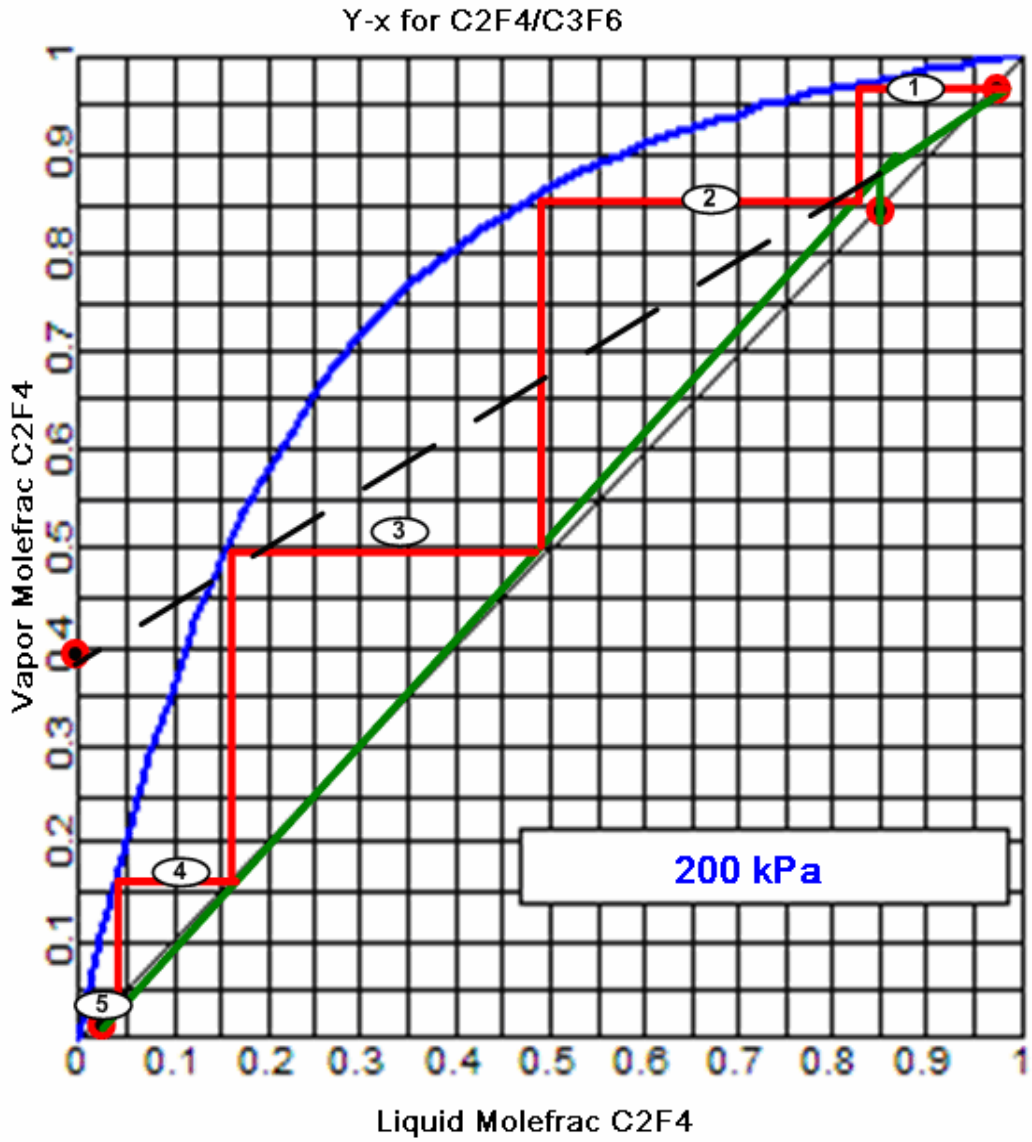
Assume tray spacing 0.6m

$l_t := 0.6$

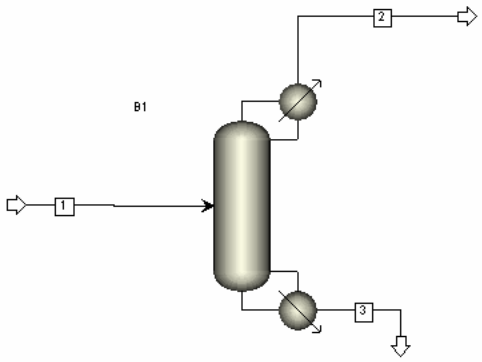
$$u_v := \left(-0.171 \cdot l_t^2 + 0.27 l_t - 0.047 \right) \cdot \left[\frac{(\rho_L - \rho_V)}{\rho_V} \right]^{0.5} \quad u_v = 0.754 \quad u_v := u_v \cdot 1 \frac{m}{sec} \quad u_v = 0.754 \frac{m}{s}$$

