기체 분리막을 활용한 Hydrocarbon 회수 사례

이 재 학

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삼성 종합 화학
공정팀

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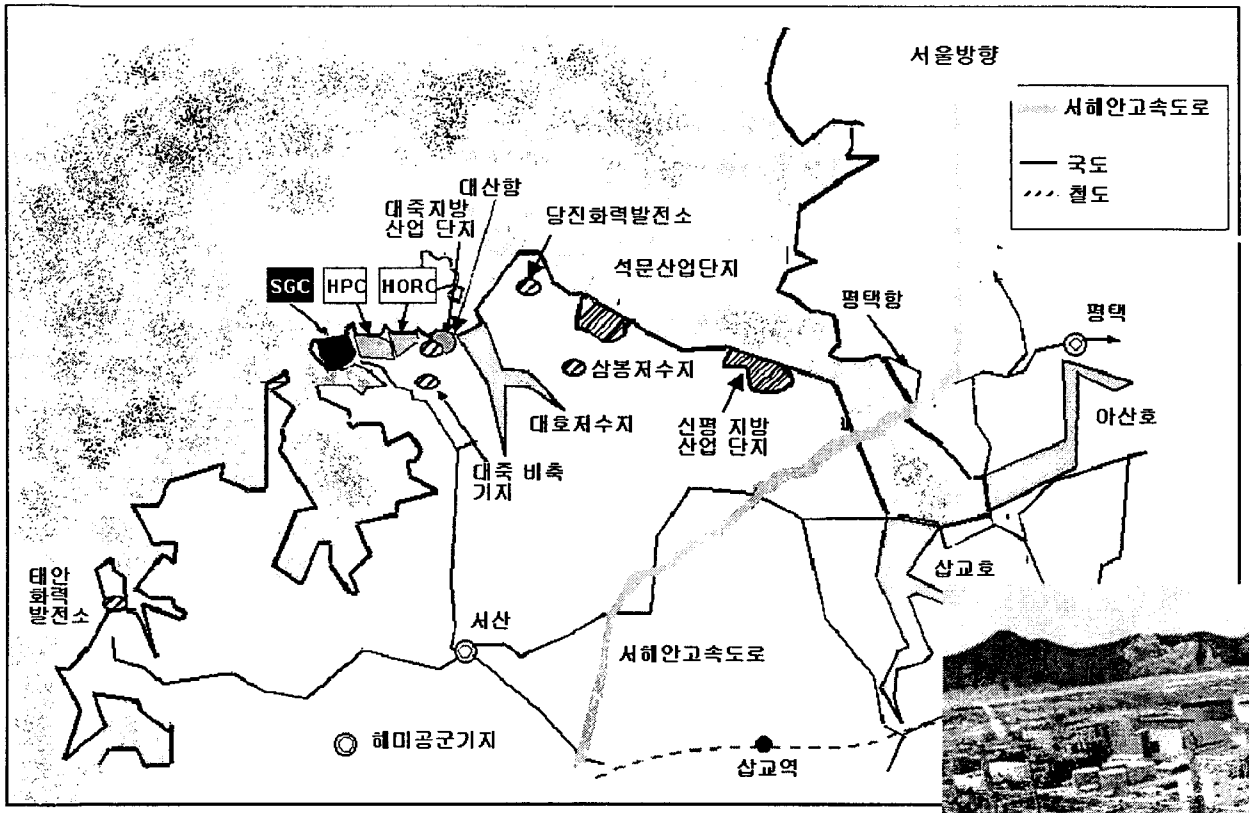
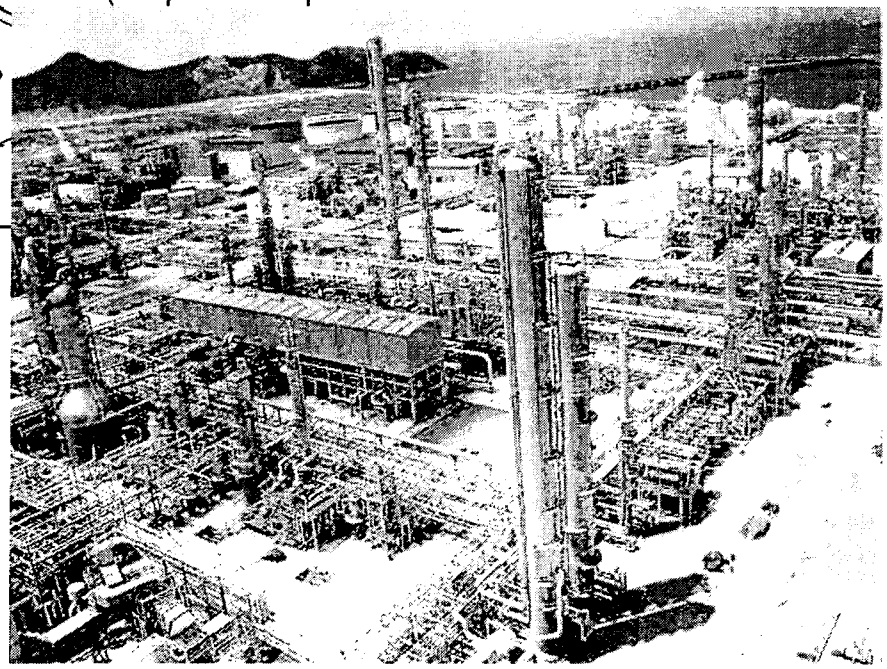
J H Lee

