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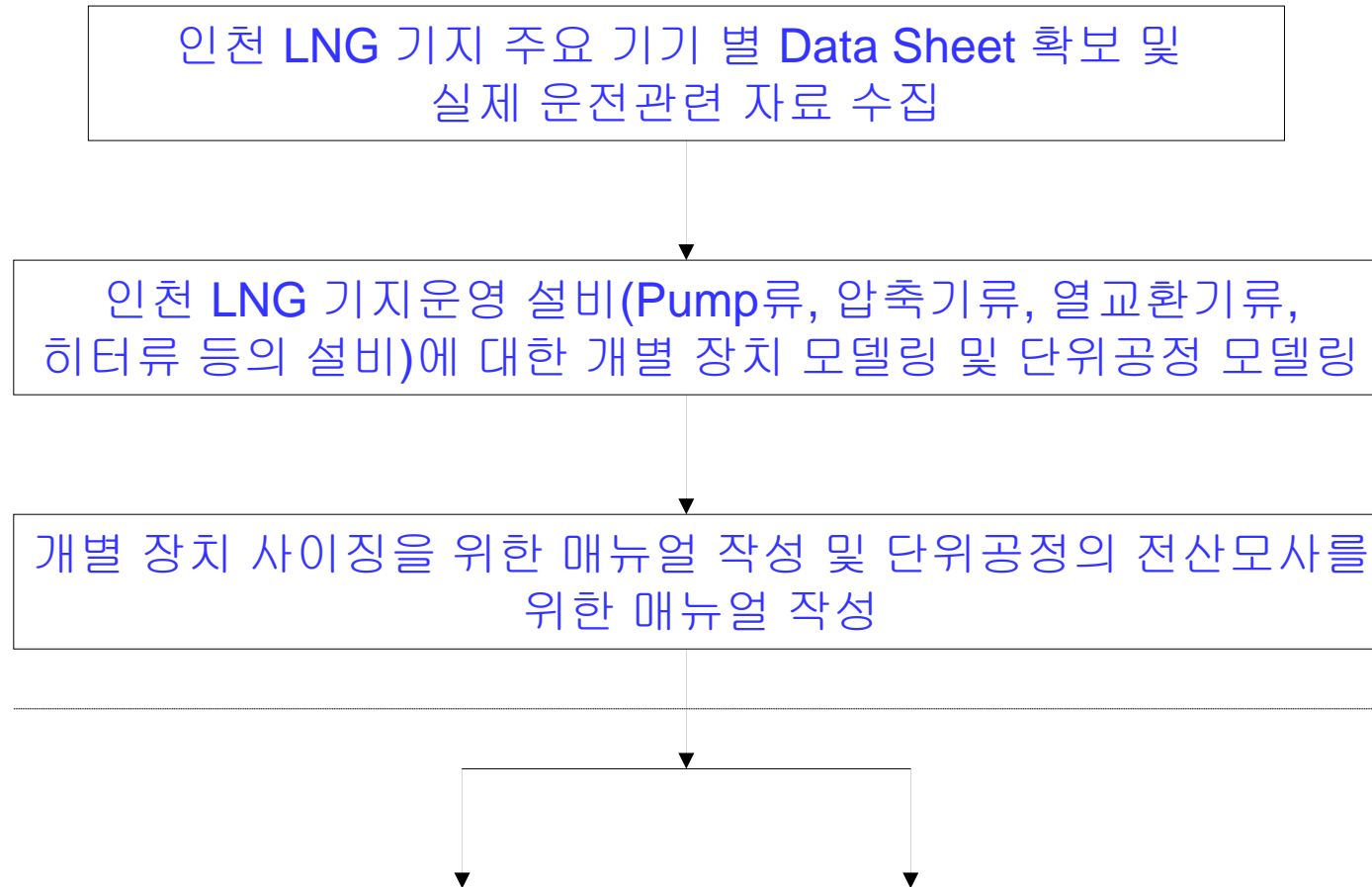
# LNG 생산기지 실제 조업 데이터 분석을 통한 생산성 향상 및 에너지 절감 연구

