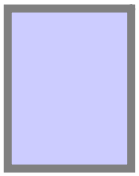
방향족 회수공정의 열역학 물성과 모사

고 민 수
서울대학교 열물성연구실

- 방향족 회수공정의 용매로서 ***N*-formylmorpholine (NFM)**및 **Sulfolane**은 사용
  - **U.S. patent no. 5401386, Morrison et al.(1995)/ reforming process**
  - **U.S. patent no. 4776927, Emmrich et al.(1988)/ NFM**
  - **U.S. patent no. 4488936, Preusser et al.(1984)/ NFM control**
  - **U.S. patent no. 5310480, Vidueira (1994)/ sulfolane**
  - **U.S. patent no. 5225072, Vidueira et al. (1993)/ sulfolane**
  - **U.S. patent no. 706853, 4058454, 4046676, 4046675, Asselin et al. (1976, 1976, 1977, 1977, 1977)/ sulfolane, UOP**
  - **U.S. patent no. 559077, Somekh et al. (1975)/ sulfolane, UCC**
  - **U.S. patent no. 6565742 B1, gentry et al. (2003)/ sulfolane, GTC**

- 운전비와 초기 설치비를 최적화하기 위해 상용 모사기를 사용
  - **Extractive distillation column**의 모사**:**
    - ✓ **ASPEN PLUS simulator: rigorous distillation model "RADFRAC"**
    - ✓ **HYSYS simulator**
    - ✓ **PRO/II simulator**
  - **Solvent Rate(**또는 **feed to solvent ratio)** 의 최적화
  - **Heat network**의 최적화**(Pinch)**

- 용매에 대한 열역학적 물성치의 부족
  - 순수물성**: Tc, Pc, ω, vapor pressure**
  - 상평형 **:**
    - ✓ 용매와 방향족간의 이성분계 **VLE** 문헌 정보
    - ✓ 용매와 비방향족간의 이성분계 **LLE** 실험
    - ✓ **NRTL**으로 **Data Correlation**



용매와 탄화수소간의 이성분계 액**-**액 상평형 실험에서 얻은
실험데이터를 공정모사기에 열역학적 모델 파라미터로서 제공

Components	Feed Naphtha (Seria, 65-134C)	Reforming oil	Extract
C4,C5		11.3	
C6	15.9	14.2	
C7	29.9	24	
C8	16.2	10.7	
CC6	21.5	6.4	
CC7	46.1	4.8	
CC8	29.9	1.9	
Benzene	1.3	13.2	13.1
Toluene	10.2	44.1	42
xylene	16.7	40.4	36.6
Total(kL/day)	187	170	91.7

▪ 1단계

접촉개질법: 고옥탄가의 가솔린 제조

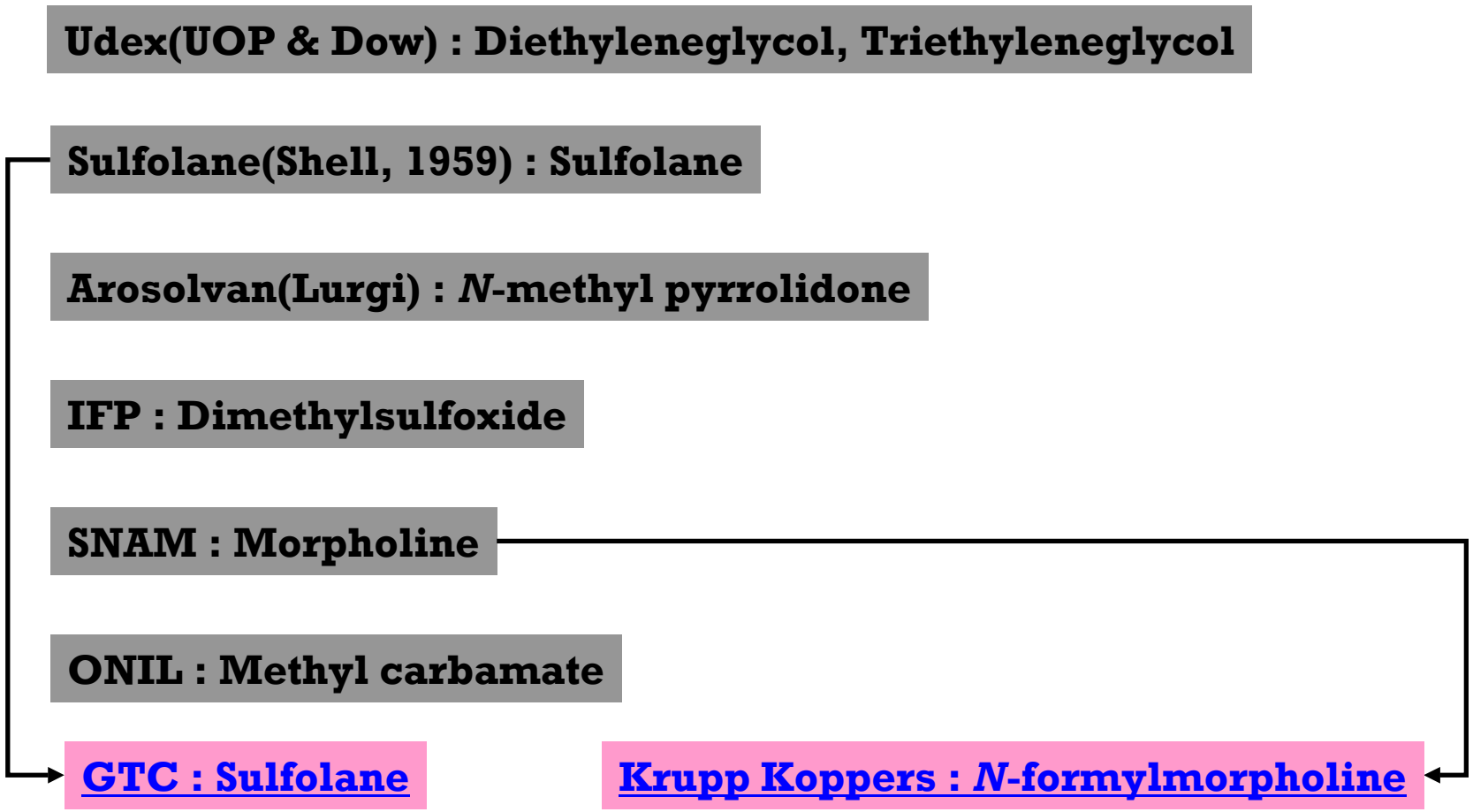
열분해법: olefin 제조

▪ 2단계

공비 증류 (Acetone, Methanol, Furfural)

추출증류 (Phenol, Cresol, Sulfolane, *N*-formylmorpholine)

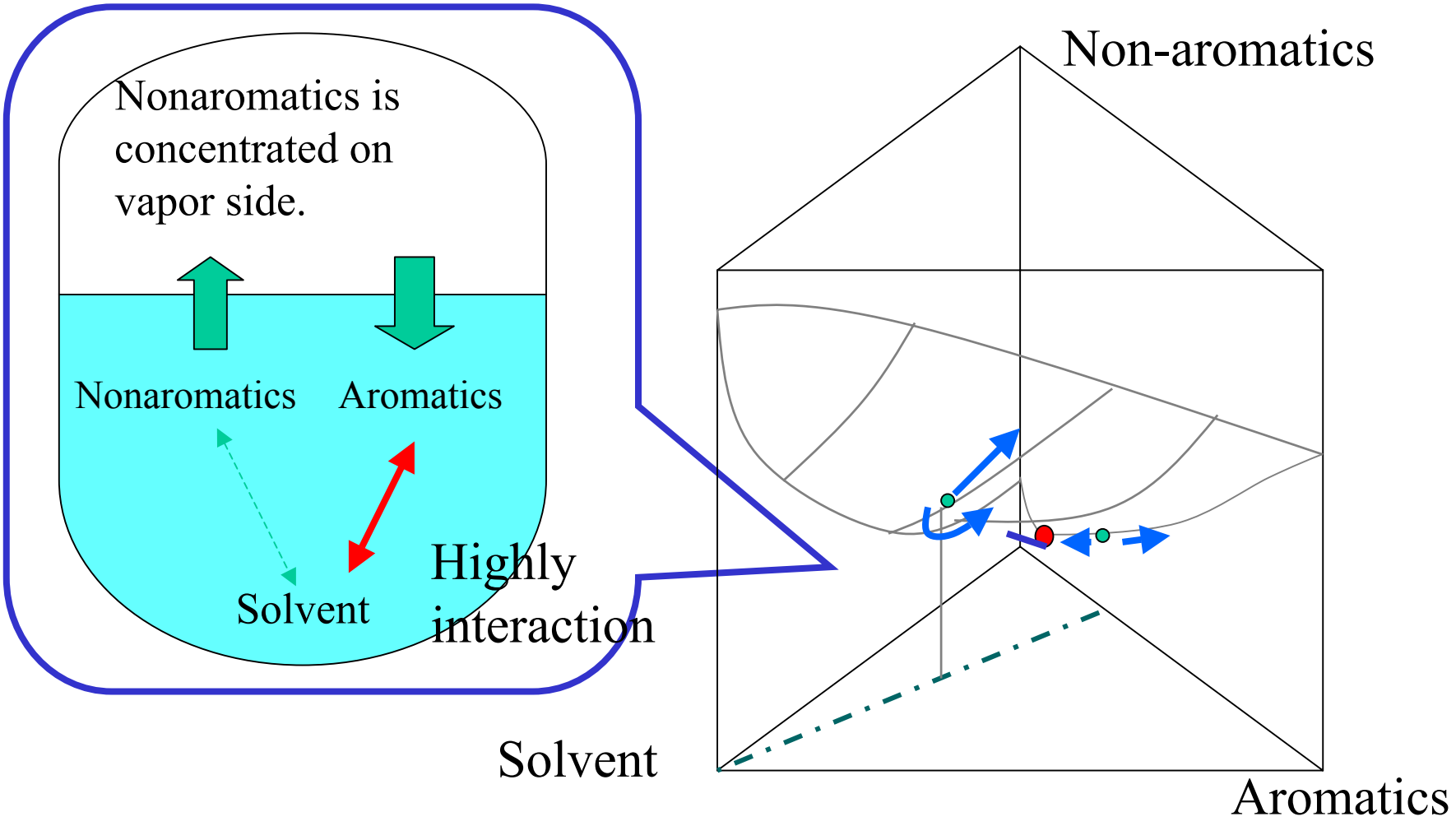
추출 (Diethyleneglycol, Sulfolane, *N*-methyl pyrrolidone)