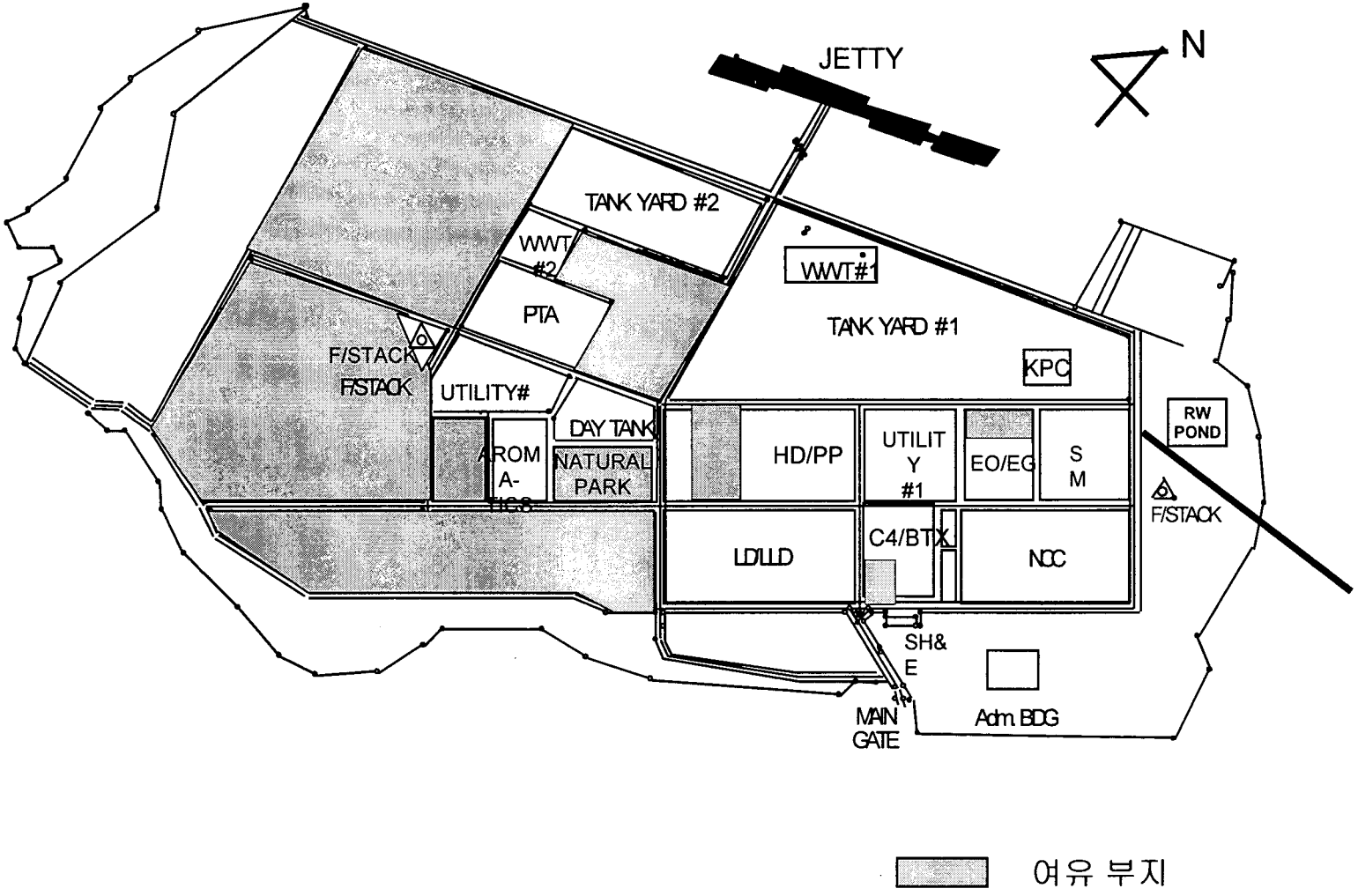
목 차

1.삼성 종합 화학 소개


서울방향
서해안고속도로
국도
철도
대산항
대죽지방
산업 단지
당진화력발전소
SGC
HPC
HORC
석문산업단지
평택항
평택
삼봉저수지
아산호
대호저수지
신평 지방
산업 단지
대죽 비축
기지
삽교호
태안
화력
발전소
서산
서해안고속도로
헤미공군기지
삽교역

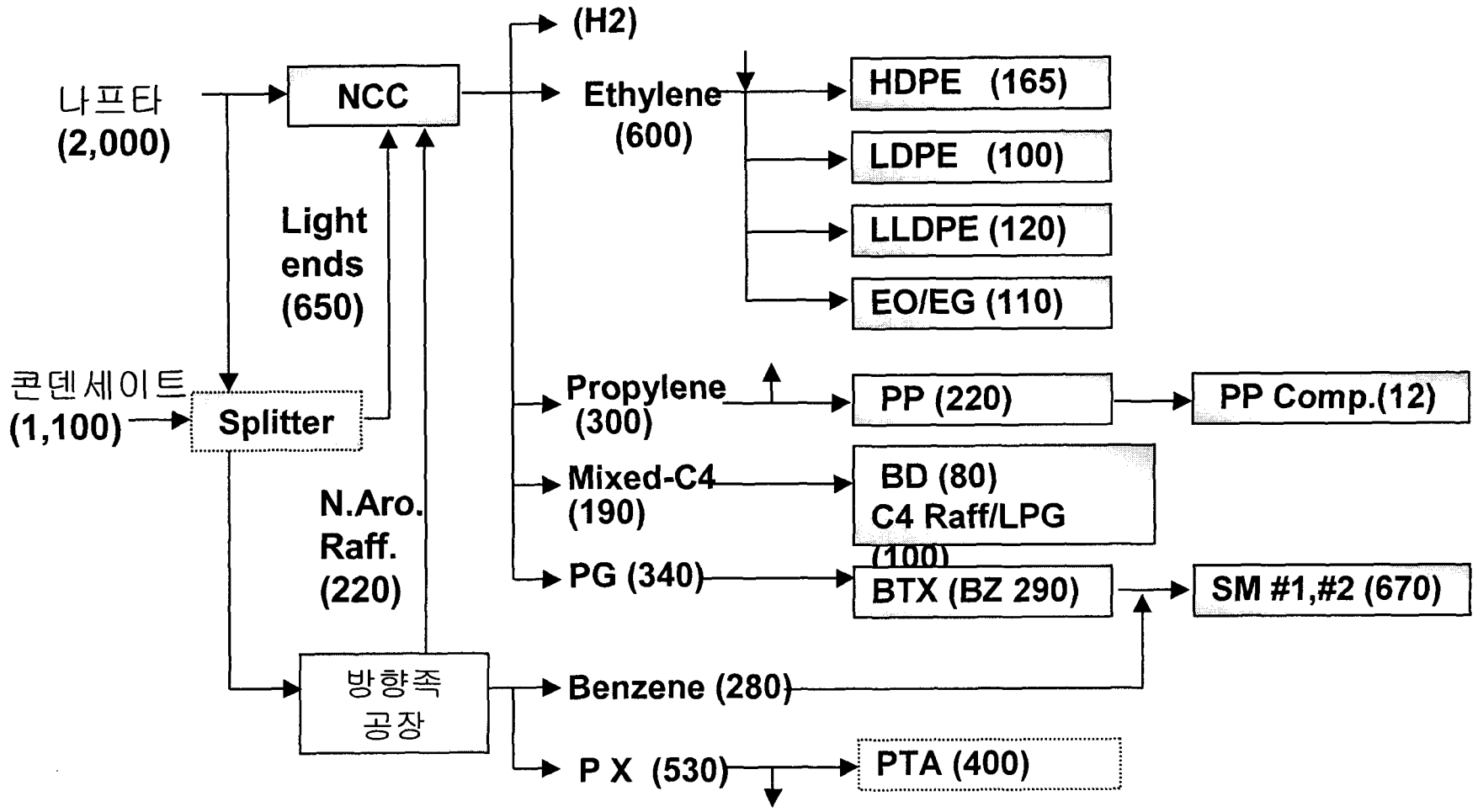


공장 **Layout**


JETTY
N
TANK YARD #2
WWT #2
PTA
WWT#1
TANK YARD #1
KPC
F/STACK
F/STACK
UTILITY#
DAY TANK
AROM A-
NATURAL PARK
HD/PP
UTILIT Y #1
EO/EG
S M
RW POND
F/STACK
LD/LLD
C4/BTX
NCC
SH& E
MAIN GATE
Adm BDG
여유 부지