2005년 12월 16일(금)  
동양대학교 생명화학공학과  
조 정 호

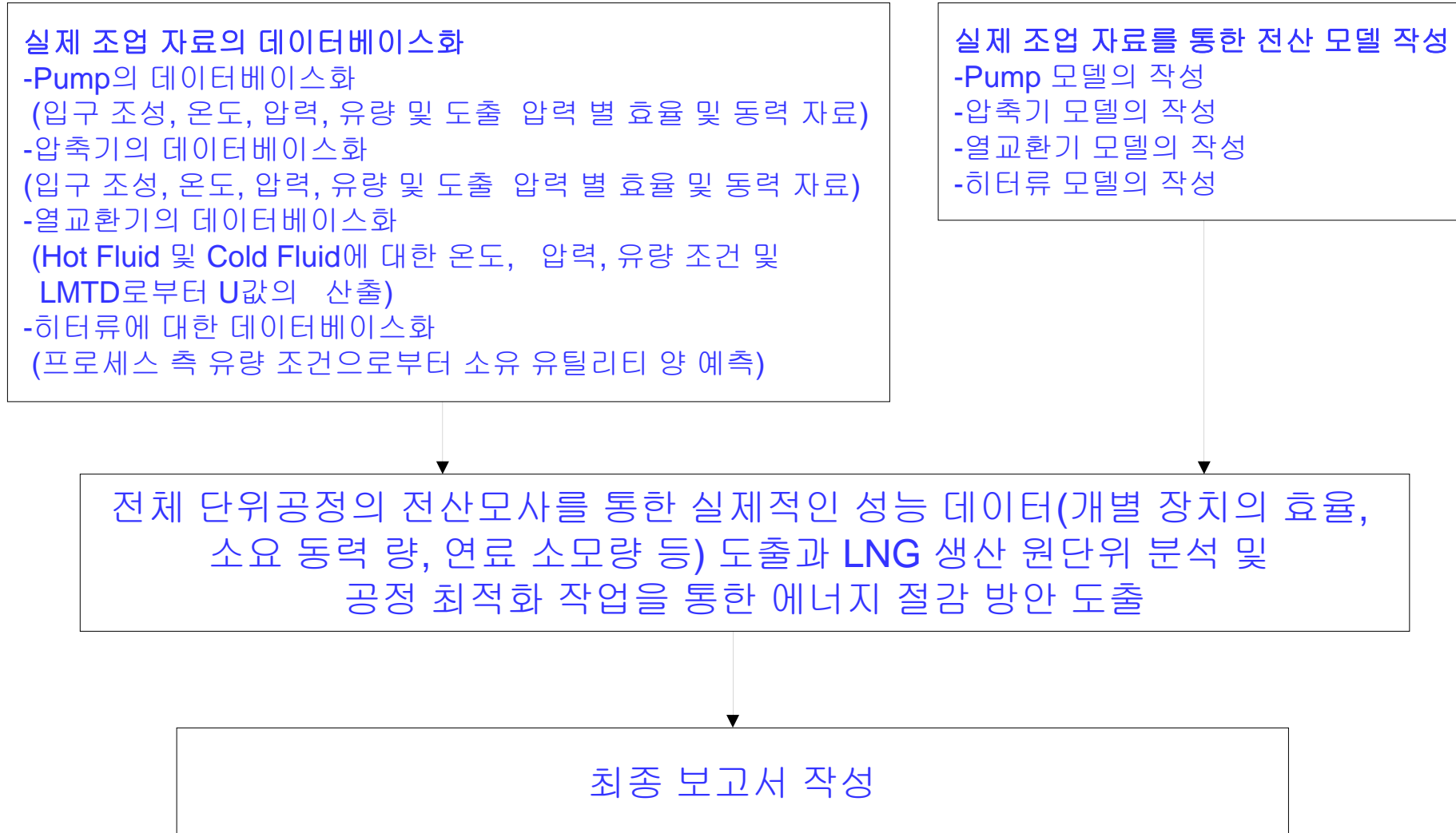
# 대학협력과제 연구협약 사항

협약 과제 명	LNG 생산기지 실제 조업데이터 분석을 통한 생산성 향상 및 에너지 절감 연구
협약 기간	2005년 7월 ~ 2006년 6월 (12개월)
협약 금액	30,000천원
협약 당사자	협약자: 한국가스공사 연구개발원장 협약 대상자: 동양대학교 산학협력단장 연구 책임자: 동양대학교 생명화학공학과 조정호

# 연구개발 추진체계: 1차년도 (2005년 7월 ~ 12월)



# 연구개발 추진체계: 2차년도 (2006년 1월 ~ 6월)



# LNG Composition: Mole%

	Case 1	Case 2	Case 3	Case 4
	Lean	Rich	Max N <sub>2</sub>	Typical
Nitrogen	0.00	0.00	1.00	0.04
Methane	96.74	85.12	94.33	89.26
Ethane	1.89	8.63	1.97	8.64
Propane	0.68	4.14	2.50	1.44
i-Butane	0.34	1.10	0.10	0.27
N-Butane	0.34	0.90	0.10	0.35
i-Pentane	0.01	0.10	0.00	0.00
N-Pentane	0.00	0.01	0.00	0.00
MW	16.791	19.320	17.189	17.924
GHV	9,882	11,163	9,975	10,450
Sp. Gr.	0.434	0.478	0.448	0.455

# Binary Interaction Parameters: Aspen Plus

	1)	2)	3)	4)	5)	6)	7)	8)
1) Nitrogen		0	0	0	0	0	0	0
2) Methane			0	0	0	0	0	0
3) Ethane				0	0	0	0	0
4) Propane					0	0	0	0
5) i-Butane						0	X	X
6) N-Butane							0	0
7) i-Pentane								0
8) N-Pentane								

$$BIP's = \frac{8 \times 7}{2!} = 28$$

26 pairs of BIP's are available in Aspen Plus database.

# Binary Interaction Parameters: Aspen Plus

Component i	NITROGEN	NITROGEN	NITROGEN	NITROGEN	NITROGEN	NITROGEN	NITROGEN	METHANE
Component j	METHANE	ETHANE	PROPANE	I-BUTANE	N-BUTANE	I-PENTAN	N-PENTAN	ETHANE
Temperature units	C	C	C	C	C	C	C	C
Source	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT
k <sub>ij</sub>	0.0278	0.0407	0.0763	0.0944	0.07	0.0867	0.0878	-7.80E-03
T <sub>lower</sub>	-273.15	-273.15	-273.15	-273.15	-273.15	-273.15	-273.15	-273.15
T <sub>upper</sub>	726.85	726.85	726.85	726.85	726.85	726.85	726.85	726.85

Component i	METHANE	METHANE	METHANE	METHANE	METHANE	ETHANE	ETHANE	ETHANE
Component j	PROPANE	I-BUTANE	N-BUTANE	I-PENTAN	N-PENTAN	PROPANE	I-BUTANE	N-BUTANE
Temperature units	C	C	C	C	C	C	C	C
Source	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT
k <sub>ij</sub>	9.00E-03	0.0241	5.60E-03	-7.80E-03	0.019	-2.20E-03	-0.01	6.70E-03
T <sub>lower</sub>	-273.15	-273.15	-273.15	-273.15	-273.15	-273.15	-273.15	-273.15
T <sub>upper</sub>	726.85	726.85	726.85	726.85	726.85	726.85	726.85	726.85

Component i	ETHANE	PROPANE	PROPANE	PROPANE	PROPANE	I-BUTANE	N-BUTANE	I-PENTAN
Component j	N-PENTAN	I-BUTANE	N-BUTANE	I-PENTAN	N-PENTAN	N-BUTANE	N-PENTAN	N-PENTAN
Temperature units	C	C	C	C	C	C	C	C
Source	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT	EOS-LIT
k <sub>ij</sub>	5.60E-03	-0.01	0	7.80E-03	0.0233	1.10E-03	0.0204	0
T <sub>lower</sub>	-273.15	-273.15	-273.15	-273.15	-273.15	-273.15	-273.15	-273.15
T <sub>upper</sub>	726.85	726.85	726.85	726.85	726.85	726.85	726.85	726.85

# Soave-Redlich-Kwong Equation of State

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□ Functional Form:

$$P = \frac{RT}{V - b} - \frac{a \alpha}{V(V + b)}$$

□ Energy and Size Parameters:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad b = \sum_i x_i b_i$$

□ Mixing Rule:

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$$



# Binary Interaction Parameters: PRO/II

	1)	2)	3)	4)	5)	6)	7)	8)
1) Nitrogen		0	0	0	0	0	0	0
2) Methane			0	0	0	0	0	0
3) Ethane				0	0	0	X	0
4) Propane					0	X	0	0
5) i-Butane						0	X	X
6) N-Butane							X	0
7) i-Pentane								X
8) N-Pentane								

$$BIP's = \frac{8 \times 7}{2!} = 28$$

22 pairs of BIP's are available in PRO/II database.