$$D_c := \sqrt{\left(4 \cdot \frac{u_w}{\pi \cdot \rho_V \cdot u_v} \right)} \qquad D_c = 0.226m$$

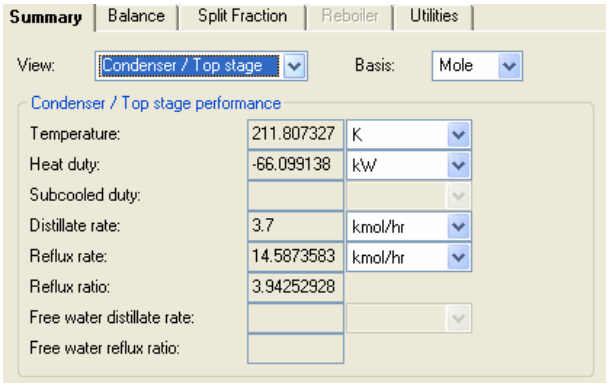
C-6: C_2F_4/C_3F_6 Distillation conceptual design (continued)

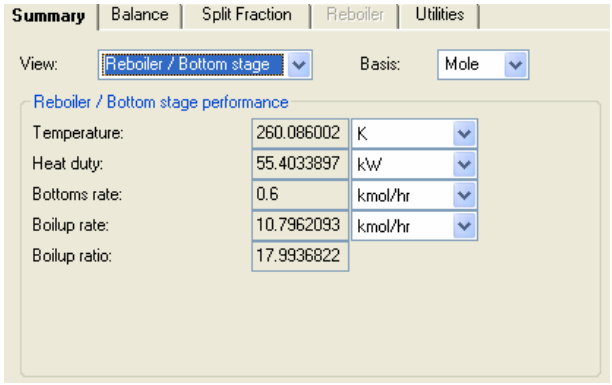


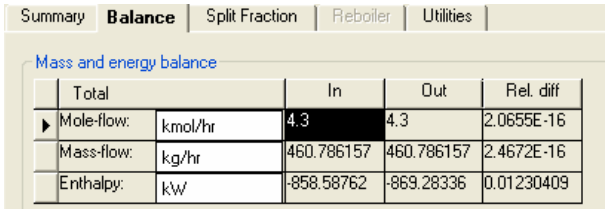
C-7: C_2F_4/C_3F_6 Distillation Aspen Simulation