생산 계통도

( ) : 천톤/365일
▭ : 공장



2.Gas Membrane 적용 사례

□ Project 배경

1) Off gas의 Value 향상

Hydrocarbon mixture + Inert Gas ====> Fuel gas

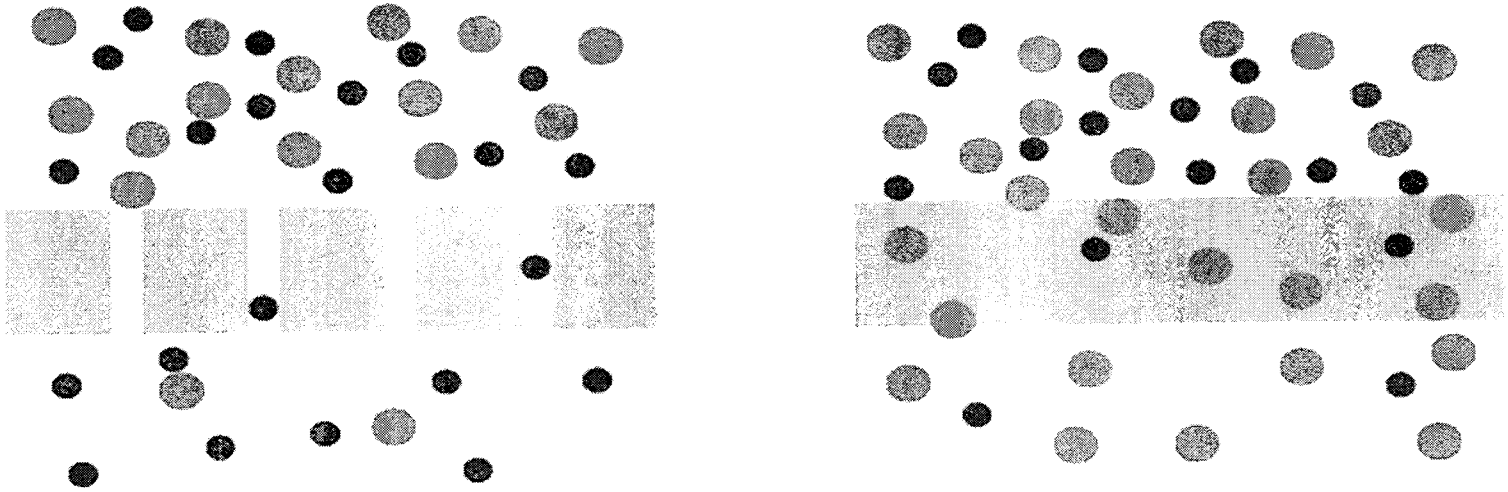
2)경제적인 분리 scheme발굴 : Energy saving

3) Debottlenecking tool

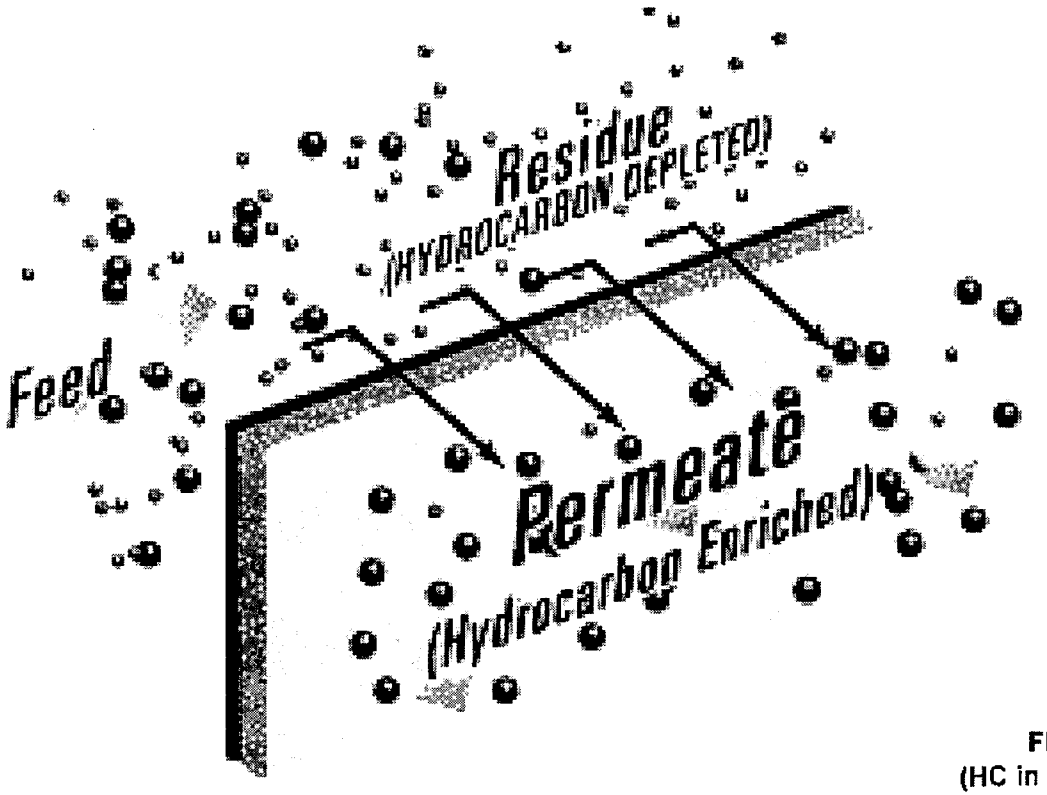
☐ Gas Membrane 특징

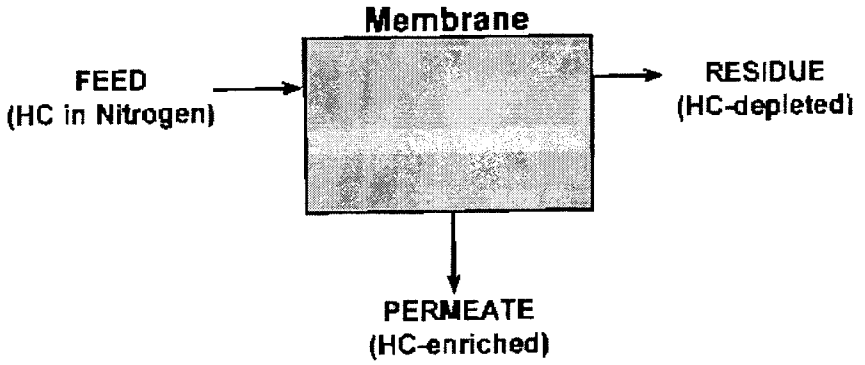
Size Selective

Solubility Selective



Gas 분리 Scheme





Permeability/Selectivity특성

Membrane Selectivity

MTR MEMBRANE TECHNOLOGY & RESEARCH

$$\alpha = \frac{\text{Permeability (HC)}}{\text{Permeability } (N_2)}$$

$$\alpha = \frac{k_{HC}}{k_{N_2}} \cdot \frac{D_{HC}}{D_{N_2}}$$

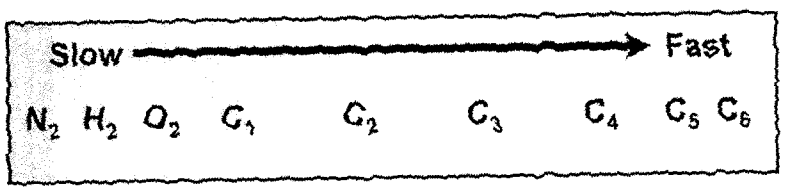
ratio of solubilities — ratio of diffusivities