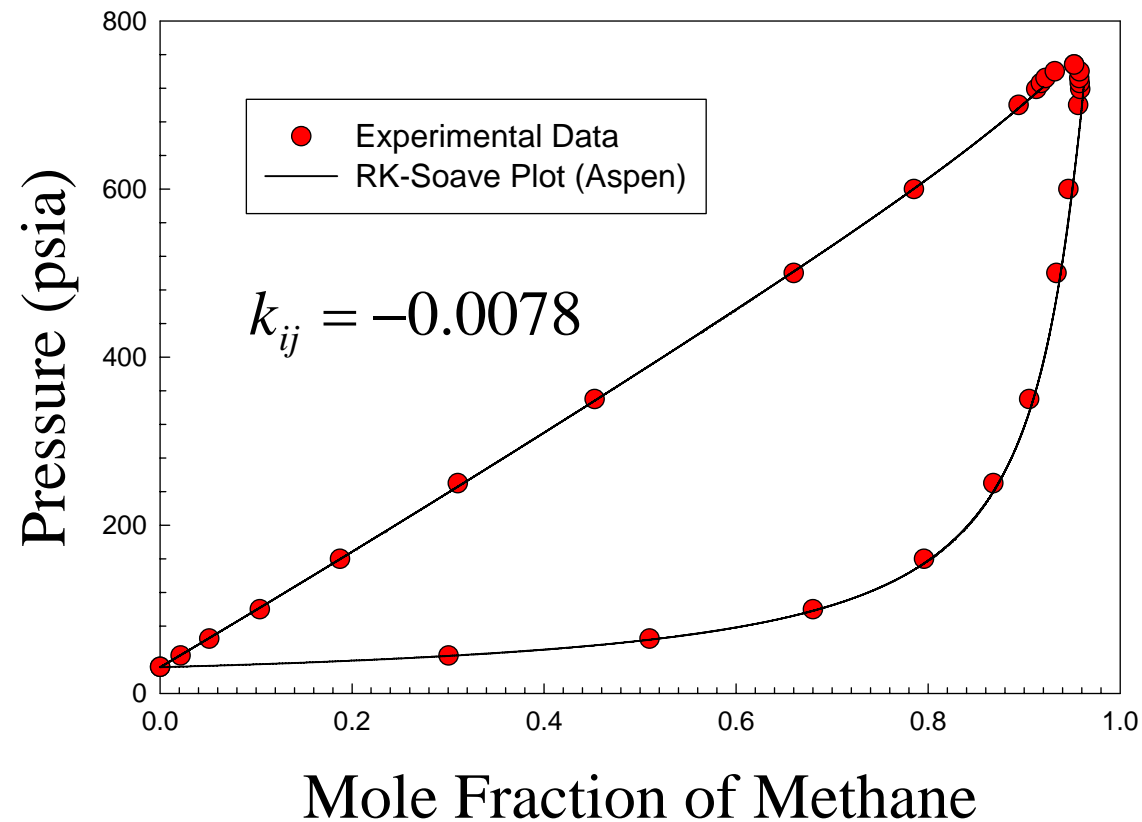
# Binary Interaction Parameters: PRO/II

## SRK INTERACTION PARAMETERS

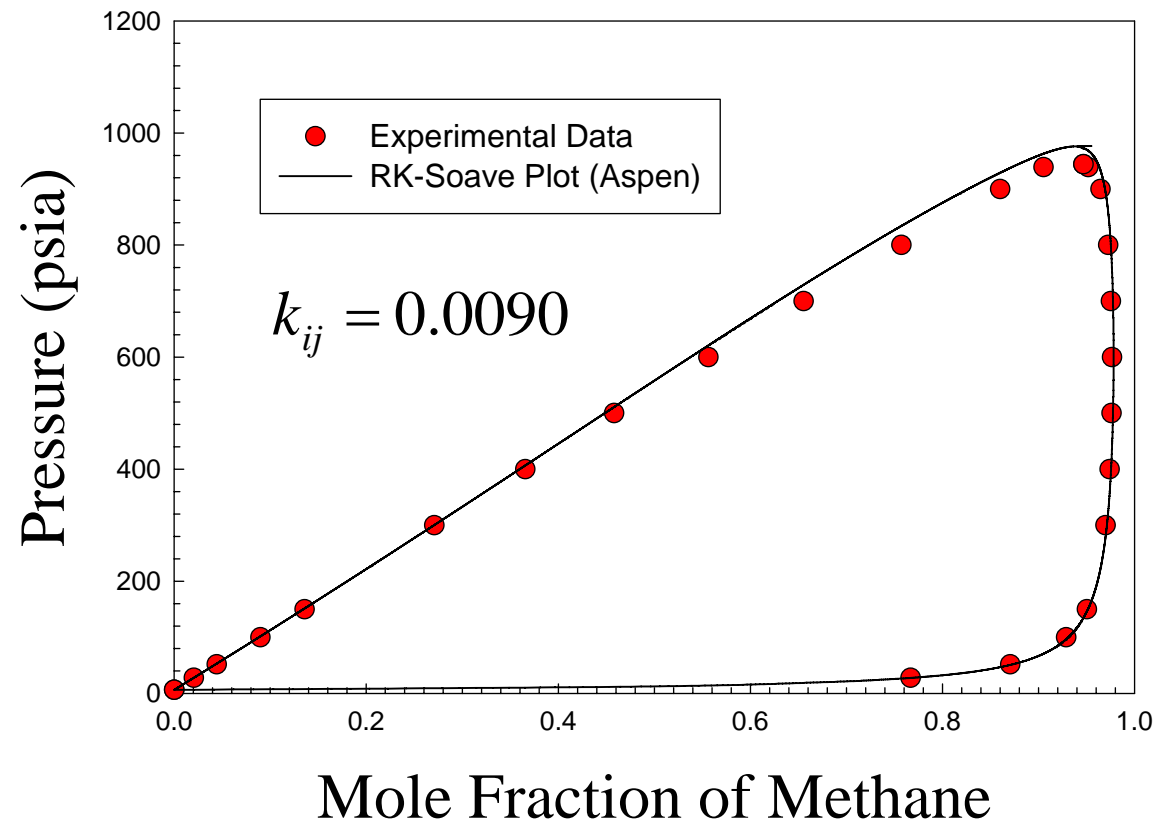
$$K_{IJ} = A(I,J) + B(I,J)/T + C(I,J)/T^{**2}$$

I	J	KA(I,J)	KB(I,J)	KC(I,J)	UNITS	FROM
1	2	0.0300	0.00	0.00	DEG K	SIMSCI BANK
1	3	0.0600	0.00	0.00	DEG K	SIMSCI BANK
1	4	0.0900	0.00	0.00	DEG K	SIMSCI BANK
1	5	0.1130	0.00	0.00	DEG K	SIMSCI BANK
1	6	0.1130	0.00	0.00	DEG K	SIMSCI BANK
1	7	0.1400	0.00	0.00	DEG K	SIMSCI BANK
1	8	0.1400	0.00	0.00	DEG K	SIMSCI BANK
2	3	-7.800E-03	0.00	0.00	DEG K	SIMSCI BANK
2	4	9.000E-03	0.00	0.00	DEG K	SIMSCI BANK
2	5	0.0241	0.00	0.00	DEG K	SIMSCI BANK
2	6	5.600E-03	0.00	0.00	DEG K	SIMSCI BANK
2	7	-7.800E-03	0.00	0.00	DEG K	SIMSCI BANK
2	8	0.0190	0.00	0.00	DEG K	SIMSCI BANK
3	4	-2.200E-03	0.00	0.00	DEG K	SIMSCI BANK
3	5	-1.000E-02	0.00	0.00	DEG K	SIMSCI BANK
3	6	6.700E-03	0.00	0.00	DEG K	SIMSCI BANK
3	8	5.600E-03	0.00	0.00	DEG K	SIMSCI BANK
4	5	-1.000E-02	0.00	0.00	DEG K	SIMSCI BANK
4	7	7.800E-03	0.00	0.00	DEG K	SIMSCI BANK
4	8	0.0233	0.00	0.00	DEG K	SIMSCI BANK
5	6	1.100E-03	0.00	0.00	DEG K	SIMSCI BANK
6	8	0.0204	0.00	0.00	DEG K	SIMSCI BANK