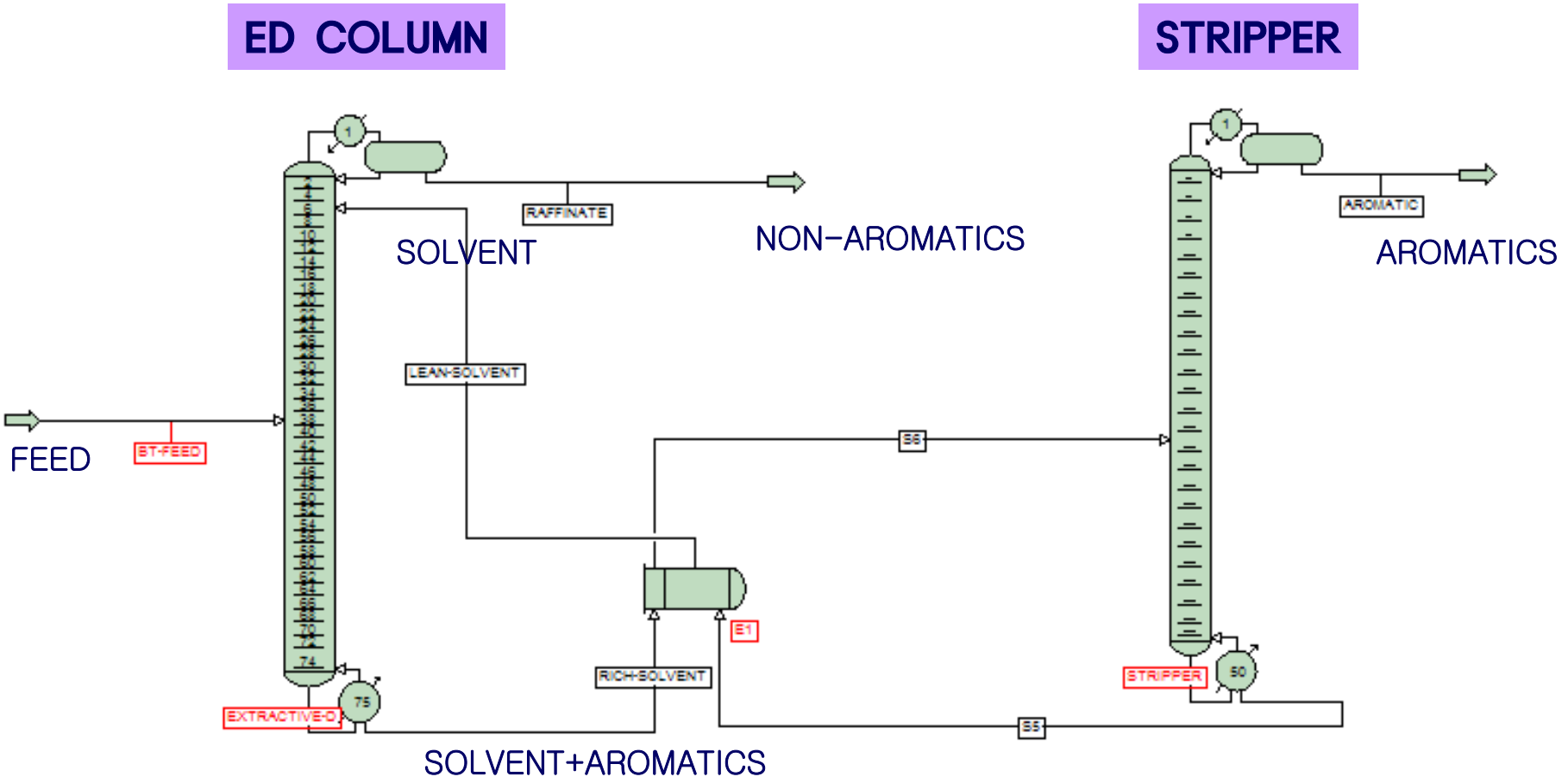


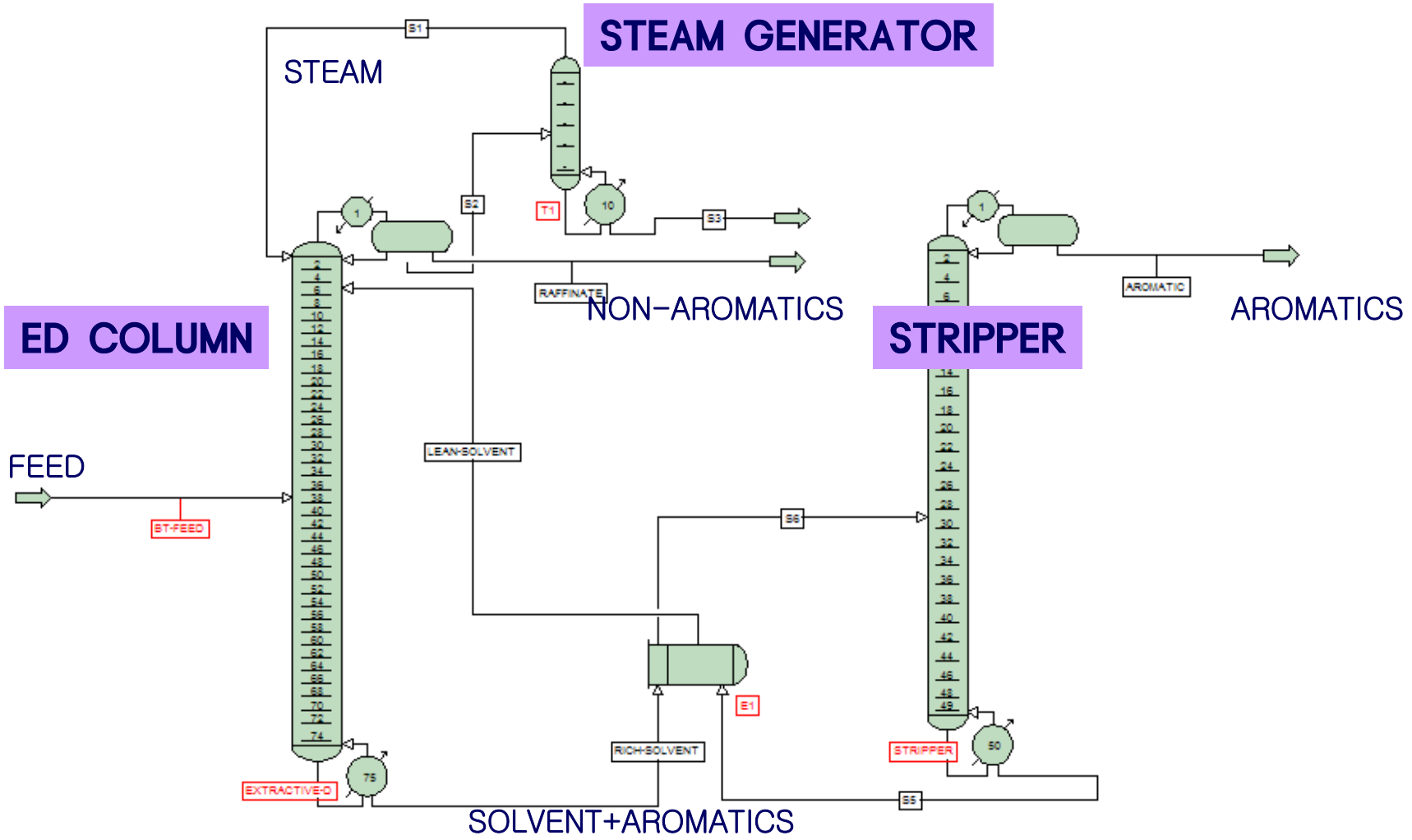
일반적으로 추출공정에 도입되는 방향족 함량비가 높아야 하며, 벤젠이 desired product 이므로 추출증류공정을 선호