In MTR's membrane k_{HC}/k_{N_2} *is the dominant term*

Membrane Permeability

MTR MEMBRANE TECHNOLOGY & RESEARCH

Permeability (HC) = $P_{HC} = k_{HC} \cdot D_{HC}$

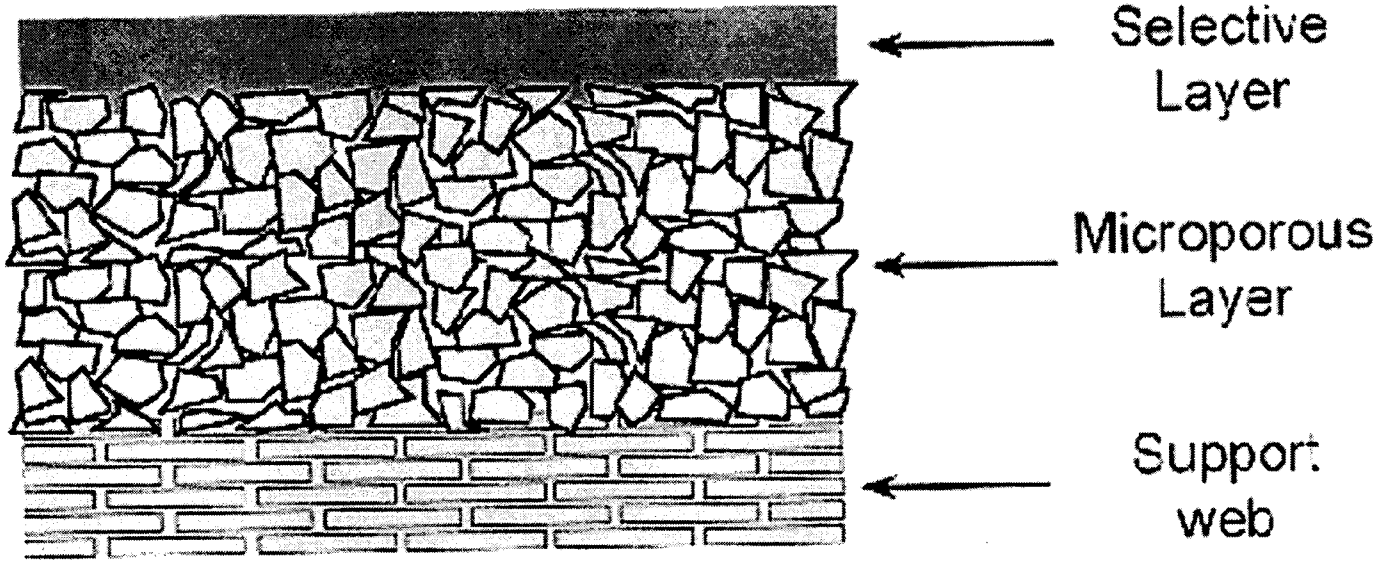


Temperature ↑, Permeability ↑

Membrane 구조

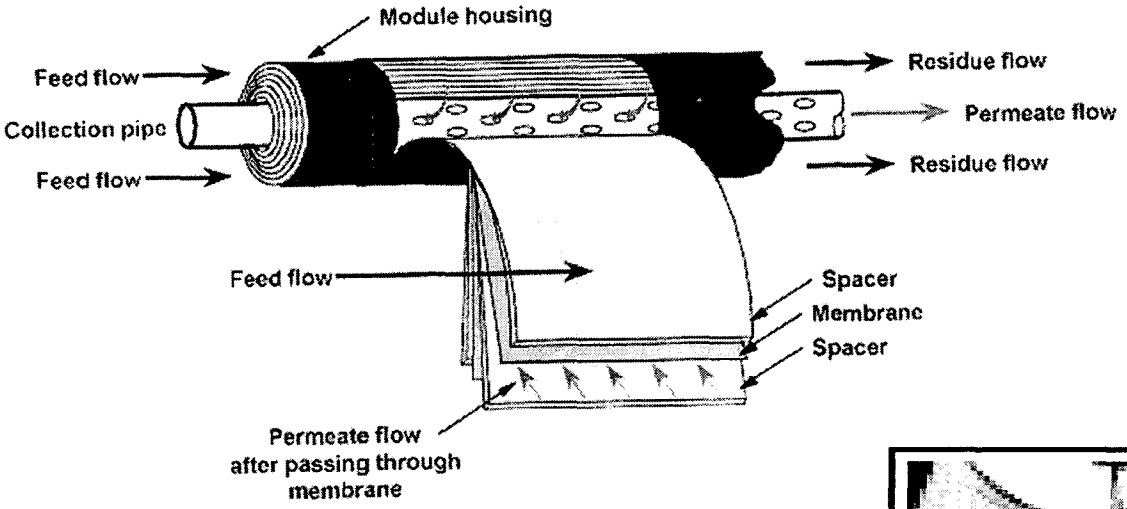
MTR Multilayer Composite Membrane

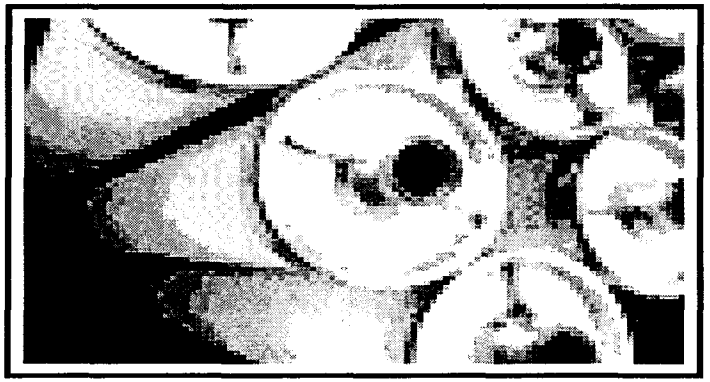
MTR MEMBRANE TECHNOLOGY & RESEARCH



Membrane 구조

MEMBRANE TECHNOLOGY & RESEARCH





□ 적용 사례

1)적용 검토 대상

- **Fuel**로 사용되는 **Off Gas**

  HDPE / PP / LLDPE Reactor Off gas (HC + N2)

  EO Rx Off gas (N2 + Argon)

- **H2 Rich Gas (87 Mol %)**의 정제
- 수소 **PSA**의 **Debottlenecking (Membrane +PSA)**
- **PP Rx Loop H2** 제거 (물성 **control**용)