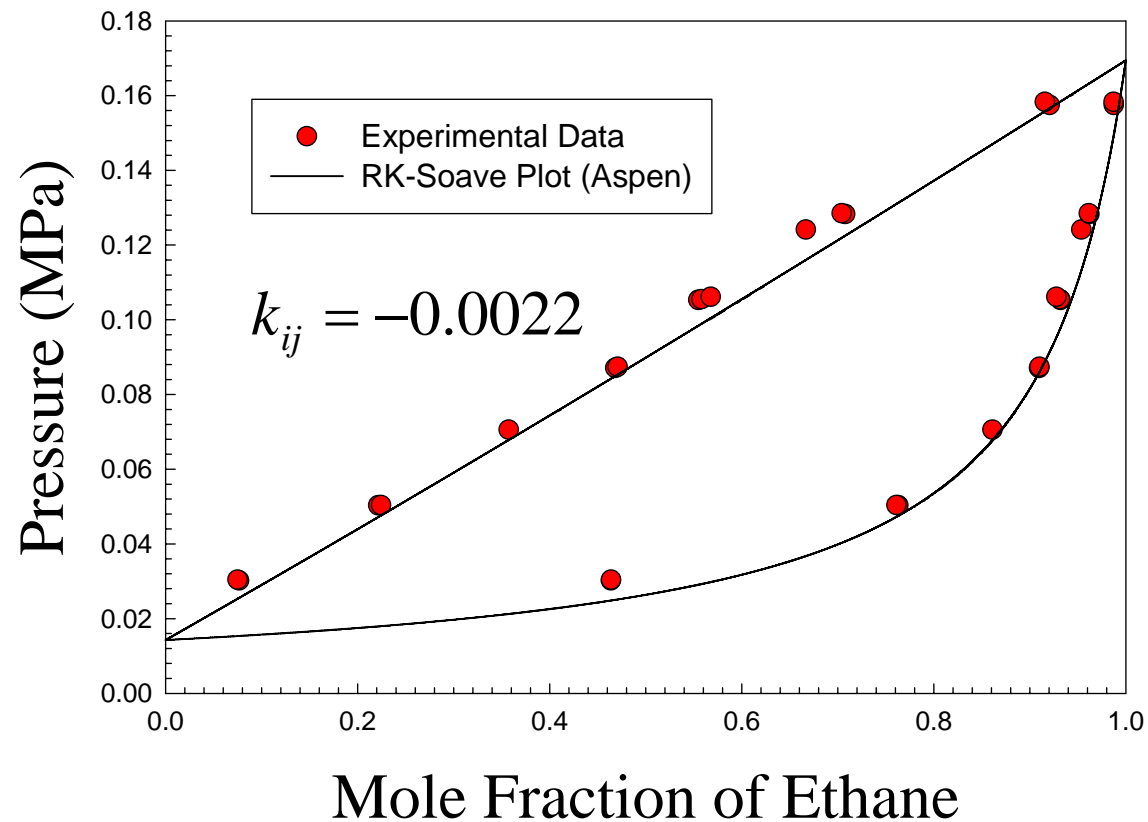
# Key Binary 1: P – X - Y Data: Methane + Ethane at -99.8°F



# Key Binary 2: P – X - Y Data: Methane + Propane at -75.0°F



# Key Binary 3: P – X - Y Data: Ethane + Propane at 195K



# LNG Composition: Mole%

	Case 1	Case 2	Case 3	Case 4
	Lean	Rich	Max N <sub>2</sub>	Typical
MW	16.791	19.320	17.189	17.924
	<i>(16.791)</i>	<i>(19.318)</i>	<i>(17.225)</i>	<i>(17.925)</i>
GHV (Kcal/Nm <sup>3</sup> )	9,882	11,163	9,975	10,450
	<i>(9,875)</i>	<i>(11,154)</i>	<i>(9,940)</i>	<i>(10,446)</i>
Sp. Gr.	0.434	0.478	0.448	0.455
	<i>(0.439)</i>	<i>(0.485)</i>	<i>(0.454)</i>	<i>(0.461)</i>

# Typical LNG Properties

	Typical	
Nitrogen	0.04	
Methane	89.26	
Ethane	8.64	
Propane	1.44	
i-Butane	0.27	
N-Butane	0.35	
i-Pentane	0.00	
N-Pentane	0.00	
MW	17.924	(17.925)
GHV	10,450	(10,446)
Density (Kg/m <sup>3</sup> )	455	(461)
BP at 1.13Kg/cm <sup>2</sup>	-158.53	(-158.95)
Viscosity at -160°C (cP)	0.142	(0.15076)
Cp (Kcal/kg°C)	0.8	(0.789)