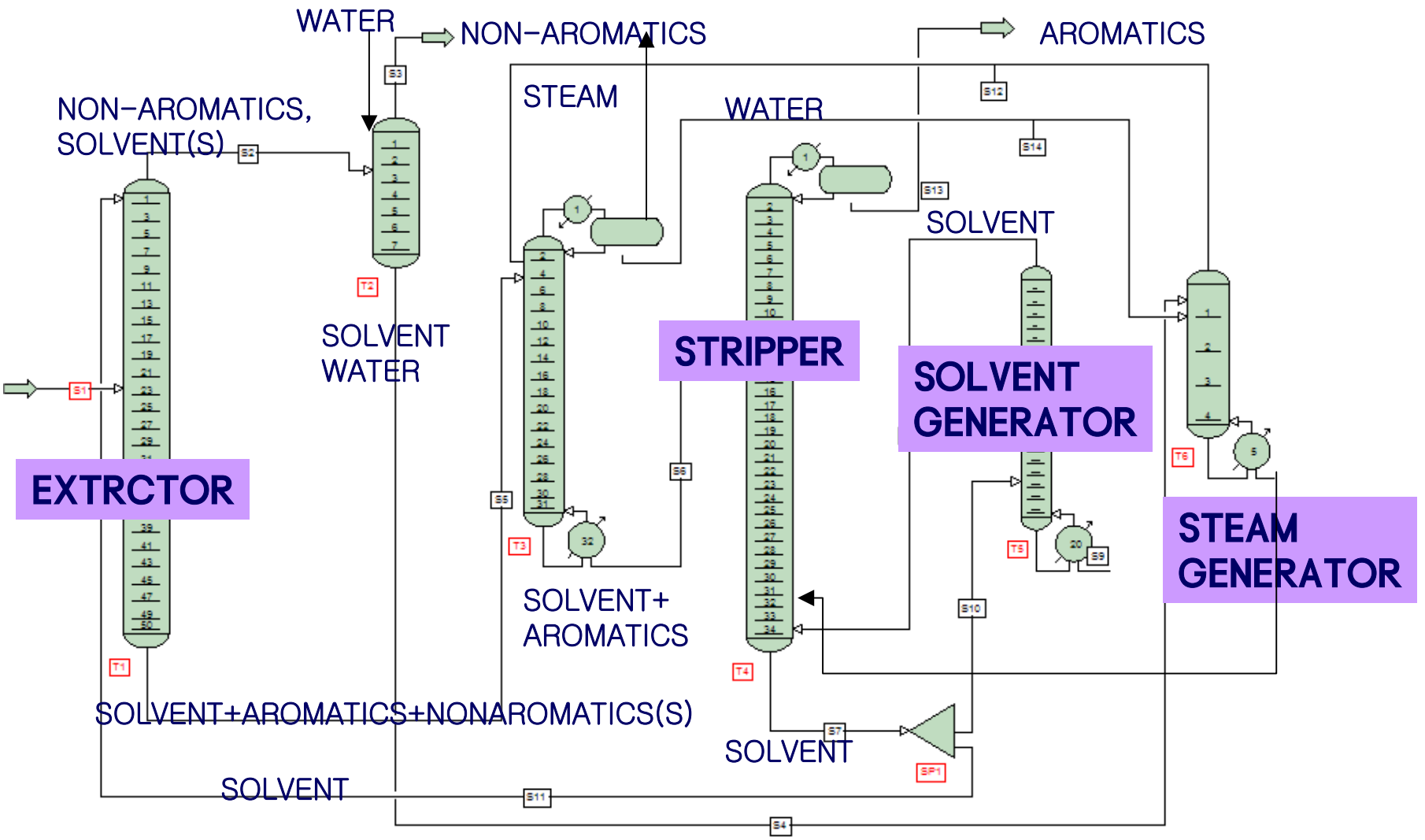
Licensor	Krupp Koppers	GTC	Shell
Type	Extractive Distillation	Extractive Distillation	Extraction
Solvent	NFM	Sulfolane+Alpha	Sulfolane
No. of Column (up stream)	2	3	Extractor = 1 Distil. Column = 5
Solvent / Feed Ratio (Mass)	3.43	3.58	3.97
Aromatics wt % in Feed	89.65 %	67.27% (Rich) 59.34% (Lean)	70.22% (Rich) 65.04% (Lean)
Aromatics Recovery %	Benzene > 99.5% for Overall Plant	99.3 wt% in ED Col.	> 99.5 wt% in Extractor
Keynote	Mainly Benzene Recovery	BTX recovery	BTX recovery
Present status (domestic)	3	1	11

NFM 추출증류공정: 공정 운전면에서 좀더 안정성을 보임


Nonaromatics is concentrated on vapor side.
Nonaromatics
Aromatics
Solvent
Highly interaction
Non-aromatics
Solvent
Aromatics

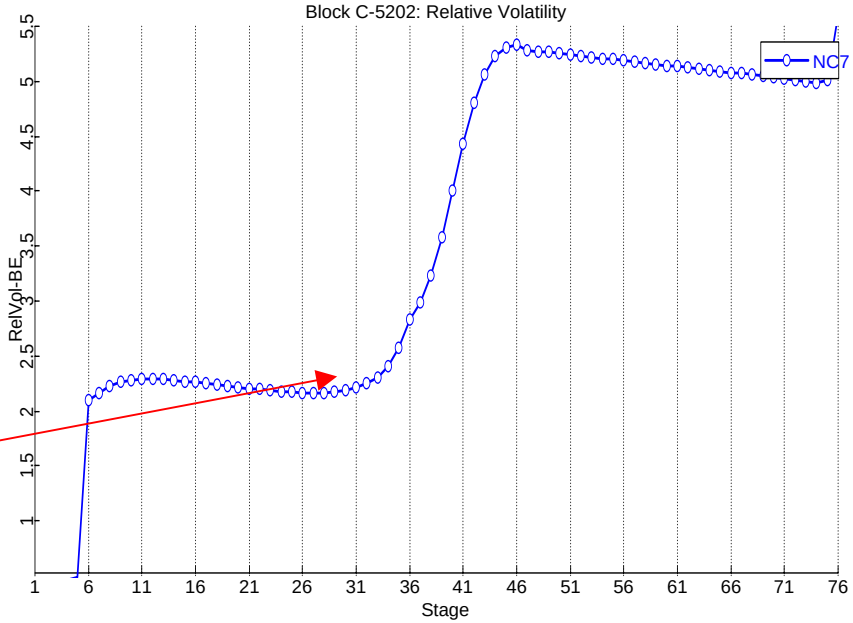

ED COLUMN
STRIPPER
RAFFINATE
NON-AROMATICS
SOLVENT
AROMATIC
AROMATICS
LEAN-SOLVENT
FEED
BT-FEED
S6
E1
RICH-SOLVENT
EXTRACTIVE-D
75
STRIPPER
50
S5
SOLVENT+AROMATICS


STEAM GENERATOR
STEAM
B1
T1
10
B2
B3
1
RAFFINATE
NON-AROMATICS
ED COLUMN
STRIPPER
AROMATIC
AROMATICS
FEED
BT-FEED
LEAN-SOLVENT
B6
E1
RICH-SOLVENT
EXTRACTIVE-D
75
STRIPPER
50
B5
SOLVENT+AROMATICS


WATER
NON-AROMATICS
AROMATICS
NON-AROMATICS,
SOLVENT(S)
STEAM
WATER
SOLVENT
WATER
STRIPPER
SOLVENT
GENERATOR
STEAM
GENERATOR
EXTRCTOR
SOLVENT+
AROMATICS
SOLVENT+AROMATICS+NONAROMATICS(S)
SOLVENT
SOLVENT
S1
S2
S3
S4
S5
S6
S7
S8
S9
S10
S11
S12
S13
S14
T1
T2
T3
T4
T5
T6
SP1

용매 존재하에 **heptane/benzene**의 상대휘발도

Solvent	NC7/Benzene# (0.57 at 100C)
Techtiv-100$	2.44
Sulfolane	2.00
N-methylpyrolidone	1.95
N-formylmorpholine	1.89, 2.25&
Gylcol blends	1.35



Ref: GTC technology corporation

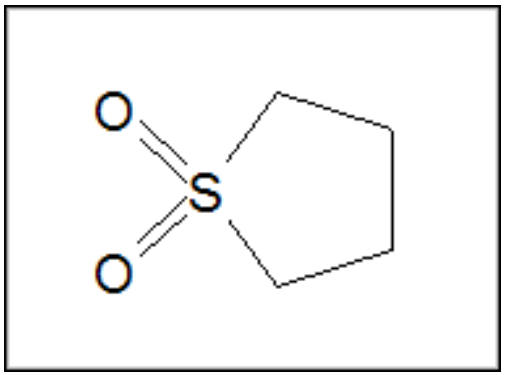
BP: NC7; 371.58 K(98.4), BZ;353.24 K(80.1)

 # is the relative volatility of non-aromatic and aromatic components in the presence of a solvent

$ is co-solvent, sulfolane+α, which is utilized in the GT-BTX process

& is the real value with NFM extractive distillation process

M.W. : 120.17 g/mol
m.p. : 300 K (27℃)
b.p. : 560 K (287 ℃)
density (at 25 ℃) : 1.265 g/cm^3
solubility in water (at 298.15 K) : fully miscible
TC: 853 K
PC: 50.3 bar
ω: 0.38234
Sulfolane은 장시간 공기와 접촉시 산화됨



Ref: Supplier of data sheet for sulfolane : AspenTech, DIPPR

“ ”

	NC5	NC6	NC7	NC8	CP5	CH6	MCP	MCH	ECH	DMCH	BE	TOL	EBE	NFM
NC5														
NC6	A[1]													
NC7	B[2]	A												
NC8	C[3]	A	A											
CP5	C	C	C	C										
CH6	C	A	A	A	A									
MCP	A	A	C	C	C	A								
MCH	A	A	A	C	C	A	C							
ECH	C	C	C	A	C	C	C	C						
DMCH	C	C	C	C	C	C	C	C	C					
BZ	A	A	A	A	A	A	A	A	C	C				
TOL	A	A	A	C	C	A	A	A	C	C	C			
EBE	C	C	A	A	C	A	C	C	A	C	A	C		
NFM	D[4]	D	D	D	D	D	D	D	D	C	D	D	C	

1. The VLE-IG and VLE-LIT are databanks for vapor-liquid applications. A[1]: The databanks VLE_IG was developed by AspenTech using binary vapor-liquid equilibrium data from the Dortmund databank. B[2]: The databank VLE_LIT contains binary parameters obtained from the literature. The both of VLE-IG and VLE-LIT are used with thermodynamic models, such as Wilson, NRTL, and UNIQUAC models and with ideal-gas model for vapor phase model. C[3]: R-PCES is obtained by UNIFAC model. D[4]: USER is obtained by regressing of experimental data [1-5]. E5: LLE-ASPEN was developed by AspenTech using binary liquis-liquid equilibrium data from the Dortmund databank.
2. IC5: Isopentane, NC5: Pentane, NC6: Hexane, NC7: Heptane, NC8: Octane, CP5: Cyclopentane, CH6: Cyclohexane, CH7: Cycloheptane, CO8: Cyclooctane, OLE: olefin(1-heptene), MCP: Methylcyclopentane, MCH: Methylcyclohexane, DMCH: Dimethylcyclohexane, BZ: Benzene, TOL: Toluene, EBE: Ethylbenzene, P-X: *p*-Xylene, M-X: *m*-Xylene, O-X: *o*-Xylene, SUL: Sulfolane, NFM: *N*-Formylmorpholine, WAT: Water.
3. Total number of binary systems is 91 for NFM process (=14C2).