Heat and Material Balance Table				
Stream ID		1	2	3
From			B1	B1
To		B1		
Phase		VAPOR	VAPOR	LIQUID
Substream: MIXED				
Mole Flow	kmol/hr			
TFE		3.685714	3.683764	1.95012E-3
HFP		.6142857	.0162358	.5980499
Mole Frac				
TFE		.8571429	.9956119	3.25020E-3
HFP		.1428571	4.38806E-3	.9967498
Mass Flow	kg/hr			
TFE		368.6289	368.4339	.1950421
HFP		92.15723	2.435755	89.72148
Mass Frac				
TFE		.8000000	.9934323	2.16915E-3
HFP		.2000000	6.56768E-3	.9978309
Total Flow	kmol/hr	4.300000	3.700000	.6000000
Total Flow	kg/hr	460.7862	370.8696	89.91652
Total Flow	cum/hr	51.96701	30.69051	.0612844
Temperature	K	298.0000	211.8073	260.0860
Pressure	kPa	200.0000	200.0000	200.0000
Vapor Frac		1.000000	1.000000	0.0
Liquid Frac		0.0	0.0	1.000000
Solid Frac		0.0	0.0	0.0
Enthalpy	kJ/kmol	-7.1882E+5	-6.6713E+5	-1.1017E+6
Enthalpy	kJ/kg	-6707.917	-6655.661	-7351.681
Enthalpy	kW	-858.5876	-685.6618	-183.6215
Entropy	J/kmol-K	-1.2307E+5	-1.4872E+5	-2.3684E+5
Entropy	J/kg-K	-1148.436	-1483.735	-1580.421
Density	kmol/cum	.0827448	.1205585	9.790406
Density	kg/cum	8.866898	12.08418	1467.199
Average MW		107.1596	100.2350	149.8609
Liq Vol 60F	cum/hr	.3024685	.2441060	.0583625
*** LIQUID PHASE ***				
MUMX	cP			.7021370







C-8: Storage Tank conceptual design

Storage Tanks heat losses

Assumptions

2m diameter

$50\,\frac{W}{m^2}$ Heat loss to enviroment

Condensers to match distillation column condenser

Tank dimensions

$D := 2m \quad Vol := 10m^3 \quad k := 1000$

$h := Vol \cdot \frac{4}{\pi \cdot D^2} \qquad h = 3.183\,m$

$Area := \pi \cdot D \cdot h \qquad Area = 20\,m^2$

Two Tanks

$Heat\_loss := 2Area \cdot 50\,\frac{W}{m^2} \qquad Heat\_loss = 2\,k \cdot W$

Condensers

$Duty_{condensers} := 66kW$

Total cooling requierments

$Q_{tanks} := Duty_{condensers} + Heat\_loss$

$Q_{tanks} = 68\,kW$

APPENDIX D: ECONOMIC ANALYSIS

D-1 Cost estimation 2500 t/aC_2F_4 & 625 t/a C_3F_6 equipment cost estimation

Method Peters and Timmerhaus
Plant design and Economics 3rd Ed (p166)

$$Cost_{equipment(a)} = Cost_{equipment(b)}\left(\frac{capcity_{ecuipmet(a)}}{capcity_{ecuipmet(b)}}\right)^{n}$$

Historical data from old TFE Plant Necsa

Equipment Description	Cost 1995 Equip. (b)	Capacity 1995 Equip. (b)	Cost 2008 New cost equip. (a)	New Capacity equip.(a)	*n = factor	Total
Plasma arc system						
Power supply	N/A	1MW	** R3/W	10MW	-	1 unit = MR30
Plasma reactor	MR 0.1	100 kg/h	MR 0.297plasma	925 kg/h	0.49	10 units = RM2.9
Filter tank	MR 0.1	100 kg/h	MR 0.925	925 kg/h	0.49	1 of MR2.97
Compressors	MR 1	50 kg/h F2 comp.	MR 7.49	925 kg/h	0.69	2 units = RM 14.97
Separation plant						
Absorption Column	C_4F_8 absorption MR 0.5 (Necsa)	0.3m dia by 3m	MR0.92	0.3m dia by 8m	0.62	1 unit = MR 0.92
n-Hexane Dist.	Limonene C_4F_8 Dist MR1 (Necsa	109 kg/h C_4F_8 Feed	MR 2.73	550 kg/h C_xF_y Feed	0.62	1 unit = MR 2.73
Membrane	N/A	N/A	***$400m^2	6084 m^2	-	1 unit = MR 18.25
C_xF_y Dist.	MR1	133 kg/h C_xF_y Feed	MR 2.89	457	0.86	1 unit = MR 2.89
C_2F_4 Storage	MR1	2000 kg C_2F_4 liq. cryogenic	MR 19.5	15000 kg C_2F_4 liq. cryogenic	0.59 *2.5 (stainless)	1 unit = MR 19.5
C_3F_6 Storage	N/A	N/A	1 MR Comp.	80kg/h	-	1 unit = MR 1