# LNG Vapor Properties

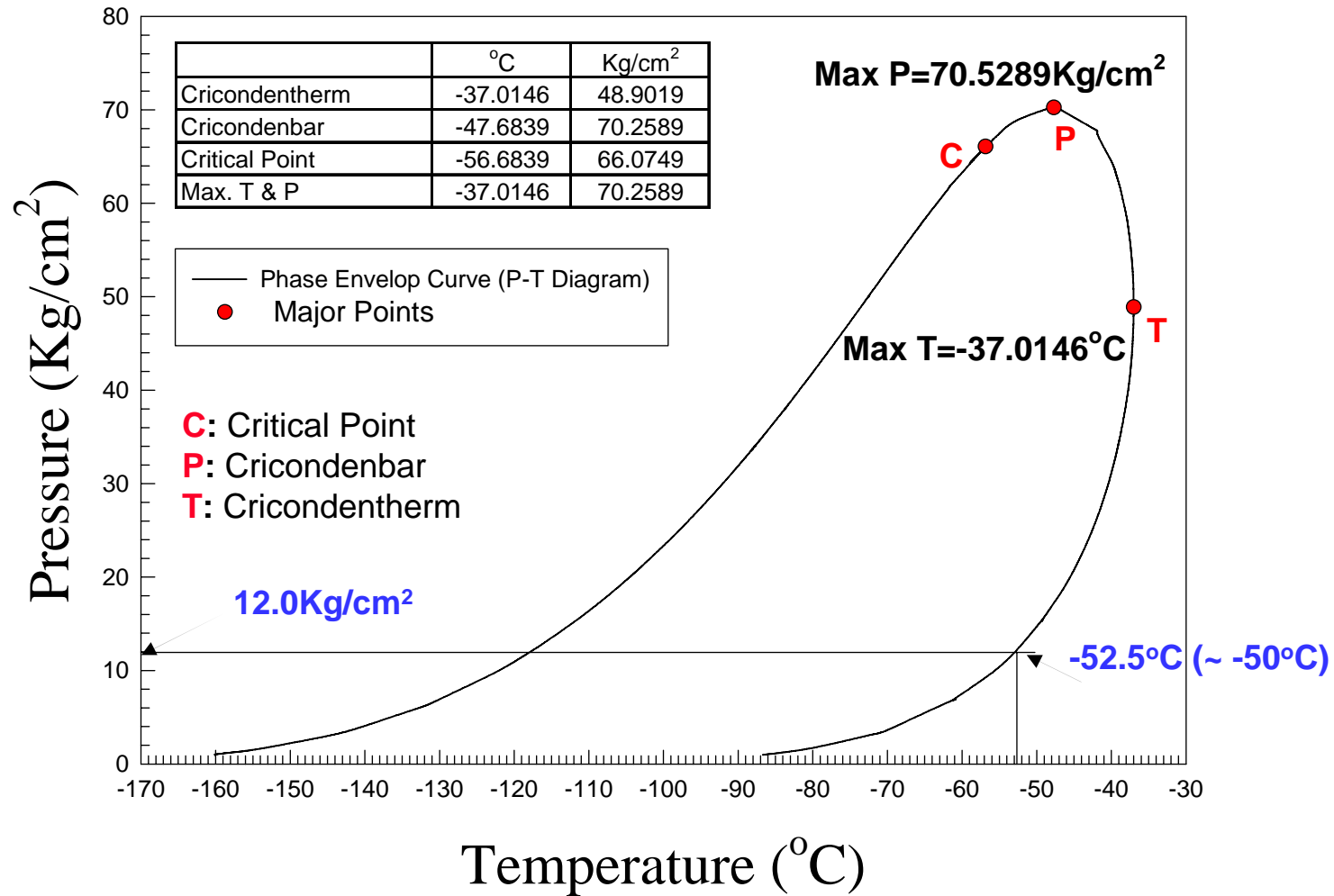
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	By KOGAS	<i>Simulation</i>
Components	Mole%	<i>Mole %</i>
Nitrogen	0.34	<i>1.2071</i>
Methane	99.64	<i>98.7783</i>
Ethane	0.02	<i>0.0146</i>
Total	100.00	<i>100.00</i>
MW	16.090	<i>(16.4783)</i>
Density (Kg/m <sup>3</sup> ) *	1.525	<i>(1.564)</i>
Viscosity at -160°C (cP) *	0.0057	<i>(0.00560)</i>
Cp (Kcal/kg°C) *	0.50	<i>(0.488)</i>

The '\*' means that physical properties were measured at -130°C, 1.13 Kg/cm<sup>2</sup> abs.



# Phase Envelop for Typical LNG Stream



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# LNG, BOG 물성추산을 위한 열역학 모델 개발 (I):

순수성분의 액체의 밀도를 정확하게 추산하기 위한  
상태방정식의 *Functional form*과 *Correlation equation*의  
적용성의 검토를 중심으로....

# LNG, BOG 물성추산을 위한 열역학 모델 개발 (I)

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## □ Liquid

- Benedict-Webb-Rubin-Starling (with necessary data)
- Lee-Kesler-Ploecker (mainly hydrocarbons)
- API (mainly hydrocarbons)
- Rackett
- Costald
- LIBRARY

## □ VAPOR:

- All Equations of State

# Critical Compressibility Factors

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- Experimental values for critical compressibility:
  - 0.2880 for CH<sub>4</sub>
  - 0.2840 for C<sub>2</sub>H<sub>6</sub> &
  - 0.2800 for C<sub>3</sub>H<sub>8</sub>
  
- PR and SRK equation of state are still used to estimate phase equilibria calculation for non-ideal systems since what is the most important thing in the design of chemical process is K-values, *not the liquid densities.*

# Density Methods

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## □ Equations of State

- 2-parameter cubic equations of state (SRK, PR)
  - ▶ These equations are acceptable for calculation of vapor density but not generally not acceptable for liquid density, even for hydrocarbons. Error in the liquid is about 15%. SRK is better for C1 and C2, PR is better for C5 – C8, both are bad for C9+.
  - ▶ Because of this, our SRK and PR CEOS use the API density method for the liquid density.
- 3-parameter cubic equation of state (TCC)
  - ▶ A 3<sup>rd</sup> parameter has been added to improve the density calculations for this cubic EOS.

# Density Methods

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## □ API

- This density method uses the density of the component at 60 F and weight-averages it to get a mixture density at 60 F. This is then corrected to the temperature of interest using the equation.

$$\rho_{act} = \rho_{60} \left[ \frac{C_{act}(T_r, P_r)}{C_{60}(T_r, P_r)} \right]$$

- $C_{60}$  and  $C_{act}$  are found based on the Kays rule reduced temperature and pressure from the API Technical Data Book.
- This method is only for liquid densities and is recommended only for  $T_r < 0.9$ . For hydrocarbon systems, the accuracy is usually within 1%.

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# LNG, BOG 물성추산을 위한 열역학 모델 개발 (II): 순수성부의 증기압을 잘 추산하기 위한 Alpha form의 개발을 중심으로....

# Alpha form: All Started with RK EOS

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- The RK EOS (1949) was the first to introduce the concept of a temperature dependency in the attractive term of the vdw EOS.
- Thus the alpha function used in RK equation of state is given by:

$$\alpha_i(T) = \frac{1}{T_{ri}^{1/2}}$$

- Thermodynamic researchers prior to Redlich-Kwong have known that “*a*” is .....



# Requirements for Alpha form

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- Requirements for alpha form:
  - The  $\alpha$  function must be finite and positive for all temperature.
  - The  $\alpha$  function must equal unity at the critical point.
  - The  $\alpha$  function must approach a zero value as the temperature approaches infinity.
  
- The trend from now is to set the coefficients of alpha function component dependently by regressing the experimental vapor pressure data vs. temperatures.

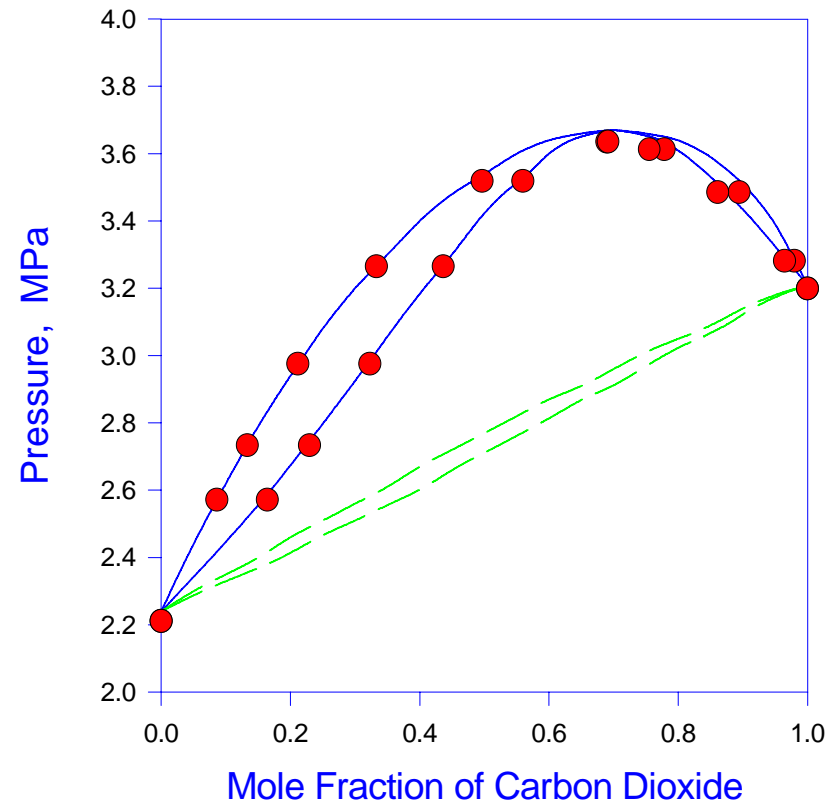
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# LNG, BOG 물성추산을 위한 열역학 모델 개발 (III):

혼합물의  $K$ -value (기액 평형 관계식)을 잘 추산하기 위한  
*Mixing rules*의 개발을 중심으로....