Ref: MinSu Ko, Sangyonp Na, Jungho Cho, and Hwayong Kim, "Simulation of the Aromatic Recovery Process by Extractive Distillation", *The Korean Journal of chemical Engineering*, 2002, 19(6)

	IC5	NC5	NC6	NC7	NC8	CP5	CH6	CH7	CO8	OLE	BZ	TOL	EBE	P-X	M-X	O-X	SUL	WAT
IC5																		
C5	C[3]																	
C6	A[1]	A																
C7		B[2]	A															
C8			A	A														
N5																		
N6		A	A	A	A	A												
N7						A	A											
N8																		
OLE				A	A													
BE		A	A	A	A	A	A			A								
TOL	A	A	A	A	A		A			A	A							
EBE				A	A		A				A	A						
P-X			A	A	A		A				A	A	A					
M-X				A			A				A	A	A	A				
O-X				A			A						A		A			
SUL	D[4]	D	D	E	D	D	E	D	D	D	A,D	A,D	D	D	D	A		
WAT	E[5]	E	E	E	E	E	E	E		E	E	E	E	E	E	E	E	

1. The VLE-IG and VLE-LIT are databanks for vapor-liquid applications. A[1]: The databanks VLE_IG was developed by AspenTech using binary vapor-liquid equilibrium data from the Dortmund databank. B[2]: The databank VLE_LIT contains binary parameters obtained from the literature. The both of VLE-IG and VLE-LIT are used with thermodynamic models, such as Wilson, NRTL, and UNIQUAC models and with ideal-gas model for vapor phase model. C[3]: R-PCES is obtained by UNIFAC model. D[4]: USER is obtained by regressing of experimental data [1-5]. E5: LLE-ASPEN was developed by AspenTech using binary liquis-liquid equilibrium data from the Dortmund databank.
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3. Total number of binary systems is 153 for sulfolane process (=18C2).

Ref: MinSu KO, Jungho CHO, Hwayong KIM, and Hyo Kwang BAE, "SIMULATION OF EXTRACTIVE DISTILLATION PROCESS", Korea-Japan Separation Technology (2002. 10).

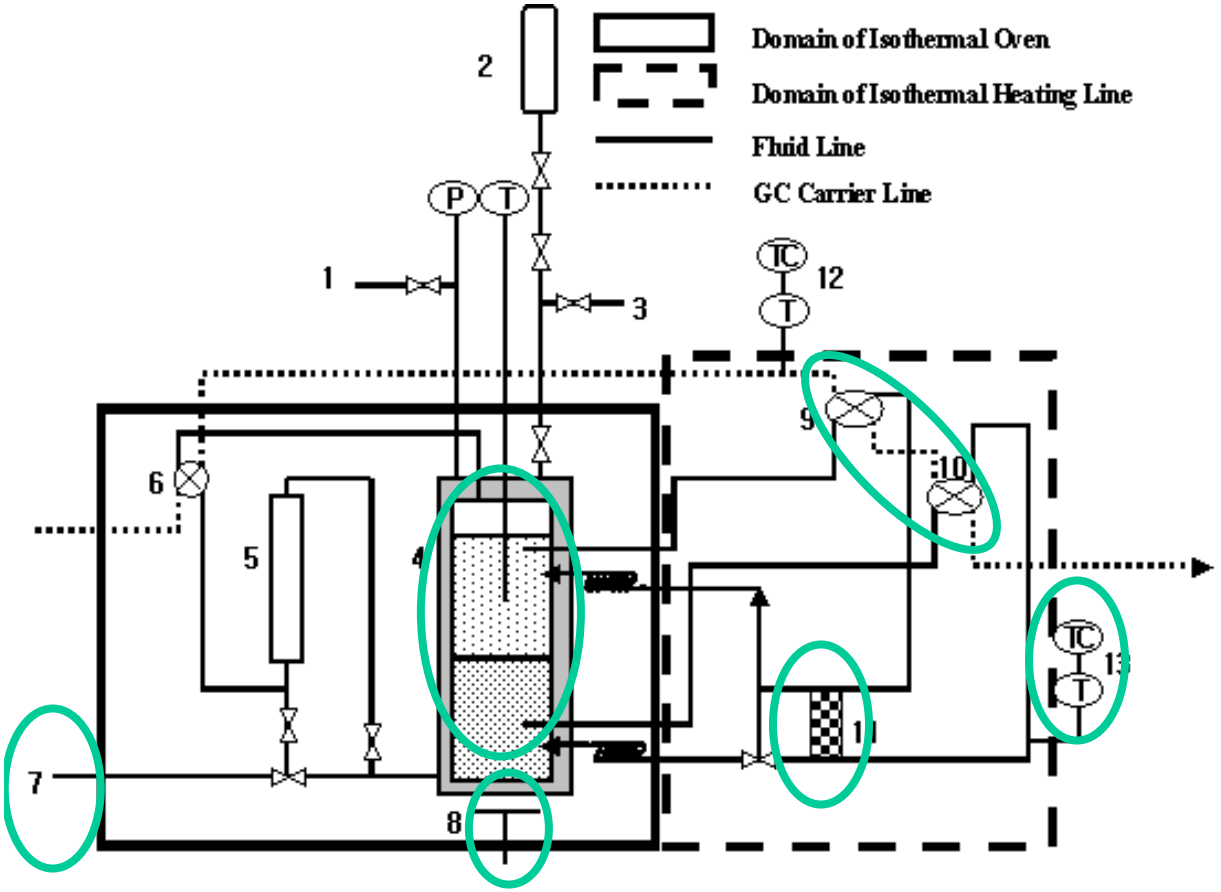
- 용매와 탄화수소간의 이성분계 액-액 상평형 측정

✓용매 **+ Alkanes**
Pentane, Hexane, Heptane, Octane

✓용매 **+ Isoalkanes**
Isopentane, Isohexane

✓용매 **+ Cycloalkanes**
Cyclopentane, Cyclohexane, Cyclooctane

✓용매 **+ Branched-cycloalkanes**
Methylcyclopentane, Methylcyclohexane, Ethylcyclohexane



1. vacuum line for the removal of air with vacuum pump,
2. bottle for charge a reagent,
3. air line (8 kg_f/cm^2) for the leak test
4. equilibrium cell with the view window (quartz)
5. magnetic pump (chromium plating)
6. 6-way valve for vapor
7. discharge line with vacuum
8. magnetic stirrer
9. sampling loop for the light phase
10. sampling loop for the heavy phase
11. circulating mini pump
12. temperature controller (domain of preheating carrier line)
13. temperature controller (domain of circulating fluid line)

- 장치특징
  - **recirculation type**
  - **Temperature range : room temp. ~ 200ºC**
  - **Pressure range : max. 30 Bar**
- 온도 측정
  - **Platinum resistance thermometer (1502A by Hart Scientific, Inc.)**
  - **Its uncertainty : ±0.006 K**
- 분석
  - **GC : HP 5890 Series II**
  - **Detector : TCD**
  - **Column: 6 ft × 1/8” packed by Chromosorb WHP 100/120 coated with OV-101**
  - **Liquid-phase compositions : maximum relative error of 0.1%**
  - **Sampling Temperature Deviation: less 0.005K (at least 10min)**

The mixture was fed into the equilibrium cell that was initially evacuated

↓

The mixture was stirred for at least 1 hr with the magnetic stirrer

↓

The mixture left to settle for at least 2 hr

↓

The samples were analyzed by gas chromatography

- GC setting
  - Injector와 detector의 온도 : 250°C or 300°C
  - Oven Temperature Programming:

  - Carrier gas의 유량 : 23 or 30 $cm^3 \cdot min^{-1}$ (Helium)

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right)$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = \frac{A_{ij}}{T} \qquad G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

파라미터의 온도의존성 표현

$$\tau_{ij} = a_{ij} + b_{ij} / T + c_{ij} \ln T + f_{ij} T \quad : \text{ASPEN PLUS}$$

$$\tau_{ij} = a_{ij} + b_{ij} / T + c_{ij} T + d_{ij} T^2 \quad : \text{PRO/II}$$

Tauij = Aij + Bij/T + Cij/T/T + Fij T + Gij ln(T); Alphaij = Alp1ij + Alp2ij T
Tauij = (Aij + Bij T) / RT; Alphaij = Alp1ij
Tauij = Aij + Bij/T + Fij T + Gij ln(T); Alphaij = Alp1ij + Alp2ij T
Tauij = (Aij + Bij t + Cij/T) / RT; Alphaij = Alp1ij + Alp2ij t (T in K, t in C)
Tauij = Aij + Bij/T; Alphaij = Alp1ij