2)적용 시 **Key Point**

■ 경제성

적정규모의 처리용량

Driving force for membrane treat

추가 **compressor** 필요여부

Upgrading value

단지 **Synergy**

■ 안정성 /운전성

설치 시 공정 변화의 영향

Explosion limit의 영향

3) 선정

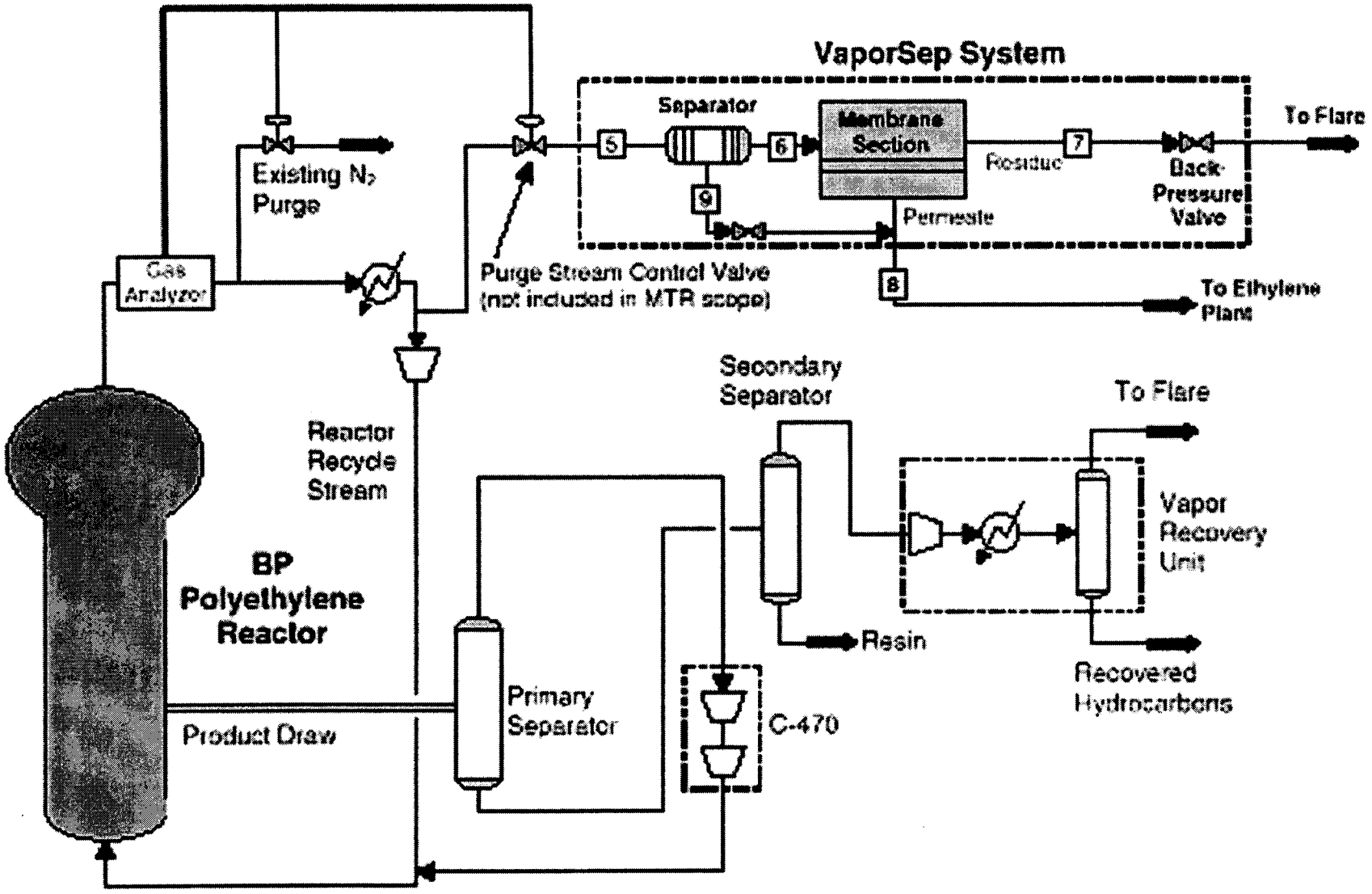
- **LLDPE Reactor Off gas**중 에틸렌 회수
- **EO Rx OFF gas**중 에틸렌회수

	LLDPE Off gas	**EO Off gas**
현재 사용	Fuel	Fuel
Membrane 설치후 목표-1	반응기 **Recycle**	반응기 **Recycle**
공정의 영향	**Ethane**의 농축	**Ethane**의 농축
대책-1	**Purge flow**의 증가	**EDC Control**
결론	**Not acceptable**	**Acceptable**
목표-2	NCC Plant integration	
Limitation	N2 Content	

4)Project History

- ❖ **2000.9 ~ 2001.2 :** 타당성 검토
- ❖ **2001. 3 :**발주
- ❖ **2001.10 ~ 12 :** 현장 도착 및 설치 공사
- ❖ **2002.12 ~ 1 :**시 운전
- ❖ **2002.2 :**정상 운전 중