# Binary Interaction Parameters (1 of 2)

- Good representation of vapor-liquid equilibria: “Adequate mixing rules”
- CO<sub>2</sub>-ethane at 270K
- Dashed line: SRK with  $k_{ij} = 0$
- Straight line: Regressed



# Binary Interaction Parameters (2 of 2)

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- Using nonzero  $K_{ij}$  generally improves VLE representation
- $K_{ij}$  is not a magic number. It corrects for the inadequacy of the model, or the deficiency in corresponding states theory.
- $K_{ij}$  for one EOS should not be used directly in another EOS.
- The order of expected accuracy for VLE calculations using  $K_{ij}$  obtained:  
regressed from data > estimated from correlation > zero value

# Advanced (Panagiotopoulos) mixing rules

- Panagiotopoulos and Reid proposed an asymmetric mixing rule containing two parameters for SRK and PR equations of state (denoted as SRKP and PRP).
- The Panagiotopoulos mixing rule

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad b = \sum_i x_i b_i$$

$$a_{ij} = \sqrt{a_i a_j} \left[ (1 - k_{ij}) + (k_{ij} - k_{ji}) x_i \right]$$

Refer to Discussion 14.hwp

# Fugacity Coefficient of Component 'i':

General Two Parameter Cubic EOS and Panagiotopoulos Mixing Rules

- The fugacity coefficient expression of component 'i' in a mixture applicable to general two parameter equation of state and Panagiotopoulos mixing rules are as:

$$\begin{aligned} \ln \hat{\phi}_i = & \frac{2\bar{b} - b_i}{b} (Z - 1) - \ln \frac{P(v - b)}{RT} \\ & + \left[ \sum_l x_l (a_{lk} + a_{il}) - \sum_l \sum_w x_l^2 x_m \sqrt{a_l a_m} (k_{lm} - k_{ml}) \right. \\ & \left. + x_i \sum_l x_l \sqrt{a_i a_l} (k_{il} - k_{li}) + \frac{a(2\bar{b}_i - b)(u - 4w)}{b(4w - u^2)} \right] \\ & \times \frac{1}{\sqrt{u^2 - 4w}} \ln \frac{2v + b(u - \sqrt{u^2 - 4w})}{2v + b(u + \sqrt{u^2 - 4w})} \end{aligned}$$

# Fugacity Coefficient of Component 'i': SRK

- The fugacity coefficient expression of component 'i' in a mixture applicable to SRK equation of state is as:

$$\ln \hat{\phi}_i = -\ln \frac{P(v-b)}{RT} + \frac{b_i}{b} (Z-1) + \frac{a}{bRT} \left[ \frac{2\bar{a}_i}{a} - \frac{b_i}{b} \right] \ln \left( \frac{v+b}{v} \right)$$

where:

$$\bar{a}_i = \sum_l x_l a_{li}$$

Refer to Discussion 10.hwp

# Fugacity Coefficient of Component 'i': PR

- The fugacity coefficient expression of component 'i' in a mixture applicable to PR equation of state is as:

$$\ln \hat{\phi}_i = \frac{b_i}{b} (Z - 1) - \ln \frac{P(v - b)}{RT} + \frac{a}{2\sqrt{2}bRT} \left[ \frac{2\bar{a}_i}{a} - \frac{b_i}{b} \right] \ln \frac{v + (1 - \sqrt{2})b}{v + (1 + \sqrt{2})b}$$

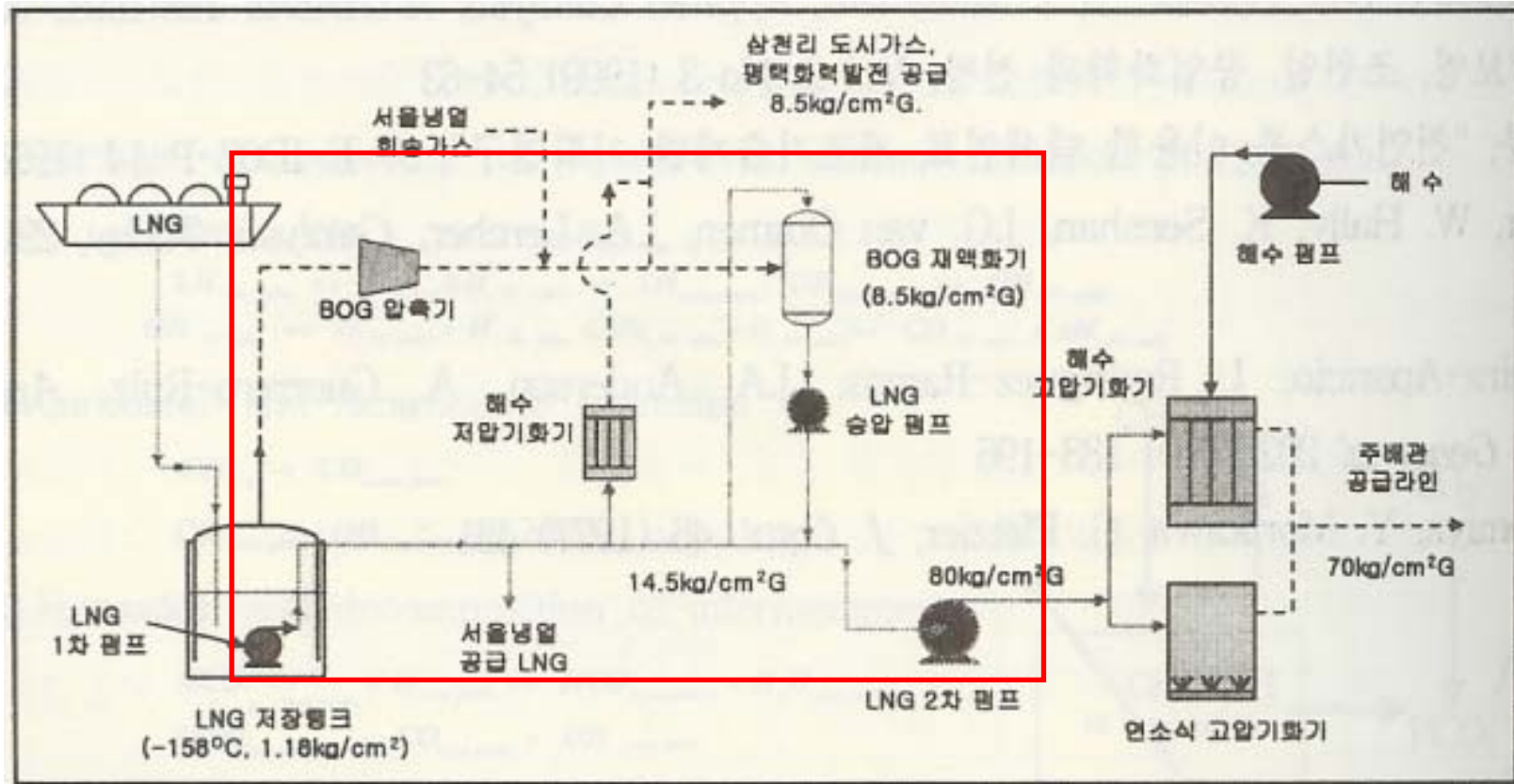
where:

$$\bar{a}_i = \sum_l x_l a_{li}$$

Refer to Discussion 11.hwp



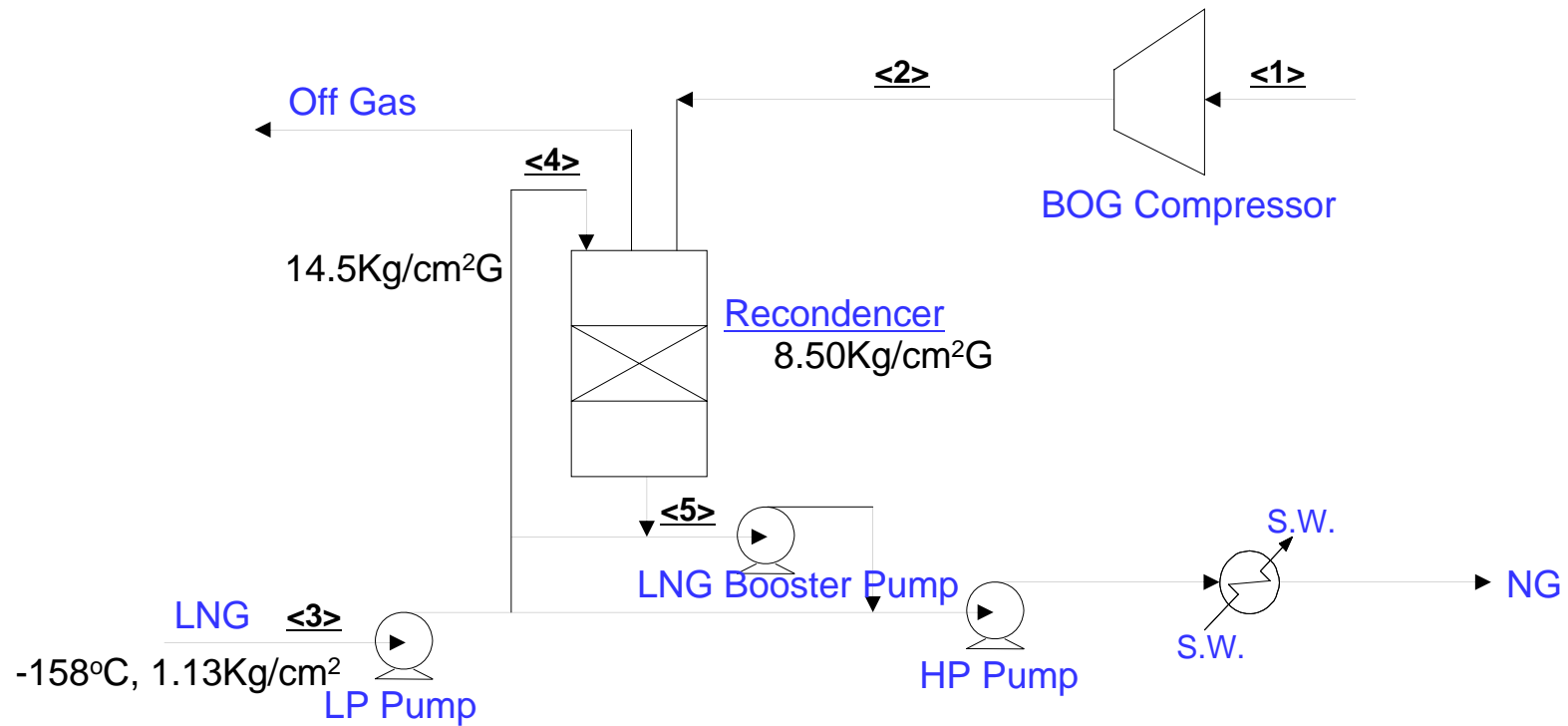
# 실제 공정에 적용 (1): LNG 기지 공정 개요도



# 실제 공정에 적용: LNG 재액화기

- **BOG 재 액화기(R/C) 내 혼합물질들의 상 거동 현상 규명.**
  - 재 액화기로 인입되는 BOG에 대하여
    - 1) 다양한 LNG 조성(Typical, Lean, Rich, Max N<sub>2</sub>)에서 발생하는 BOG의 조성 및 물성 추산
  - 온도, 압력 변화에 따른 열역학적인 물성 규명
    - 1) 인천, 평택, 통영 세 기지에서 재 액화기로 인입되는 BOG의 온도조건이 틀림.
    - 2) 현 운전조건이 아닌 다른 조건에서 분석
  - R/C로 인입되는 LNG
    - 1) LNG 조성에 따른 인입 조건에서의 열역학적인 물성 규명
    - 2) BOG 조성, 인입온도, 압력변화에 따른 LNG 혼합률에 따른 재액화 LNG(R/C 토출라인)의 열역학적인 상태 규명
    - 3) Two-stage Compression System에서 총 동력을 최소화시키는 최적의 중간 압력의 결정 문제
    - 4) 재액화기로 주입되는 LNG 최소량의 결정