: HYSYS

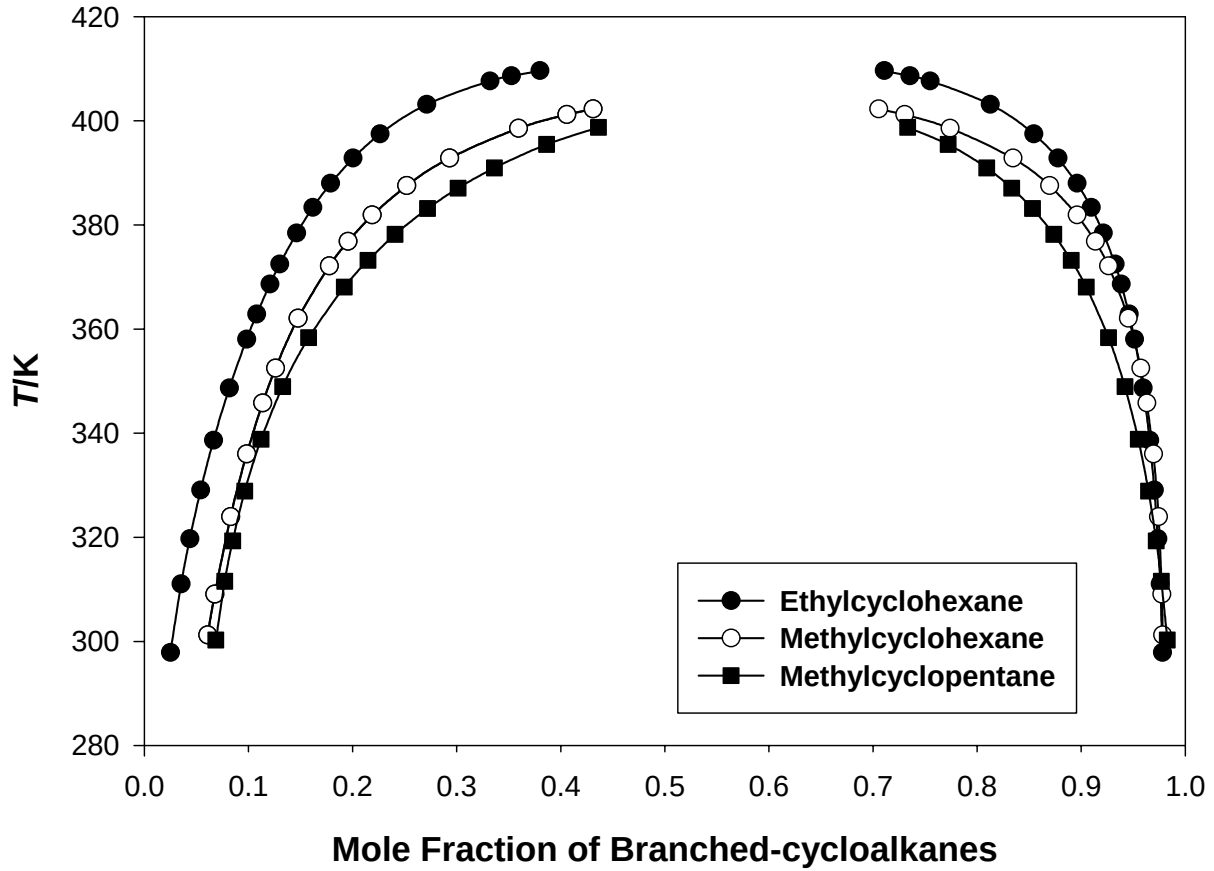
NRTL의 **3**개의 **adjustable parameter**를 가지고 **VLLE**의 상거동과 **Critical region**의 **flat**함을 표현할 수 없음**(Hradetzky and Lempe, 1991)**

- The temperature-dependent binary parameters
  - Evalution of the binary parameters for the models :

    nonlinear regression method based on the maximum-likelihood
  - The objective function :

    Measurable variables : T, x'_1, x''_1

$$OF = \sum_{k=1}^{N} \left\{ \left(\frac{T_k^{cal} - T_k^{\exp}}{\sigma_{T_k}} \right)^2 + \sum_{i=1}^{2} \sum_{j=1}^{2} \left(\frac{x_{ij}^{cal} - x_{ij}^{\exp}}{\sigma_{x_{ijk}}} \right)^2 \right\}$$

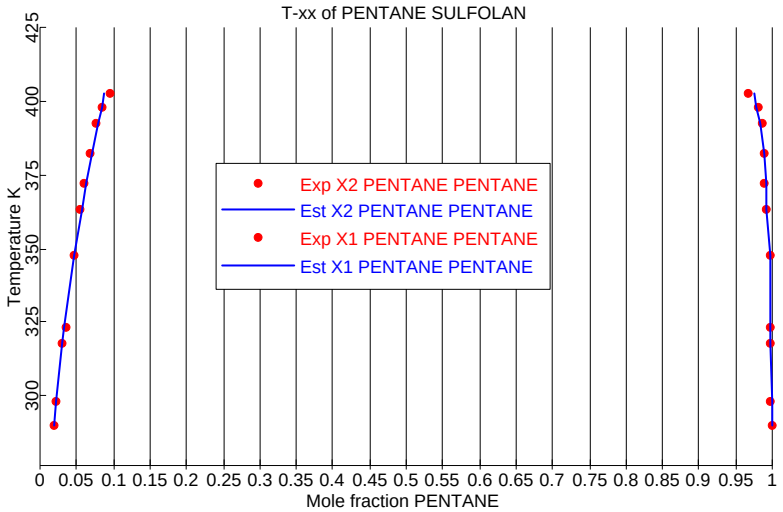


UCST동영상

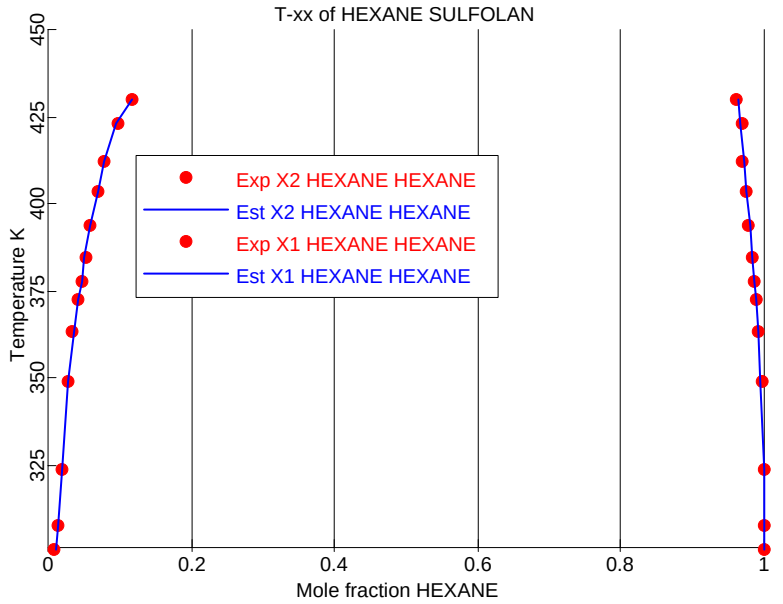
Solubility: Methylcyclopentane > Methylcyclohexane > Ethylcyclohexane

Ref: MinSu Ko, Sangyoup Na, Soyoung Kwon, Sungjin Lee, and Hwayong Kim, "Liquid-Liquid Equilibria for the Binary Systems of N-Formylmorpholine with branched-cycloalkanes", Journal of Chemical and Engineering Data, 2003, 48(3), 699-702.

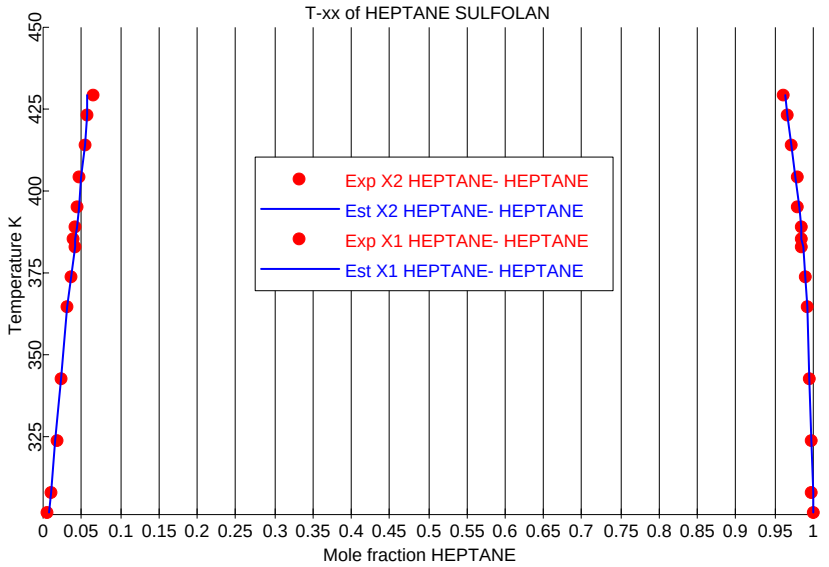
Temperature K	Exp X1	Calc X1	Exp X2	Calc X2
290.15	0.9996	0.9994	0.0184	0.0185
298.15	0.9983	0.9991	0.0215	0.0212
318.06	0.9985	0.9983	0.0303	0.0304
323.15	0.9974	0.998	0.0347	0.0334
347.45	0.9974	0.996	0.0465	0.0455
363.21	0.9921	0.9931	0.0538	0.0568
371.99	0.9897	0.9909	0.0606	0.063
382.24	0.9888	0.9877	0.068	0.0703
392.71	0.9866	0.983	0.0766	0.0784
397.94	0.9801	0.9792	0.0854	0.0834
402.44	0.9681	0.9746	0.0964	0.0882



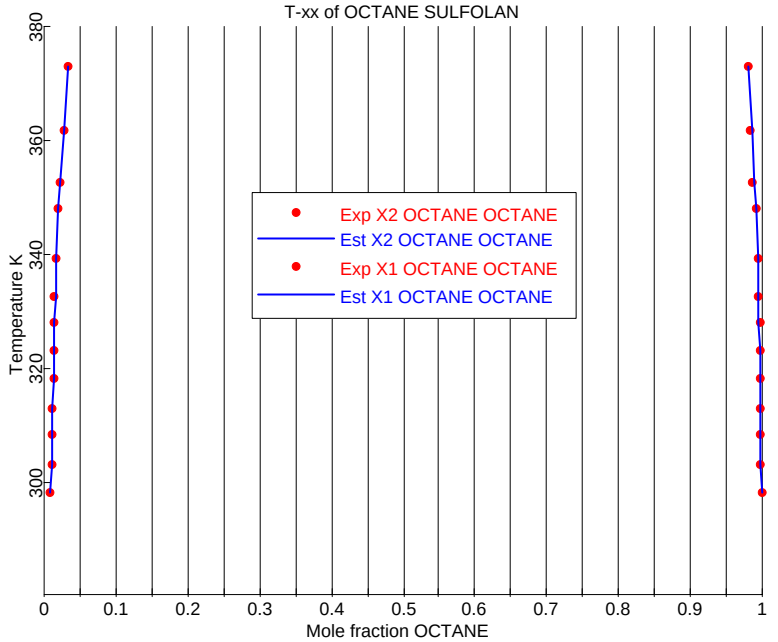
Temperature K	Exp X1	Calc X1	Exp X2	Calc X2
300.3	0.9999	0.9999	0.0092	0.0103
307.43	0.9995	0.9996	0.015	0.0135
323.51	0.9987	0.9988	0.0203	0.0184
348.72	0.9966	0.9956	0.0276	0.0284
363.36	0.9918	0.9917	0.0332	0.0369
372.41	0.9893	0.9888	0.0432	0.0427
377.72	0.9849	0.9867	0.0469	0.0467
384.43	0.9842	0.9841	0.052	0.0514
393.92	0.9788	0.9799	0.0584	0.0594
403.51	0.9756	0.9754	0.0698	0.0687
412.29	0.9706	0.971	0.0794	0.079
422.92	0.9681	0.9657	0.098	0.0959
429.93	0.9608	0.9623	0.1161	0.117