* Peters and Timmerhaus, Plant design and Economics 3rd Ed (p166)
** Necsa specializes equipment, experience based estimation Plasma group
*** North West University cost factor/m^2 [Hein Neomagus]

D-2 Exponent for equipment cost (Pieter and Timmerhaus)

Typical exponents for equipment cost vs. capacity

Equipment	Size range	Exponent
Blender, double cone rotary, c.s.	50–250 ft^3	0.49
Blower, centrifugal	10^3–10^4 ft^3/min	0.59
Centrifuge, solid bowl, c.s.	10–10^2 hp drive	0.67
Crystallizer, vacuum batch, c.s.	500–7000 ft^3	0.37
Compressor, reciprocating, air-cooled, two-stage, 150 psi discharge	10–400 ft^3/min	0.69
Compressor, rotary, single-stage, sliding vane, 150 psi discharge	10^2–10^3 ft^3/min	0.79
Dryer, drum, single vacuum	10–10^2 ft^2	0.76
Dryer, drum, single atmospheric	10–10^2 ft^2	0.40
Evaporator (installed), horizontal tank	10^2–10^4 ft^2	0.54
Fan, centrifugal	10^3–10^4 ft^3/min	0.44
Fan, centrifugal	2×10^4–7×10^4 ft^3/min	1.17
Heat exchanger, shell and tube, floating head, c.s.	100–400 ft^2	0.60
Heat exchanger, shell and tube, fixed sheet, c.s.	100–400 ft^2	0.44
Kettle, cast iron, jacketed	250–800 gal	0.27
Kettle, glass lined, jacketed	200–800 gal	0.31
Motor, squirrel cage, induction, 440 volts, explosion proof	5–20 hp	0.69
Motor, squirrel cage, induction, 440 volts, explosion proof	20–200 hp	0.99
Pump, reciprocating, horizontal, cast iron (includes motor)	2–100 gpm	0.34
Pump, centrifugal, horizontal, cast steel (includes motor)	10^4–10^5 gpm × psi	0.33
Reactor, glass lined, jacketed (without drive)	50–600 gal	0.54
Reactor, S.S., 300 psi	10^2–10^3 gal	0.56
Separator, centrifugal, c.s.	50–250 ft^3	0.49
Tank, flat head, c.s.	10^2–10^4 gal	0.57
Tank, c.s., glass lined	10^2–10^3 gal	0.49
Tower, c.s.	10^3–2×10^6 lb	0.62
Tray, bubble cup, c.s.	3–10 ft diameter	1.20
Tray, sieve, c.s.	3–10 ft diameter	0.86