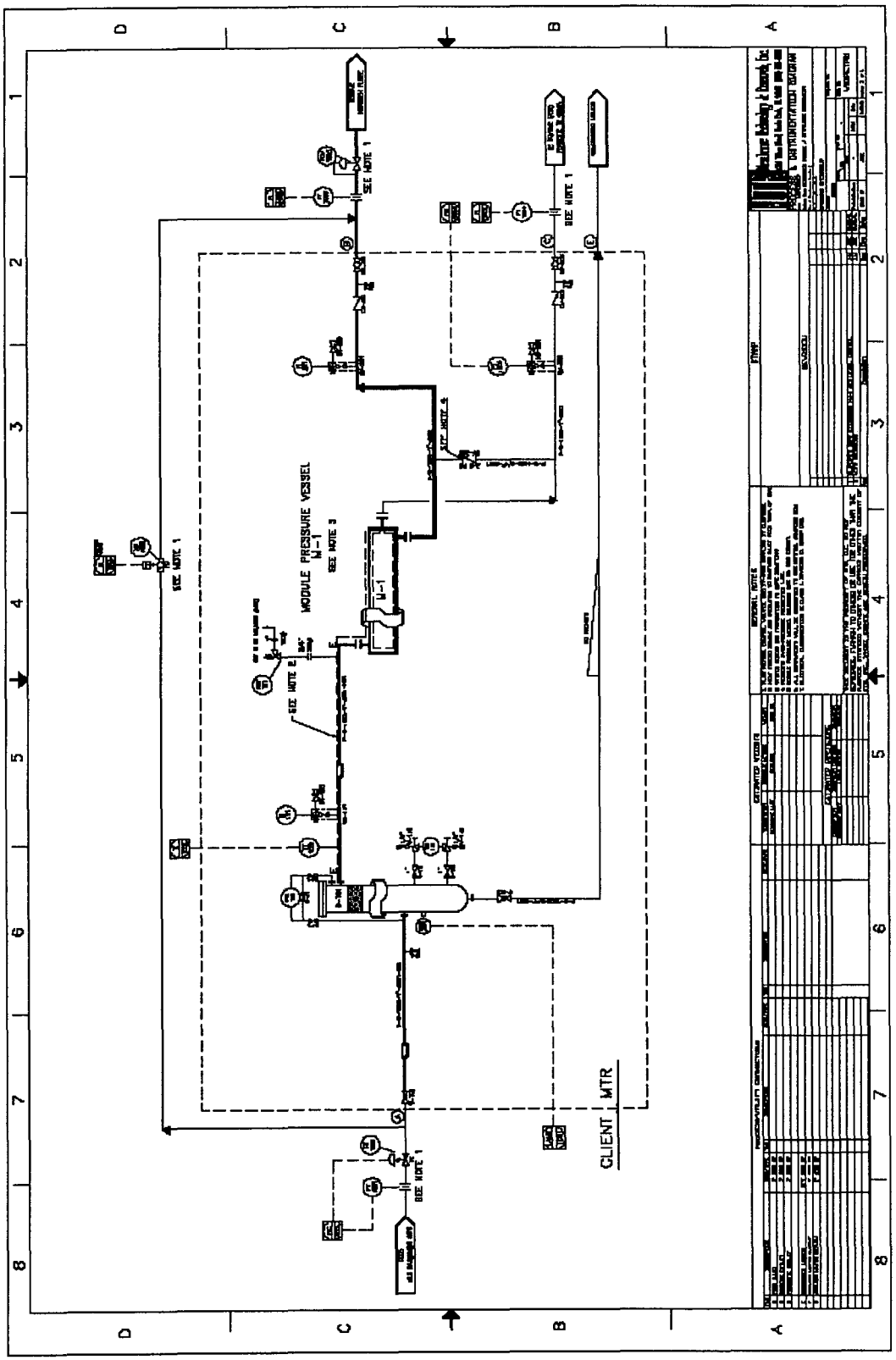
5) LLDPE OFF GAS중 에틸렌 회수 사례



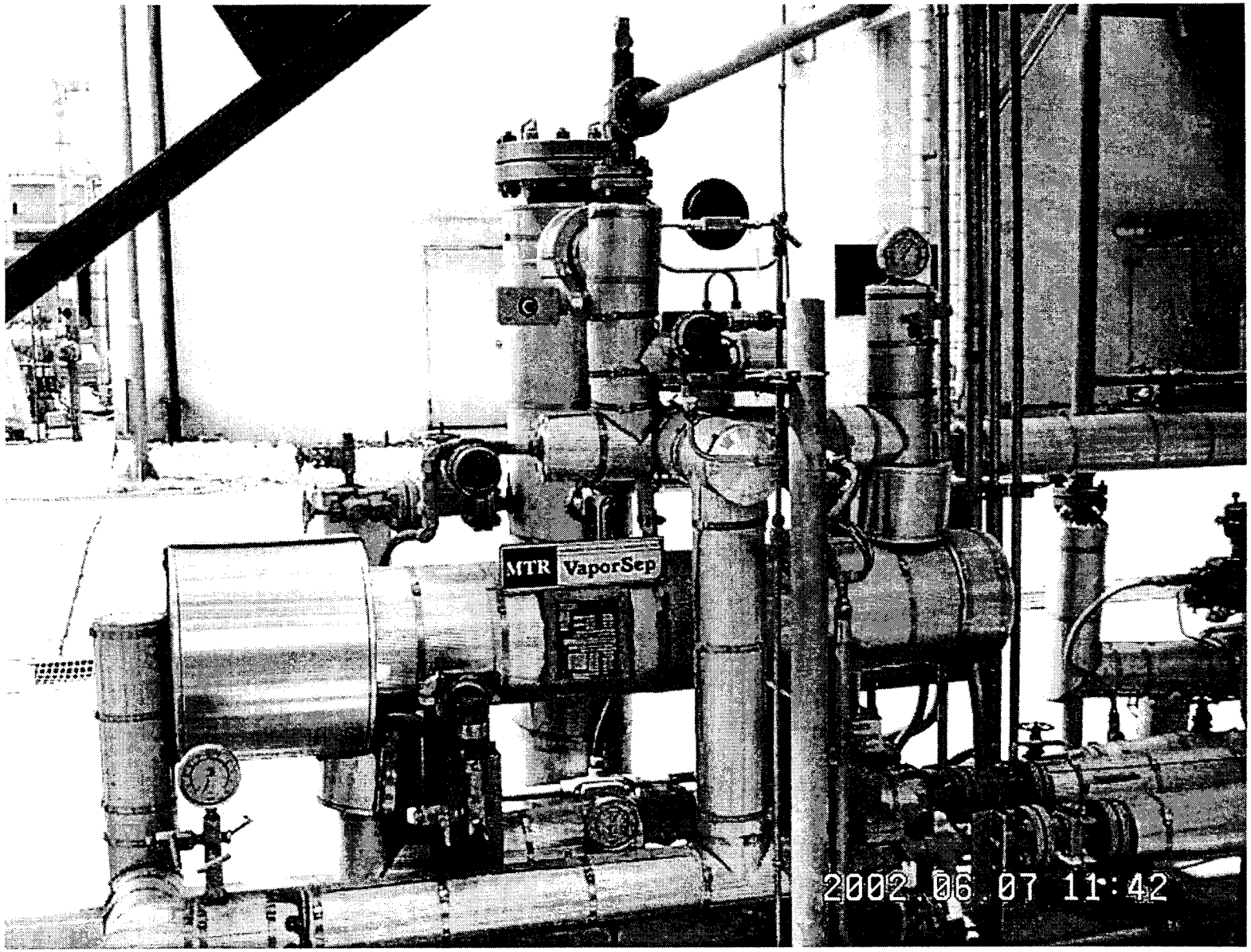
■ Design Basis

Table 1. Current Reactor Vent Stream Conditions[1]				
Polymer Grade	C_4 LLDPE		MDPE	
Flowrate (kg/hr)	300		300	
Pressure (kg/cm^2 (abs))	20		20	
Temperature (°C)	35 [2]		35 [2]	
Composition	vol%	kg/hr	vol%	kg/hr
Hydrogen	9.0	1.7	18.0	3.9
Ethane	2.0	5.7	2.8	9.0
Ethylene	49.0	130.9	49.0	146.7
N-Butane	0.5	2.8	0.4	2.5