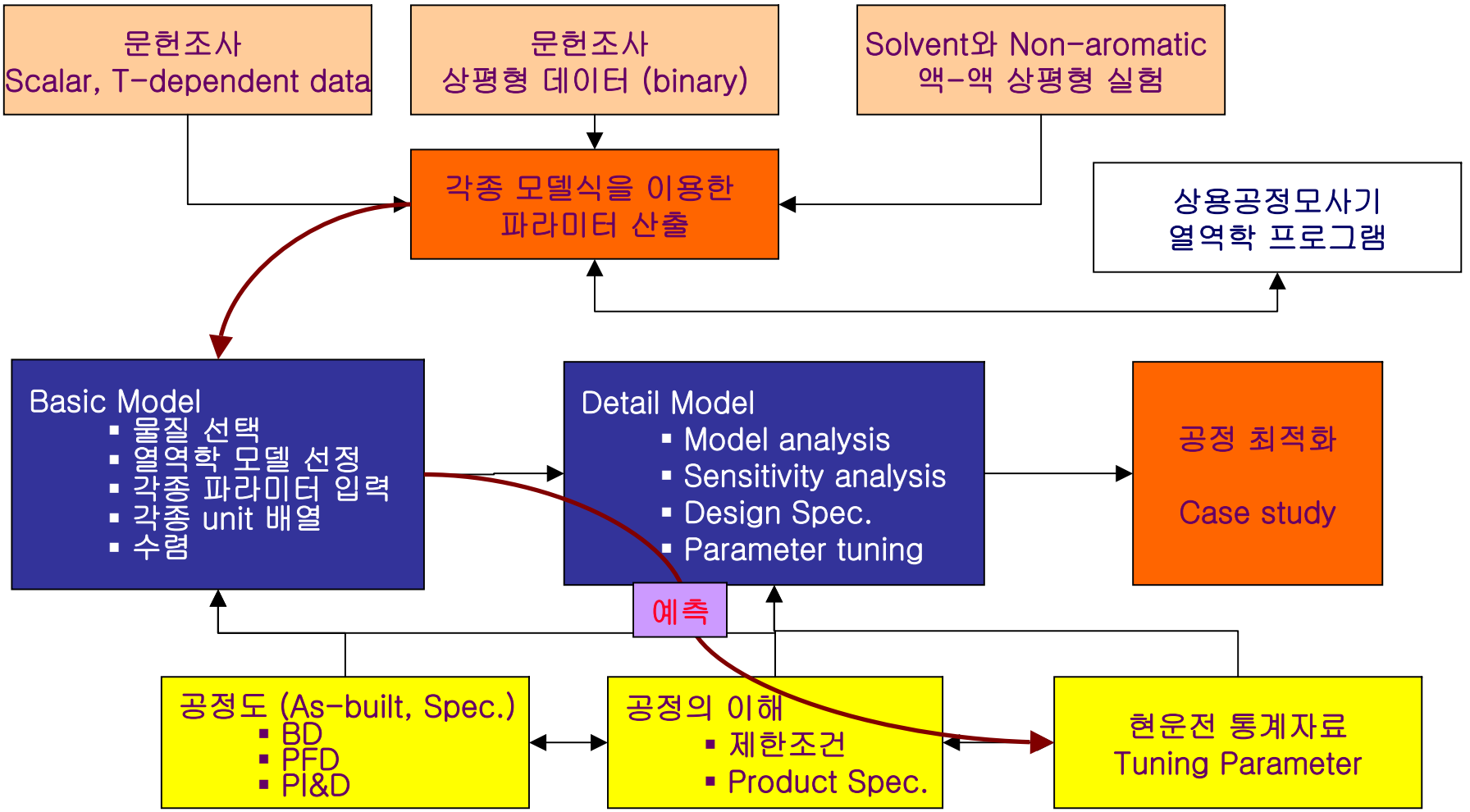


Temperature K	Exp X1	Calc X1	Exp X2	Calc X2
302.09	0.9995	0.9992	0.0059	0.0071
308.03	0.9981	0.9988	0.0109	0.01
323.93	0.9974	0.9978	0.0186	0.0151
342.74	0.9955	0.9957	0.023	0.0225
364.62	0.9934	0.9917	0.0312	0.0322
373.78	0.9893	0.9891	0.0367	0.0368
382.81	0.9854	0.986	0.0424	0.0412
385.17	0.9854	0.9852	0.0392	0.0421
389.11	0.9854	0.9838	0.0423	0.0438
395.41	0.98	0.981	0.0438	0.0467
404.3	0.9781	0.977	0.0475	0.0502
413.87	0.9716	0.9719	0.0546	0.0537
423.39	0.9661	0.9665	0.0567	0.0566
429.24	0.9603	0.9628	0.0637	0.058



Temperature K	Exp X1	Calc X1	Exp X2	Calc X2
298.15	0.999	0.9989	0.0092	0.009303
303.15	0.9986	0.9985	0.01	0.010052
308.34	0.9968	0.9979	0.011	0.011199
313.15	0.9981	0.9977	0.012	0.011564
318.25	0.9964	0.9969	0.0134	0.012806
323.15	0.9958	0.9962	0.014	0.013785
328.15	0.9959	0.9955	0.0143	0.014751
332.8	0.9957	0.9948	0.015	0.015813
339.15	0.9937	0.9932	0.0178	0.017797
348.15	0.9925	0.9909	0.0203	0.020686
352.65	0.9866	0.989	0.0233	0.022987
361.65	0.9838	0.9855	0.0287	0.027078
373.15	0.9811	0.9801	0.0322	0.033348



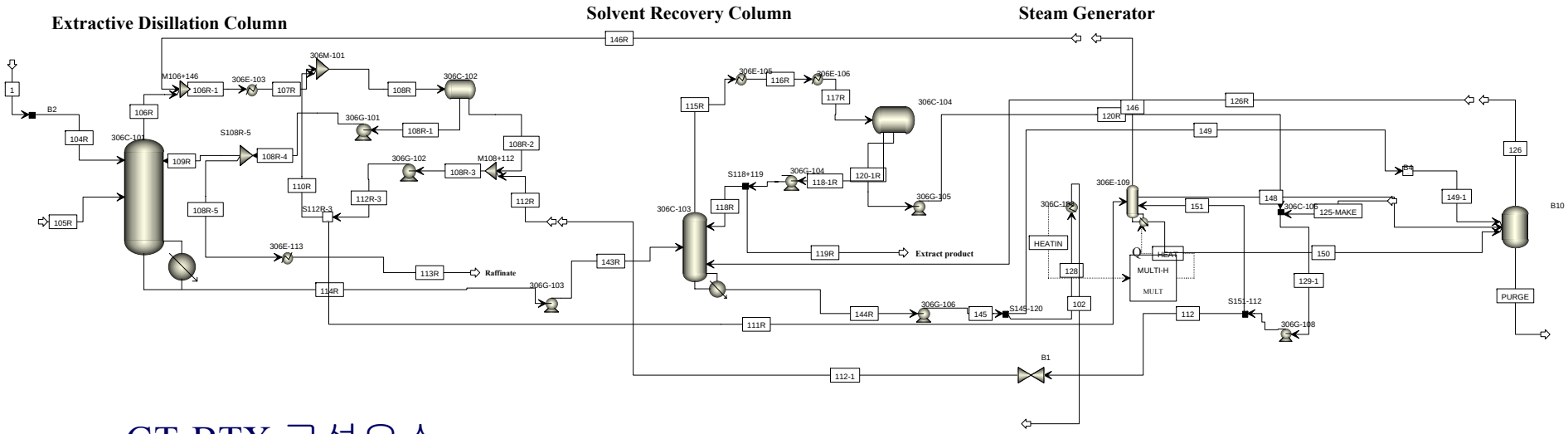

문헌조사
Scalar, T-dependent data
문헌조사
상평형 데이터 (binary)
Solvent와 Non-aromatic
액-액 상평형 실험
각종 모델식을 이용한
파라미터 산출
상용공정모사기
열역학 프로그램
Basic Model
▪ 물질 선택
▪ 열역학 모델 선정
▪ 각종 파라미터 입력
▪ 각종 unit 배열
▪ 수렴
Detail Model
▪ Model analysis
▪ Sensitivity analysis
▪ Design Spec.
▪ Parameter tuning
공정 최적화
Case study
예측
공정도 (As-built, Spec.)
▪ BD
▪ PFD
▪ PI&D
공정의 이해
▪ 제한조건
▪ Product Spec.
현운전 통계자료
Tuning Parameter

Naphtha-reforming unit (CCR) 에서 **Extractive Distillation Process**를 이용하여 방향족을 얻는 공정 **[GT-BTX^{sm} Aromatics Recovery Process]**의 모사 및 최적화

- **Basic modeling**
  - **Solvent + Nonaromatic system**의 액-액 상평형 실험: **RT～200℃**
  - **Simulation**에서 필요한 열역학적 파라미터를 제공
  - 추출증류탑의 운전온도: **91～177℃**
  - 탑내부의 상태: **VLLE**와 **VLE**가 형성