D-3: Feasible analysis

FEASIBILITY ANALYSIS OF THE < CxFy PLANT > PRODUCTION PLANT

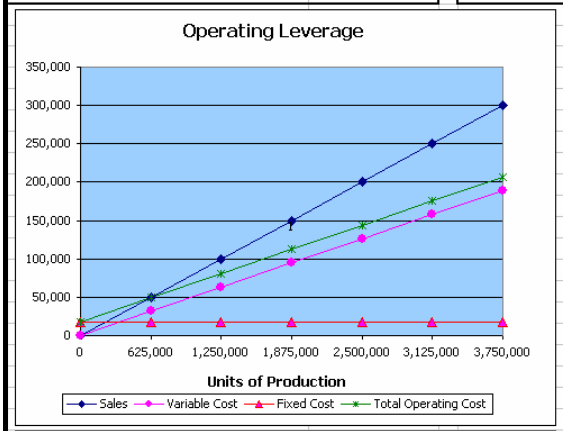
PROJECT INFORMATION:	
Cost of Equity [R150]	12.50%
-> Inflation	9.40%
Real Cost of Capital	***3.10%***
Cost of Debt [Prime]	13.50%
-> Inflation	9.40%
Real Cost of Debt	***4.10%***
Debt : Equity Ratio	100.00%
Risk Premium	
Company Tax Rate	30.00%
WACC - Nominal	**4.67%**
RADR - Nominal	**4.67%**
Cash Flows Method:	Nominal
Project Life Expectancy (yrs):	20 yrs
Amortisation period (yrs):	10 yrs
Investment rate (%):	8.00%
Accounts Receivable days:	45 days
Accounts Payable days:	30 days
Inventory days in Sales:	90 days
Salvage value/(Decomm. cost):	8,000,000
Average Sales Price / Kg	R 80.00
Average Variable Cost / 1000 Kg	R 50.38
Variable cost %	60%
Marginal Income %	40%

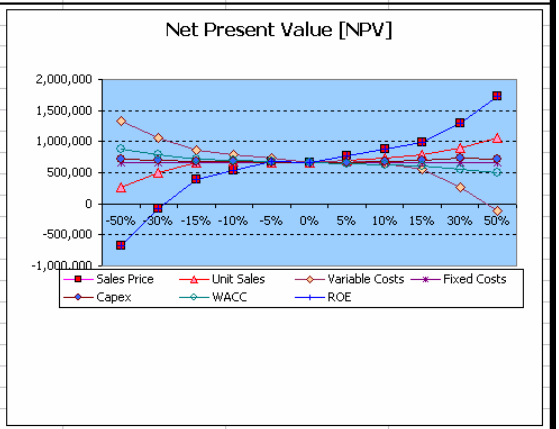
SENSITIVITY ANALYSIS:	
Minimum Sales in Kg's [Break-even]	595,306
Minimum Sales Price / Kg	R 54.62
Max Variable Cost / Kg	R 74.36
Max Fixed Cost / Kg	R 29.62

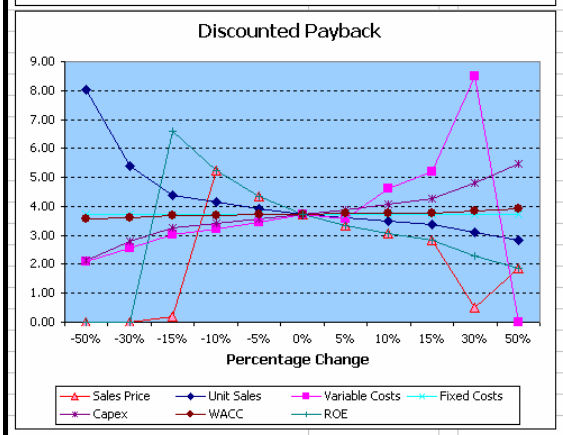
CAPITAL BUDGET DECISION TOOLS:		
Net Present Value [NPV]	Thousands	661,870
Internal Rate of Return [IRR]	%	29.17%
Modified IRR [MIRR]	%	17.16%
Payback Period	Years	3.73 yrs
Profitability Index	Times	3.67
Gross Profit %	%	33%
Earnings Before Interest & Tax	Thousands	80,318