1-Butene	20.0	106.9	10.0	59.9
N-Pentane	-	-	3.6	27.7
I-Pentane	-	-	0.4	3.1
Nitrogen	19.5	52.0	15.8	47.2

Table 3. Estimated System Performance		
Polymer Grade	C_4-LLDPE	MDPE
VaporSep System Pressure (kg/cm^2 (abs))	15	18
Ethylene Recovery		
kg/hr	72.7	89.9
%	55.6	61.2


MODULE PRESSURE VESSEL
M-1
CLIENT MTR

■ 현장설치



6) EO Off gas 에틸렌회수 Scheme

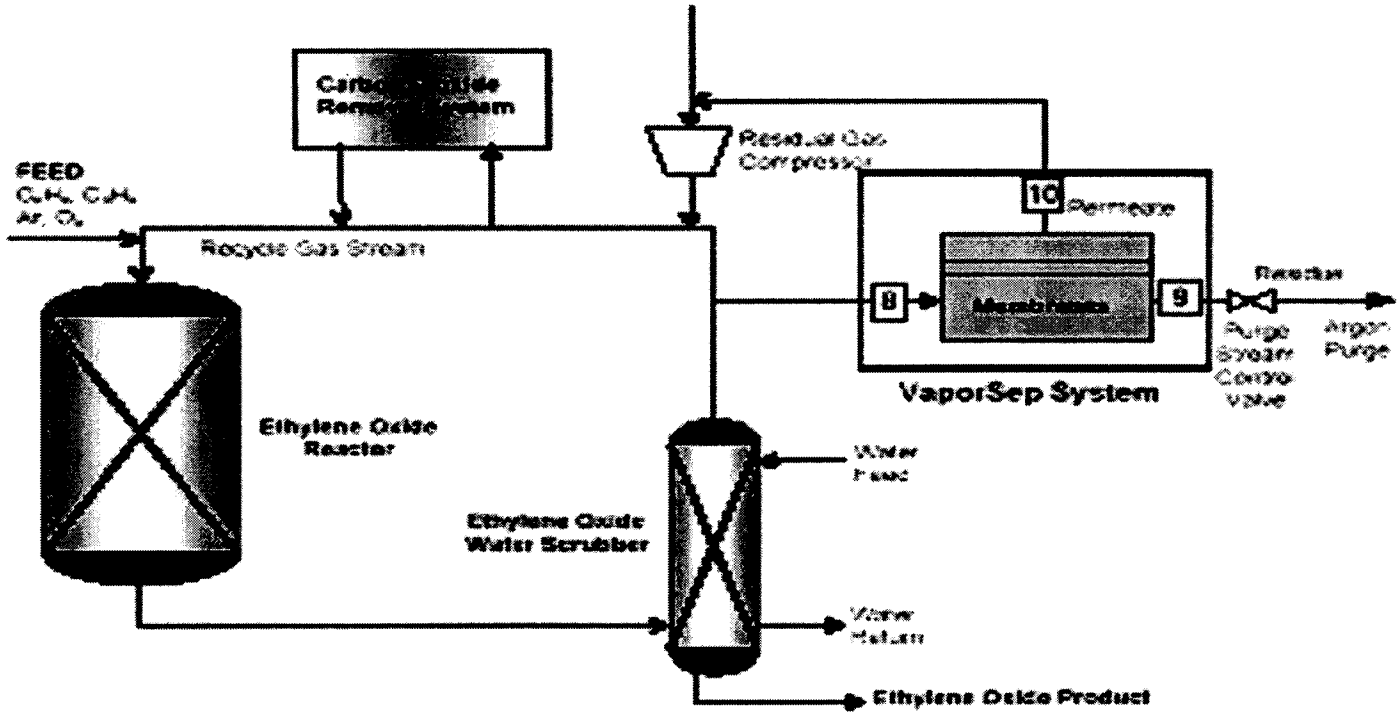
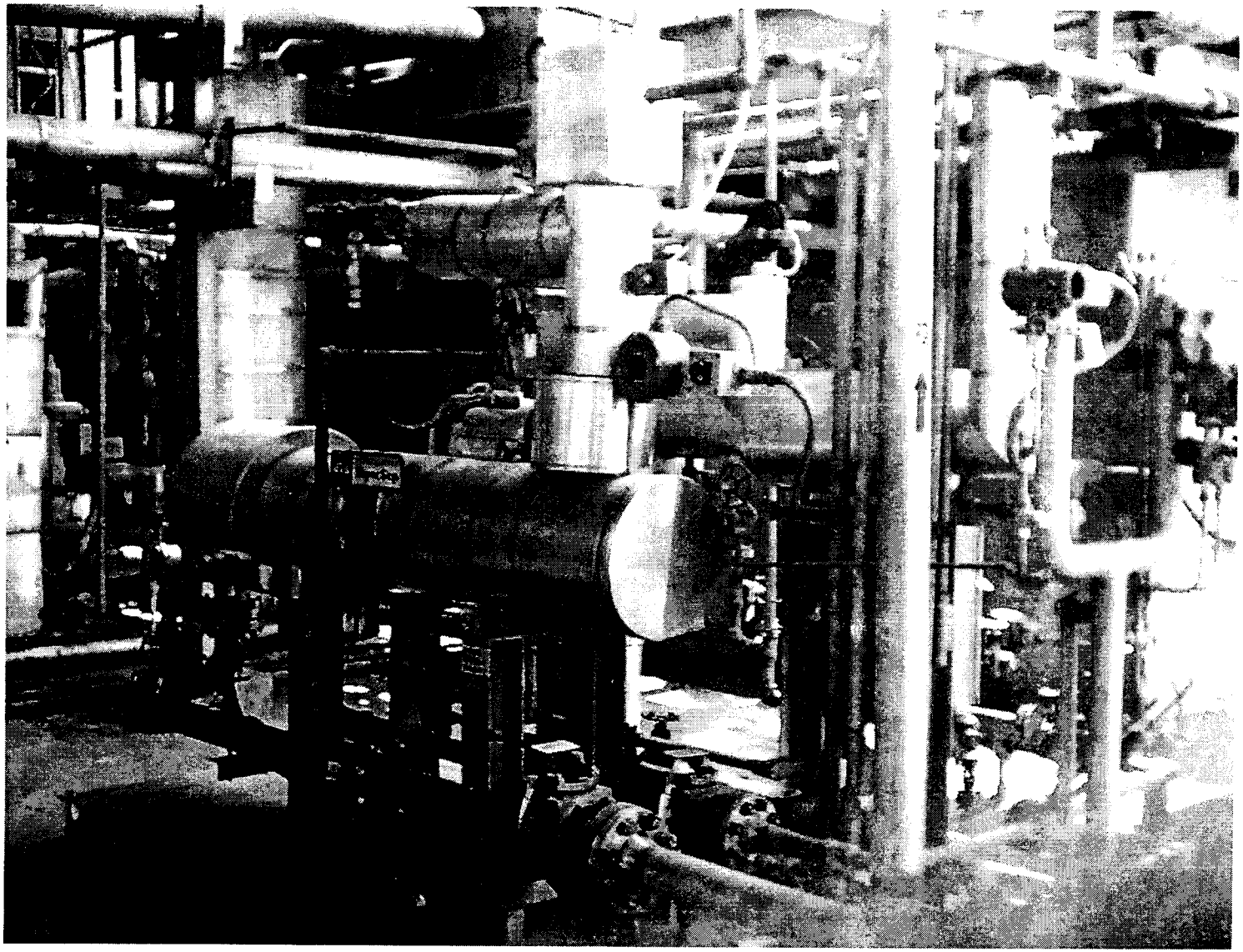