- **Modeling and Simulation**
  - **Lean Case**
  - **Rich Case**
  - **Real Operation Case : 2002-2003**년 운전 데이터의 년간 통계치를 이용

GT-BTX Process



GT-BTX 구성요소

❶ Extractive Distillation Column
❷ Solvent Recovery Column
❸ Steam Generation and Solvent Regeneration
❹ Clay Tower and Benzene Fractionation
❺ Toluene Fractionation
❻ Storage System

Modelling 및 Simulation

❶ Lean Case
❷ Rich Case
❸ Real Operation Case

Simulation에서의 두 가지 가정

❶ 용매는 Sulfolane
❷ olefin은 1-hexene

Design시 제품 품질

❶ **Raffinate안에 방향족 최소함량비: <0.01wt%**
❷ **Extract안에 비방향족 최소 함량비 : <200ppm**
❸ **Benzene의 순도: 99.9wt%**
❹ **Toluene의 순도: 99.0wt%**

Solvent to feed ratio/방향족 함량비

❶ Lean Case: 3.56/ 59.34
❷ Rich Cas: 3.59/ 67.27
❸ Operation Case: 2.97/ 75.1

	Rich Case				Lean Case					Operation Condition Case				
	Raffinate		Extract			Raffinate		Extract	Lean-S	Raffinate		Extract		Lean -S
Temperature C		40		40.4		40		40.4	154		40		40.4	154
Pressure kg/sqcmg		4.5		3.5		4.5		3.5	9		4.5		3.5	9
Vapor Frac		0		0		0		0	0		0		0	0
Mole Flow kmol/hr		524.43		1043.57		628.43		896.44	4061.85		319.44		975.64	3285.42
Mass Flow kg/hr		46282.81		92902.58		56448.41		80585.69	487626.91		28604.32		84651.65	359783.3
Volume Flow cum/hr		70.41		109.39		85.56		94.68	424.5		43.06		99.93	317.77
Enthalpy MMkcal/hr		-92.84		19.71		-28.54		3.34	-403.84		-14		5.39	-310.61
IC5	0.0992	0.099		TRACE	0.0951	0.094		TRACE	TRACE		0.082		TRACE	TRACE
C5	0.066	0.066		0	0.0634	0.063		TRACE	TRACE		0.056		TRACE	TRACE
C6	0.3635	0.362		0	0.2905	0.288		TRACE	TRACE		0.282		TRACE	TRACE
C7	0.2951	0.294		26 PPB	0.3598	0.356		4 PPM	399 PPB		0.379		9 PPM	220 PPB
C8	0.0817	0.079		0.001	0.1049	0.103		393 PPM	TRACE		0.071		0.015	TRACE
C9	0	0		0		0		0	0	0.9528	0	0.0053	0	0
N5	0.0069	0.007		0	0.0066	0.007		0	TRACE		0.008		TRACE	TRACE
N6	0.0154	0.015		0	0.0146	0.014		TRACE	TRACE		0.02		TRACE	TRACE
N7	0.0087	0.008		325 PPM	0.0127	0.012		167 PPM	TRACE		0.018		0.005	TRACE
N8	0.0029	TRACE	0.0002	0.002	0.0028	1 PPB	0.0001	0.002	TRACE		TRACE		678 PPM	204 PPM
OLEFFINS	0.0467	0.047		0	0.0412	0.041		TRACE	TRACE		0.042		TRACE	TRACE
BENZENE	0.0124	0.022	0.1986	0.194	0.0071	0.021	0.1596	0.149	67 PPB	0.0013	0.041	0.3829	0.357	100 PPM
TOLUENE	0.0016	20 PPB	0.7777	0.779	0.0012	2 PPM	0.8134	0.813	132 PPB	95 PPM	215 PPB	0.5792	0.601	0.009
EBENZENE	10 PPM	TRACE	0.006	0.006		4 PPB	0.0069	0.007	TRACE	19 PPM	TRACE	0.0103	0.006	0.001
P-XYLENE		TRACE	0.0045	0.004		3 PPB	0.0053	0.005	TRACE	29 PPM	TRACE	0.0078	0.005	767 PPM
M-XYLENE		TRACE	0.0124	0.012		10 PPB	0.0139	0.014	TRACE	10 PPM	TRACE	0.0126	0.008	0.001
O-XYLENE		TRACE	0.0006	599 PPM		TRACE	0.0008	846 PPM	TRACE	10 PPM	TRACE	909 PPM	392 PPM	152 PPM
SULFOLAN		TRACE		43 PPM		TRACE		0.007	1	0.0458	TRACE	0.001	6 PPM	0.971

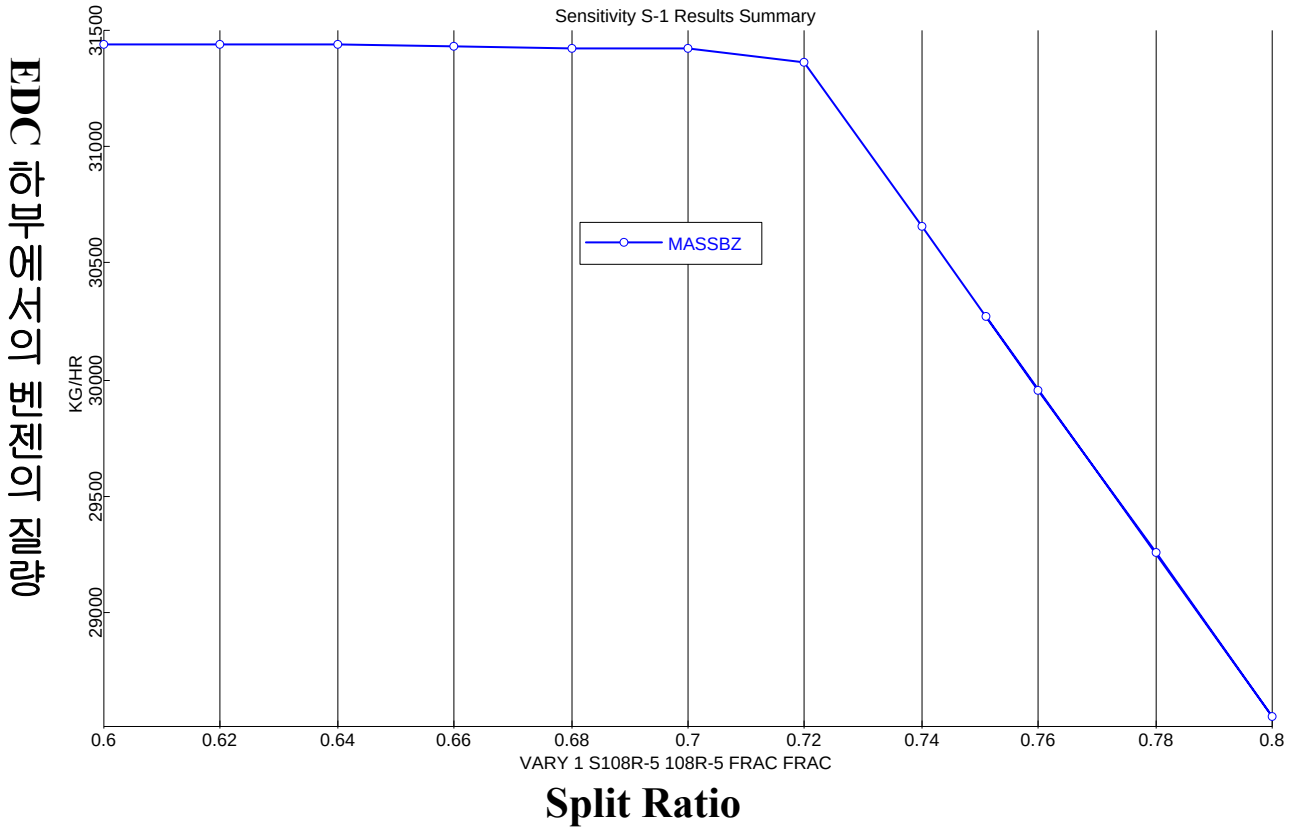
Several areas can be improved for GT-BTX unit Some of them are:

- **Optimization of solvent to feed ratio to handle variations in feed quality**
- **Minimizing reflux on columns, while employing other means to maintain low solvent concentrations in the product streams**
- **To maximize heat recovery and improve the energy efficiency for the GT-BTX unit**
- **Applying advanced controls to adjust critical process conditions in the EDC**

Optimization of solvent to feed ratio to handle variations in feed quality

- R113BZ: Raffinate에서의 Benzene의 질량분율
- R119N8: Extract에서의 Cyclooctane의 질량분율

상태	Factor	Bz MassFrac in Raffinate	Cyclooctane MassFrac in Extract	Solvent to Feed ratio
OK	1	0.04075794	0.00067759	2.96775933 (현 운전)
OK	0.95	0.04634485	0.00065625	2.81937136
OK	0.9	0.05188429	0.00063364	2.67098339
OK	0.85	0.05737453	0.00060966	2.52259543
OK	**0.8**	**0.06282973**	**0.00058427**	**2.37420746**
Error	0.75	0.06831080	0.00055748	2.2258195
Error	0.7	0.07410859	0.00052934	2.07743153



Reflux ratio =1/Split ratio -1

- Reflux ratio의 변화를 나타낼 수 있는 Split ratio로 EDC bottom에서의 벤젠의 질량변화.
- Split ratio를 증가할 수로 환류비는 감소하고 EDC bottom에서의 벤젠 생성량은 감소함
- 벤젠의 질량변화는 일정하게 유지되다가 Split ratio 0.72(환류비 0.39)일 때부터 일정하게 감소

D사 톨루엔 현황

A. 톨루엔 제품종류 : 순도 98%전후의 Commercial Toluene(반제품) 생산중
B. 톨루엔 생산량 : 5,160 Ton/년 (최근 3년 평균)
C. 판매가격 : 완제품 톨루엔 가격대비 -$45/ton 가격으로 판매

⇒ 98% TOLUENE은 상품으로서의 가치가 없으므로 이를 99.9+% >의 TOLUENE으로 정제하여 상품으로서의 가치를 높이고자 함

	Purity(%)	용 도
반제품 (Commercial Toluene)	95~99.5	Gasoline 제조공정 원료로 사용
완제품 (Nitration Toluene)	99.5~99.9	페인트, 잉크, 고무 및 접착제의 용제, 각종 석유화학제품 원료로 사용
고순도제품	99.9이상	TDI(Toluene Di-isocyanate: 폴리우레탄 원료), 의약품, 사카린 향료, 폭약 제조용

- 검토하고 있는 PROCESS로는 SULFOLANE(SOLVENT)을 이용
- 추출/추출증류공정으로서 TOLUENE의 순도를 99.6% 이상으로 올리려고 함
- TOLUENE 으로부터 EB 및 BENZENE을 분리하지 않을 경우 이론적으로는 99.6%이상의 TOLUENE은 생산하지 못함
- SOLVENT RECOVERY SYSTEM을 SIMULATION 하여 TOLUENE의 SPEC 및 UTILTIY(REBOILE STEAM, COOLING WATER, MAKE-UP SULFOLANE양 등) CONSUMPTION을 확인
- 개략적인 투자비를 산출: Sulfolane, Steam, 각종 유틸리티, 각종 단위조작 등의 가격 정보가 필요.