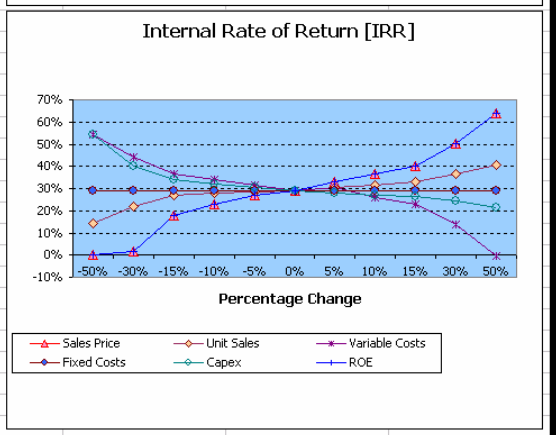
CASH FLOW:	Capex (kR)	Sales (kR)	Sales (Kg's)
Year 0	200,000		
Year 1	50,000	250,000	3,125,000
Year 2		240,000	3,000,000
Year 3		240,000	3,000,000
Year 4		240,000	3,000,000
Year 5		240,000	3,000,000
Year 6		240,000	3,000,000

SENSITIVITIES:	NPV (kR)	IRR (%)	DC-Payback
+10% Change in:			
Sales Price	875,424,334	36.53%	3.1 yrs
Unit Sales	742,671,937	31.71%	3.5 yrs
Variable Costs	650,910,289	25.87%	4.6 yrs
Fixed Costs	661,779,720	29.17%	3.7 yrs
Capex	684,441,314	27.21%	4.1 yrs
WACC	626,857,864	No Change	3.8 yrs
ROE	875,424,334	36.53%	3.1 yrs
-10% Change in:			
Sales Price	538,410,871	22.70%	5.2 yrs
Unit Sales	673,890,216	27.82%	4.1 yrs
Variable Costs	797,848,121	34.27%	3.2 yrs
Fixed Costs	661,960,623	29.18%	3.7 yrs
Capex	674,684,757	32.10%	3.4 yrs
WACC	699,053,293	No Change	3.7 yrs
ROE	538,410,871	22.70%	5.2 yrs









Enquiries: J Kotze [082 808 5103]	Version: Rev2004ajl	Filename: MSc economic analysis model R5.xls	25-May-2008