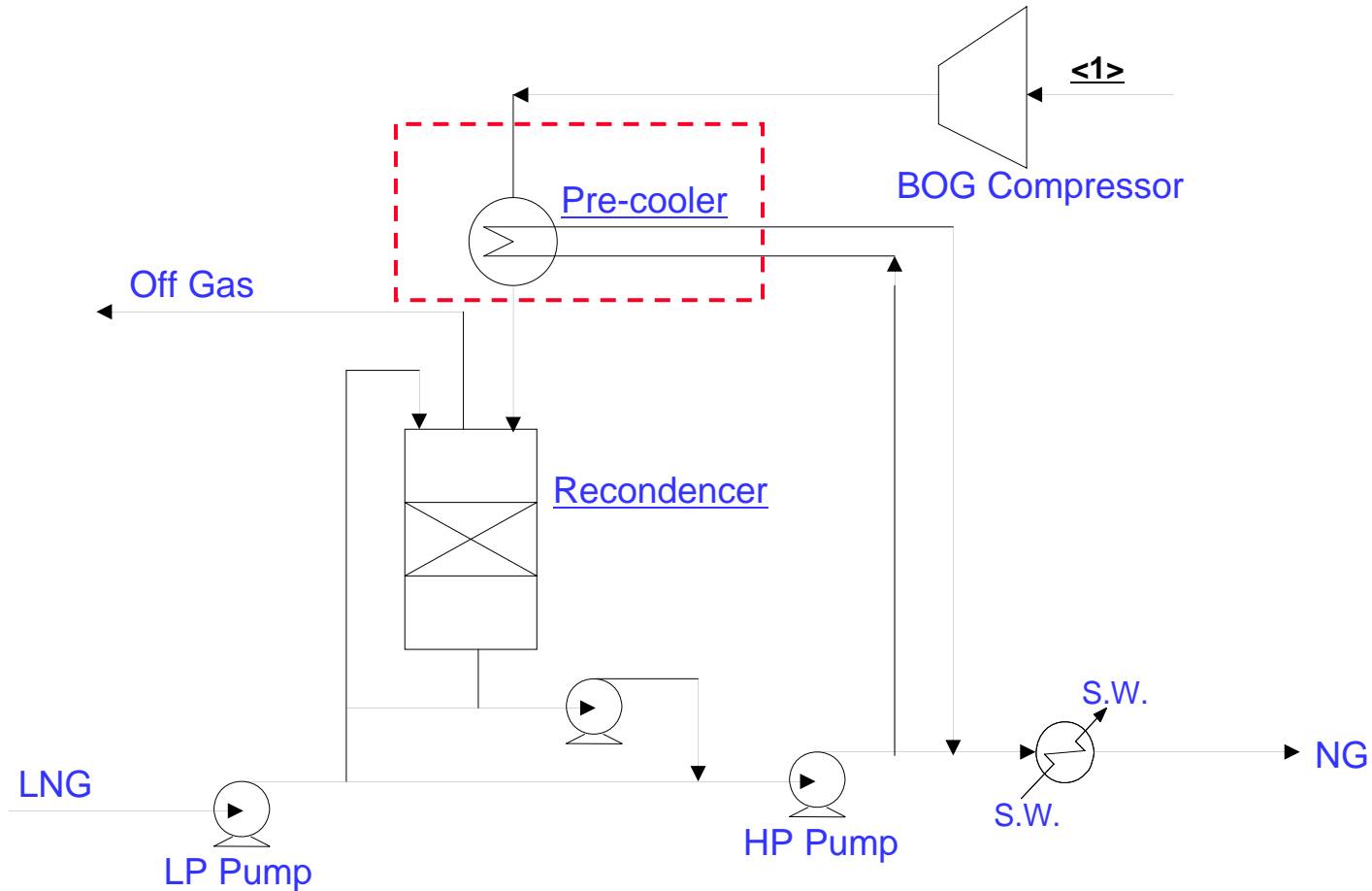
# 실제 공정에 적용: LNG 재액화기



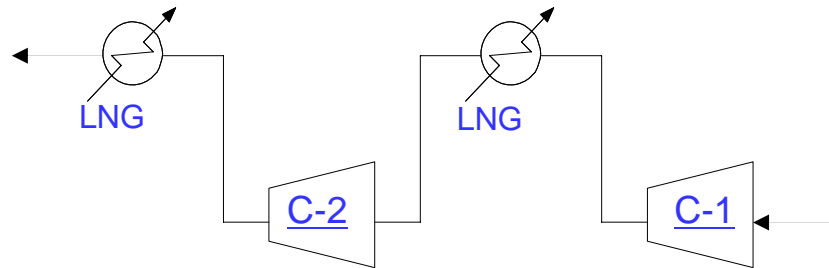
# 실제 공정에 적용: LNG 재액화기

Stream Number	1	2	3	4	5
N2	0.34	0.34	0.04	0.04	0.07
C1	99.64	99.64	89.26	89.26	90.21
C2	0.02	0.02	8.64	8.64	7.85
C3	0.00	0.00	1.44	1.44	1.31
iC4	0.00	0.00	0.27	0.27	0.25
nC4	0.00	0.00	0.35	0.35	0.32
iC5	0.00	0.00	0.00	0.00	0.00
nC5	0.00	0.00	0.00	0.00	0.00
Temperature(°C)	-120.00	26.30	-158.95	-157.89	-135.91
Phase	G	G	L	L	L
Pressure(Kg/cm <sup>2</sup> G)	0.15	8.85	1.13(A)	8.85	8.85
Flowrate (Kg/hr)	50000	50000	550000	550000	600000

# 기존 재액화기 개선 (1): Pre-cooler 설치



# 기존 재액화기 개선 (2): Intercooler 설치



- Consider the above two-stage compression system.
  - Determination of Optimum Intermediate Pressure
    - 1) Find the optimum intermediate pressure which minimized the summation of compressor power.
  - Determination of Minimum Compressor Power
    - 1) Find the minimum compressor power at the optimum intermediate pressure.

# 향후 연구 내용 및 기대효과 (1):

- 천연가스 혼합물의 열역학적 상 거동 해석에 가장 적합한 열역학 모델식의 선정 가이드 라인 작성.
  - 삼차형 상태 방정식에 대하여
    - 1) Functional Form에 대한 분석: 기상 및 액상의 밀도 추산
    - 2) API Method, Rackett Method에 대한 분석
  - Alpha Formulation에 대하여: 순수성분의 증기압 추산을 위하여
    - 1) Redlich-Kwong Alpha Form
    - 2) Soave's Original Alpha Form
    - 3) Component-dependent Alpha Form
  - Mixing Rules에 대하여: 혼합물의 K-value 추산을 위하여
    - 1) van der Waals: One fluid mixing rule
    - 2) Panagiotopoulos mixing rules
    - 3) Composition-dependent mixing rules
    - 4) 혼합물 중의 'i' 성분의 퓨개시티 계수의 유도 및 적용

# 향후 연구 내용 및 기대효과 (2):

## □ BOG 재액화 공정에 대해.....

- BOG에 대한 LNG의 혼합비의 최소화함으로써
  - 1) LNG 승압펌프 동력 최소화
  - 2) LNG 2차 펌프 동력 최소화
- 재액화기의 운전압력(현 8.5Kg/cm<sup>2</sup>G)을 떨어뜨림으로써
  - 1) BOG Compressor 동력 최소화
  - 2) BOG Compressor 동력 감소분 > Pump 동력의 증가분
  - 3) (BOG Compressor 동력)-(Pump 동력)을 최대화 시키는 최적의 재액화기의 운전 압력 결정
- Pre-cooler를 설치 함으로써
  - 1) LNG 혼합비율의 감소를 통한 Pump 동력의 최소화
- Intercooler를 설치 함으로써
  - 1) 재액화기로 주입되는 BOG의 온도를 떨어뜨림으로써 LNG 혼합비율의 감소를 통한 Pump 동력의 최소화
  - 2) BOG Compressor들의 총 소요 동력의 최소화



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# The End...