Figure 2. Process Flow Diagram of Ethylene Recovery Process in EO Plant

■ Design Basis

Table 9. Estimated VaporSep System Performance		
Description	Current Purge	Purge with VaporSep
Ethane Concentration in Recycle Gas Stream (vol %)	0.3	2.3
Permeate Stream Flow (Nm^3/hr)	-	480
Composition (kg/hr)		
Ethylene	40 0	5 0
Oxygen	10.7	10.0
Ethylene Oxide	< 0 1	< 0.1
Carbon Dioxide	18.3	0.6
Water	0.2	< 0.1
Nitrogen	1.7	1.7
Argon	15 7	15 7
Methane	51.5	26.6
Ethane	0 5	0.5
Ethylene Recovery		
kg/hr	-	35
%	-	88

■ 현장설치



7) 효과 분석

❖ 소요 투자비: **3.9** 억원 **(Two skid)**

❖ 에틸렌 **Recovery : 800 Ton/년**

(LLD: 550 톤, EO 250톤)

❖ 효과

(1) Value Upgrading

- Fuel -->원료 **(250 W/Kg)** **2** 억

(2) Vent loss방지 **0.9** 억

(3) 단지 **utility synergy** **0.5** 억

계 **3.4** 억원 **/**년

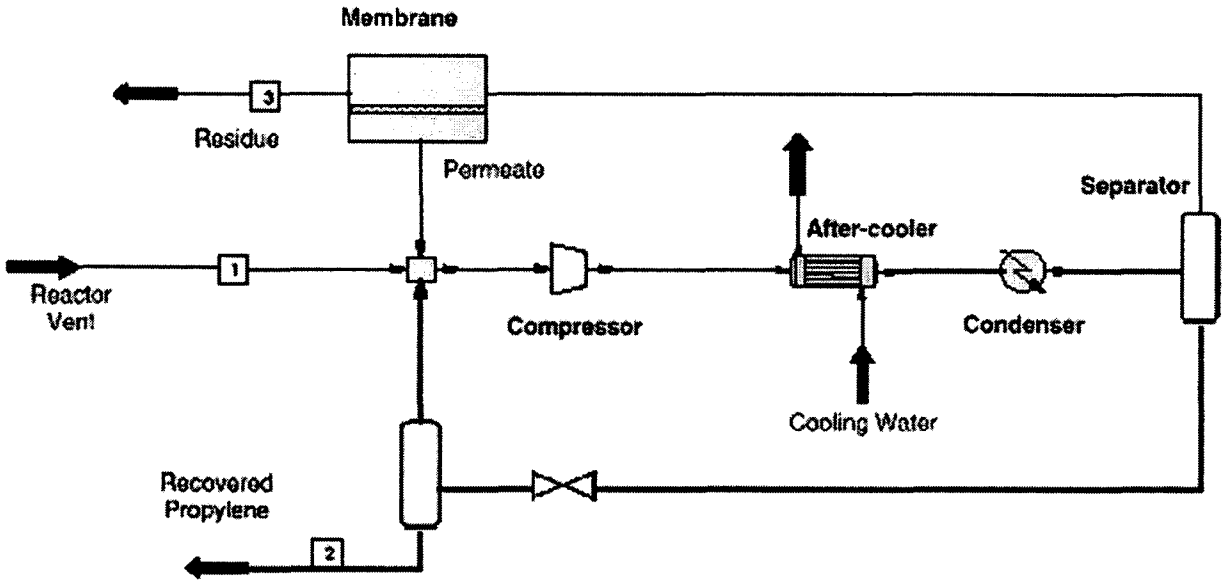
(3) 환경보호

- HC Emission 방지

- 에너지 사용의 최소화를 통한 에틸렌 생산

3.Future 계획

1) PP Off gas 적용 검토



2) 수소 제조 설비 Debottlenecking 용

3) Isomer Rx off gas

4) 설비 국산화