D-4: Financial statements

FINANCIAL STATEMENTS OF THE < CxFy PLANT > PRODUCTION PLAN

#N/A

Description	2008-09	2009-10	2010-11	2011-12	2012-13	2013-14	2014-15	2015-16	2016-17	2017-18	2018-19
		1	2	3	4	5	6	7	8	9	10
SALES [Kilograms]		*3,125,000*	*3,000,000*	*3,000,000*	*3,000,000*	*3,000,000*	*3,000,000*	*3,000,000*	*3,000,000*	*3,000,000*	*3,000,000*
SALES/REVENUE		250,000	240,000	240,000	240,000	240,000	240,000	240,000	240,000	240,000	240,000
VARIABLE COSTS		153,050	144,385	144,385	144,385	144,385	144,385	144,385	144,385	144,385	144,385
		39%	40%	40%	40%	40%	40%	40%	40%	40%	40%
MARGINAL INCOME		96,950	95,615	95,615	95,615	95,615	95,615	95,615	95,615	95,615	95,615
DIRECT FIXED COSTS		15,165	16,165	16,165	16,165	16,165	16,165	16,165	16,165	16,165	16,165
Direct Labour		4,060	4,060	4,060	4,060	4,060	4,060	4,060	4,060	4,060	4,060
Direct Material		15	15	15	15	15	15	15	15	15	15
Quality Costs		275	275	275	275	275	275	275	275	275	275
Depreciation Equip & Plant		10,000	11,000	11,000	11,000	11,000	11,000	11,000	11,000	11,000	11,000
Factory Costs		25	25	25	25	25	25	25	25	25	25
Rental Building		0	0	0	0	0	0	0	0	0	0
Product Distribution		100	100	100	100	100	100	100	100	100	100
Indirect Labour Costs		80	80	80	80	80	80	80	80	80	80
Repair & Maintenance		360	360	360	360	360	360	360	360	360	360
Other Operating Costs		250	250	250	250	250	250	250	250	250	250
		33%	33%	33%	33%	33%	33%	33%	33%	33%	33%
GROSS PROFIT/(LOSS)		81,785	79,450	79,450	79,450	79,450	79,450	79,450	79,450	79,450	79,450
BUSINESS OVERHEADS		1,467	1,442	1,442	1,442	1,442	1,442	1,442	1,442	1,442	1,442
Management & Overheads		1,017	992	992	992	992	992	992	992	992	992
Marketing Costs		350	350	350	350	350	350	350	350	350	350
Development Costs		100	100	100	100	100	100	100	100	100	100
PROFIT/(LOSS)		32%	33%	33%	33%	33%	33%	33%	33%	33%	33%
Before Interest		80,318	78,008	78,008	78,008	78,008	78,008	78,008	78,008	78,008	78,008
INTEREST	12,851	33,495	36,265	31,462	25,966	19,674	12,471	4,225	-5,216	-16,027	-29,123
Interest on Cash		-299	-1,661	-4,054	-6,818	-10,007	-13,688	-17,937	-22,842	-28,504	-35,755
Interest on Loan	12,851	33,794	37,925	35,517	32,783	29,680	26,159	22,162	17,626	12,477	6,633
		19%	17%	19%	22%	24%	27%	31%	35%	39%	45%
NET PROFIT before TAX	-12,851	46,823	41,744	46,546	52,043	58,335	65,538	73,784	83,225	94,035	107,131
TAXATION		14,047	12,523	13,964	15,613	17,500	19,661	22,135	24,967	28,211	32,139
SA Normal Tax		3,847	2,623	4,064	5,713	19,600	22,961	25,435	28,267	31,511	35,439
Deferred Taxation		10,200	9,900	9,900	9,900	-2,100	-3,300	-3,300	-3,300	-3,300	-3,300
NET PROFIT/(LOSS) TO		13%	12%	14%	15%	17%	19%	22%	24%	27%	31%
DISTRIBUTABLE RESERVES	-12,851	32,776	29,221	32,582	36,430	40,834	45,876	51,649	58,257	65,825	74,992
#N/A											
Funds (Required)/Supplied by Business Activities	-12,851	42,776	40,221	43,582	47,430	51,834	56,876	62,649	69,257	76,825	85,992
Net Profit/(Loss) after Tax	-12,851	32,776	29,221	32,582	36,430	40,834	45,876	51,649	58,257	65,825	74,992
Add: Depreciation		10,000	11,000	11,000	11,000	11,000	11,000	11,000	11,000	11,000	11,000
(Acquisition)/Disposal of Assets	-200,000	-20,000									
(Increase)/Decrease Working Cap		-41,899	15,180	13,964	15,221	-2,100	-3,300	-3,300	-3,300	-3,300	-3,300
Inventory (Incr.)/Decr.		-37,738	2,137								
Trade Debtors (Incr.)/Decr.		-30,822	1,233								
Trade Creditors Incr./(Decr.)		12,614	-712								
Deferred Tax Incr./(Decr.)		14,047	12,523	13,964	15,221	-2,100	-3,300	-3,300	-3,300	-3,300	-3,300
TOTAL FUNDS (REQUIRED)/AVAILABLE	-212,851	-19,123	55,401	57,546	62,651	49,734	53,576	59,349	65,957	73,525	82,692
NET MOVEMENT IN SHAREHOLDER FUNDING	212,851	83,794	-17,840	-20,249	-22,982	-26,085	-29,606	-33,603	-38,140	-43,289	-49,133
Funds Obtained - Equity											
Funds Obtained - Loans	212,851	83,794	37,925	35,517	32,783	29,680	26,159	22,162	17,626	12,477	6,633
Repayment - Loans			-55,765	-55,765	-55,765	-55,765	-55,765	-55,765	-55,765	-55,765	-55,765
NET INFLOW TO / (OUTFLOW FROM) BANK		64,671	37,561	37,297	39,669	23,649	23,970	25,745	27,818	30,236	33,559

D-5: Financial statements (continued)