Component		SM#1 Avg.	SM#2 Avg.	최종 저장조	비점 (℃)
TOL Product량 (kg/hr)		368.5	303.3	671.8	
TOL 함유량		98.49	98.13	98.33	110.6
BZ 함유량		0.25	0.17	0.21	80.1
NA	Methyl cyclohexane				
	Ethyl cyclopentane				
	1,1,3 Tri-methyl cyclopentane				
	2,4 Di-methyl hexane				
	TC 1,2,4 Tri-methyl cyclopentane				
	3,3 Di-methyl hexane				
	Unknown				
	TC 1,2,3 Tri-methyl cyclopentane				
	1,1,2 Tri-methyl cyclopentane				
	2,3 Di-methyl hexane				
	2 Methyl, 3 ethyl pentane				
	2 Methyl heptane				
	3 Methyl heptane				
	CT 1,2,3 Tri-methyl cyclopentane				
	T 1,4 Di-methyl cyclohexane				
	1,1 Di-methyl cyclohexane				
	C 1 Ethyl, 3 methyl cyclopentane				
	T 1 Ethyl, 3 methyl cyclopentane				
	T 1 Ethyl, 2 methyl cyclopentane				
	T 1,2 Di-methyl cyclohexane				
	Octane				
	1,1,4 Tri-methyl cyclohexane				
NA 함유량					
EB 함유량					

	Feedstock Characterization	
Flow, Kg/hr	671.9	
	Flowrate (Kg/hr)	Weight Percent
Toluene	660.581	98.32
Benzene	1.411	0.21
Methyl Cyclohexane	2.217	0.33
Dimethyl Cyclohexane	4.470	0.67
C8	1.747	0.26
Ethyl Benzene	1.075	0.16
Temperature	35.00	451.5
Pressure	2.50	849.0

E-101
FEED PREHEATER

T-101
EXTRACTION DISTILLATION COLUMN

E-102
T-101 REBOILER

E-103
T-101 CONDENSER

D-101
EXTRACTION REFLUX RECEIVER

E-108
SOLVENT REFLUX COOLER

E-104
LEAN SOLVENT & RICH SOLVENT HEAT EXCHANGER

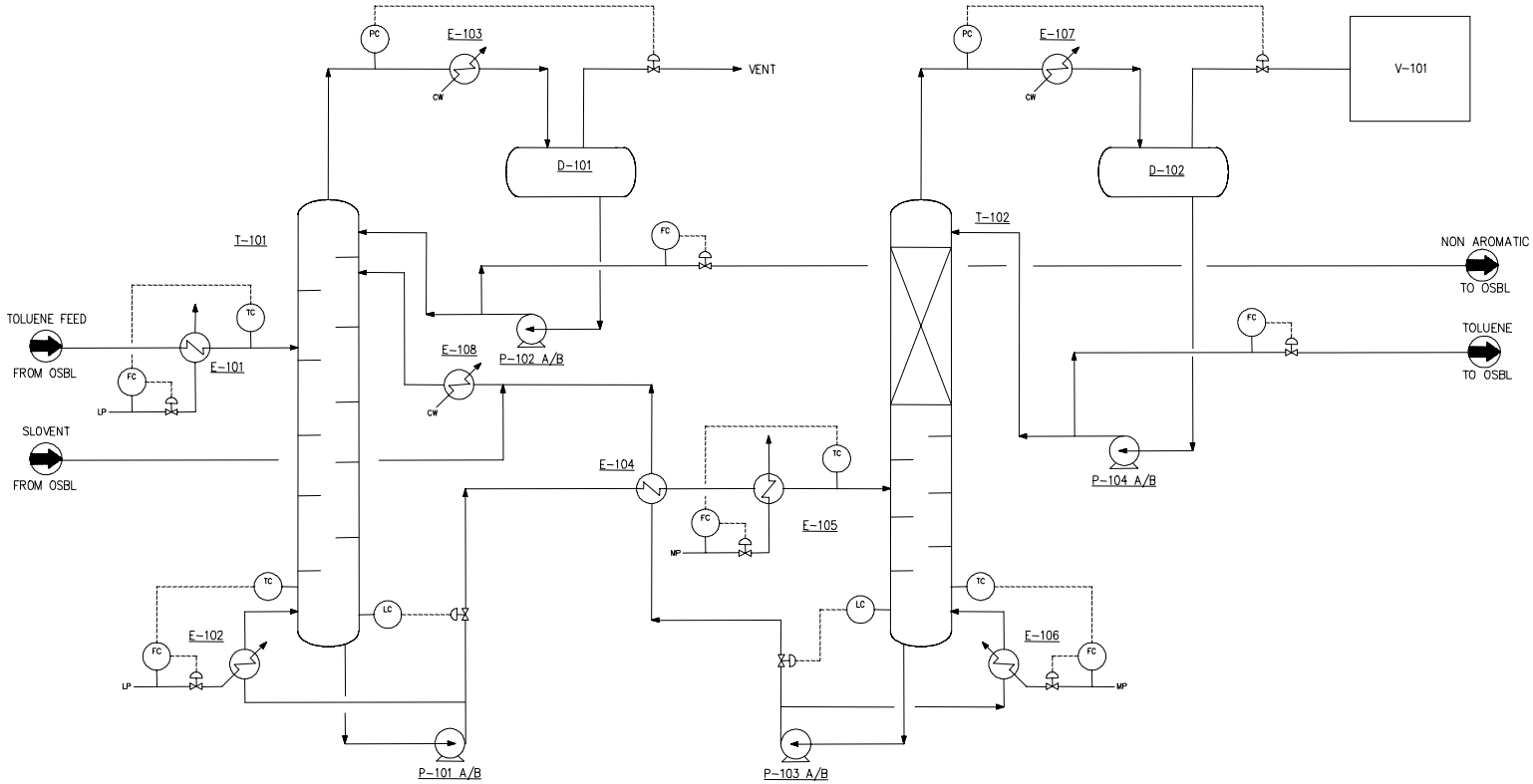
E-105
T-102 HEATER

T-102
SOLVENT RECOVERY COLUMN

E-106
T-102 REBOILER

D-102
SOLVENT RECOVERY REFLUX RECEIVER

E-107
T-102 CONDENSER



P-101 A/B
EXTRATION BTM PUMP

P-102 A/B
EXTRACTION REFLUX PUMP

P-103 A/B
SOLVENT RECOVERY RFFLUX PUMP

P-104 A/B
TOLUENE REFLUX & PRODUCT PUMP

V-101
VACUUM SYSTEM

	1	2	3	4	5	6	7
	Crude Feed	Raffinate (Nonaromatics)	Rich Solvent (Solvent + Aromatics)	Feed to Solvent Recovery Column	Toluene Rich Aromatics Product	Solvent Recovery Column BTMS Product	Lean Solvent Recycled to Extractive Distillation Column
Flow, Kg/hr	671.800	12.300	3,078.000	3,078.000	659.500	2,418.500	2,418.500
Toluene	660.581	2.321	658.261	658.261	658.260	0.001	0.001
Benzene	1.411	1.263	0.147	0.147	0.147	-	-
MCH	2.217	2.217	< 0.001	< 0.001	< 0.001	-	-
DMCH	4.470	4.763	0.007	0.007	0.007	-	-
C8	1.747	1.736	0.010	0.010	0.010	-	-
Ethyl Benzene	1.075	-	1.075	1.075	1.075	< 0.001	< 0.001
Sulfolane	0.00	< 0.001	2,418.500	2,418.500	< 0.001	2,418.499	2,418.499
Temp. (°C)	35.00	50.000	148.400	157.000	45.000	264.900	105.000
Press. (bar)	2.50						

- Toluene 회수율 : 99.65%.
- Toluene 순도 : 99.8% in weight.
- Toluene의 순도를 99.9%+>
  - ✓ 추출증류탑 앞에 B/T fractionator 를 적용
  - ✓ 용매회수탑 뒤에 B/T fractionator 를 적용

1. 공정모사 에 열역학적 모델들의 중요성
    열역학적 모델들의 선택(50%)
    선택된 모델들 사이의 각종 물성 파라미터 산출(20%)
        - 실험 데이터 (vapor pressure, VLE, LLE)
        - 예측 방법 (Joback, Ambrose, etc)

2. 물질들의 특성 이해
    물질간의 상호작용을 이해
        - 물질간의 그룹 만들기 (5%)

3. 공정의 이해
    단위 공정의 적절한 선택 (15%)
        - 증류탑 모델/ condenser와 reboiler를 열교환기 해석
        - 효율의 문제
        - 제한 조건 설정

4. 시뮬레이터의 사용능력 (10%)