FINANCIAL STATEMENTS OF THE < CxFy PLANT > PRODUCTION PLAN

#N/A

Description	2008-09	2009-10	2010-11	2011-12	2012-13	2013-14	2014-15	2015-16	2016-17	2017-18	2018-19
		1	2	3	4	5	6	7	8	9	10
CAPITAL EMPLOYED											
SHARE CAPITAL											
ACCUM SURPLUS/(DEFICIT)	(12,851)	19,925	49,146	81,728	118,158	158,993	204,869	256,517	314,775	380,599	455,591
- Opening Balance		(12,851)	19,925	49,146	81,728	118,158	158,993	204,869	256,517	314,775	380,599
- Surplus/(Deficit)	(12,851)	32,776	29,221	32,582	36,430	40,834	45,876	51,649	58,257	65,825	74,992
NET SHAREHOLDER'S FUNDS	**(12,851)**	**19,925**	**49,146**	**81,728**	**118,158**	**158,993**	**204,869**	**256,517**	**314,775**	**380,599**	**455,591**
LONG TERM LOANS	212,851	296,645	278,805	258,556	235,574	209,489	179,882	146,279	108,139	64,851	15,718
CAPITAL EMPLOYED	**200,000**	**316,570**	**327,951**	**340,284**	**353,732**	**368,481**	**384,751**	**402,797**	**422,914**	**445,450**	**471,309**
EMPLOYMENT OF CAPITAL											
FIXED ASSETS	200,000	210,000	199,000	188,000	177,000	166,000	155,000	144,000	133,000	122,000	111,000
- Assets	200,000	220,000	220,000	220,000	220,000	220,000	220,000	220,000	220,000	220,000	220,000
- Accumulated Depreciation		(10,000)	(21,000)	(32,000)	(43,000)	(54,000)	(65,000)	(76,000)	(87,000)	(98,000)	(109,000)
NET OPERATING CAPITAL		106,570	128,951	152,284	176,732	202,481	229,751	258,797	289,914	323,450	360,309
CURRENT ASSETS		133,232	167,423	204,720	244,389	268,039	292,009	317,754	345,572	375,808	409,367
- Inventory		37,738	35,602	35,602	35,602	35,602	35,602	35,602	35,602	35,602	35,602
- Accounts Receivable		30,822	29,589	29,589	29,589	29,589	29,589	29,589	29,589	29,589	29,589
- Bank		64,671	102,232	139,530	179,199	202,848	226,818	252,563	280,381	310,617	344,176
CURRENT LIABILITIES		26,661	38,472	52,436	67,657	65,557	62,257	58,957	55,657	52,357	49,057
- Accounts Payable		12,614	11,902	11,902	11,902	11,902	11,902	11,902	11,902	11,902	11,902
- Provisions		14,047	26,570	40,534	55,755	53,655	50,355	47,055	43,755	40,455	37,155
- Bank											
EMPLOYMENT OF CAPITAL	**200,000**	**316,570**	**327,951**	**340,284**	**353,732**	**368,481**	**384,751**	**402,797**	**422,914**	**445,450**	**471,309**

D-6: Variables costs

Calcium Fluoride (Fluorspar)	0.02	R 1,900.00	R 34.20
Electricity Variable	30.00	R 0.22	R 6.60
Process water	1.30	R 3.46	R 4.50
Cooling water	1.30	R 0.40	R 0.52
Demin water		R 26.07	
Carbon	4.70	R 5.00	R 23.50
Subtotal Variable Cost: HFP			**R 69.32**
Description:C2F4	**BOM:**	**Price/Unit:**	**Cost:**
Calcium Fluoride (Fluorspar)	0.005	R 1,900.00	R 8.55
Electricity Variable	111.00	R 0.22	R 24.42
Process water	1.30	R 3.46	R 4.50
Demin water	0.10	R 26.07	R 2.61
Cooling water	1.30	R 0.40	R 0.52
Carbon	1.18	R 5.00	R 5.90
Subtotal Variable Cost: TFE			**R 46.50**