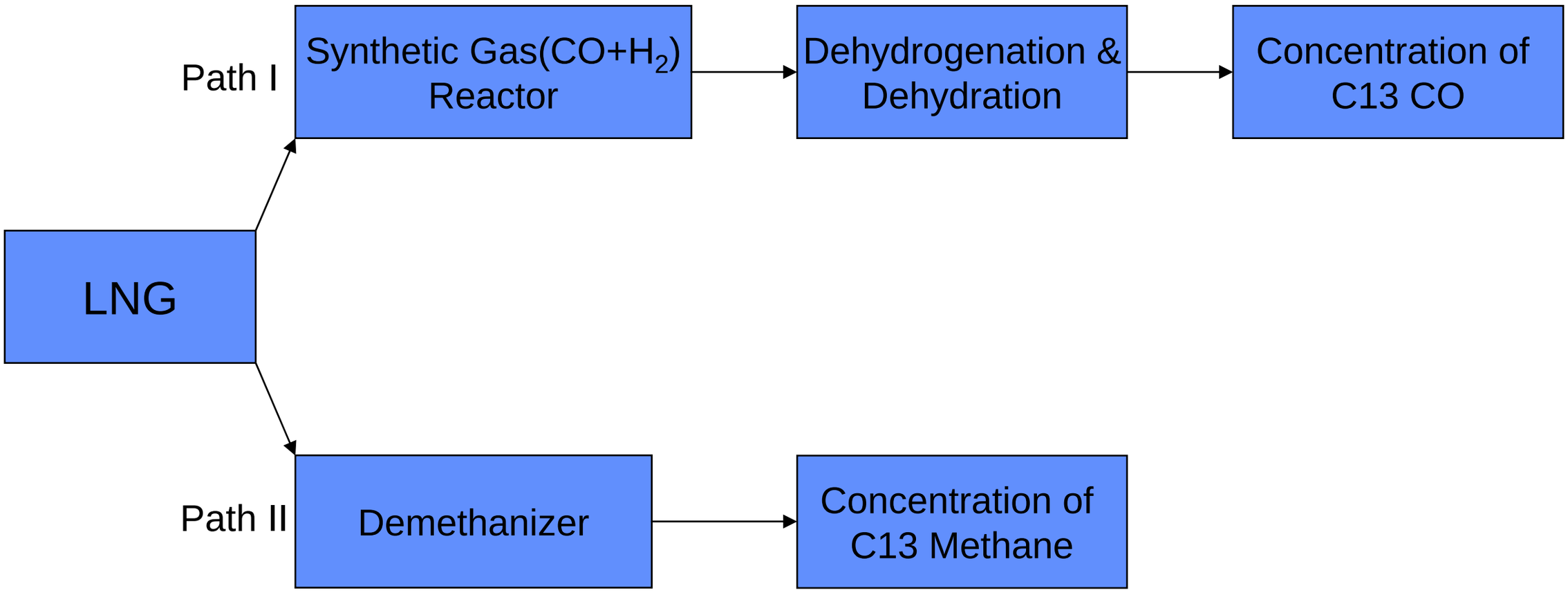
A Study on the Methane Isotope Separation Using Cryogenic Distillation

Jonghwan KIM[1], Sangjin PARK[1], Sehoon YOON[1],
Jungho CHO[2*], Young-Chul LEE[3], Taek-Yong SONG[3]
and Euy Soo LEE[1*]

Dongguk University 1
Dong Yang University 2
LNG Technology Research Center 3

Two Paths to Obtain $^{13}CH_4$ Based on a Cryogenic Distillation



Vapor Pressure Correlation of $^{12}CH_4$ Methane

- Antoine Vapor Pressure Equation is:

$$\ln P_L = 13.2093 - \frac{897.84}{T - 7.16}$$ (P_L in kPa and T in K)

- Normal boiling temperature of $^{12}CH_4$ methane is:

$$T = 7.16 + \frac{897.84}{13.2093 - \ln(101.325)} = 111.6697738K$$

Vapor Pressure Correlation of $^{13}CH_4$ Methane

- Correlation of $^{13}CH_4$ methane is:

$$\log\left(\frac{P_L}{P_H}\right)=\frac{36.9}{T^2}-\frac{0.192}{T}$$ (P_L in kPa and T in K)

- Vapor pressure expression of $^{13}CH_4$ methane is:

$$P_H=10^{\log\left[13.2093-\frac{897.84}{T-7.16}\right]-\frac{36.9}{T^2}+\frac{0.192}{T}}$$

- Normal boiling temperature of $^{13}CH_4$ methane is:

$$T=111.704475K$$ (0.0347K difference with $^{12}CH_4$ methane)

Relative Volatilities btn $^{12}CH_4$ & $^{13}CH_4$

- Definition of relative volatility of component ‘i’ and component ‘j’ is:

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\left(P_i/P\right)}{\left(P_j/P\right)} = \frac{P_i}{P_j}$$

(component ‘’ is defined as more volatile than component ‘j’)

Temperature (K)	VP of $^{12}CH_4$ (kPa)	VP of $^{13}CH_4$ (kPa)	**Alpha**
126.784	300.00	299.46	**1.0018**
120.653	200.00	199.568	**1.0022**
116.671	150.00	149.638	**1.0025**
111.510	100.00	99.714	**1.0029**
108.873	80.00	79.755	**1.0031**
105.662	60.00	59.796	**1.0034**
104.139	52.00	51.812	**1.0036**

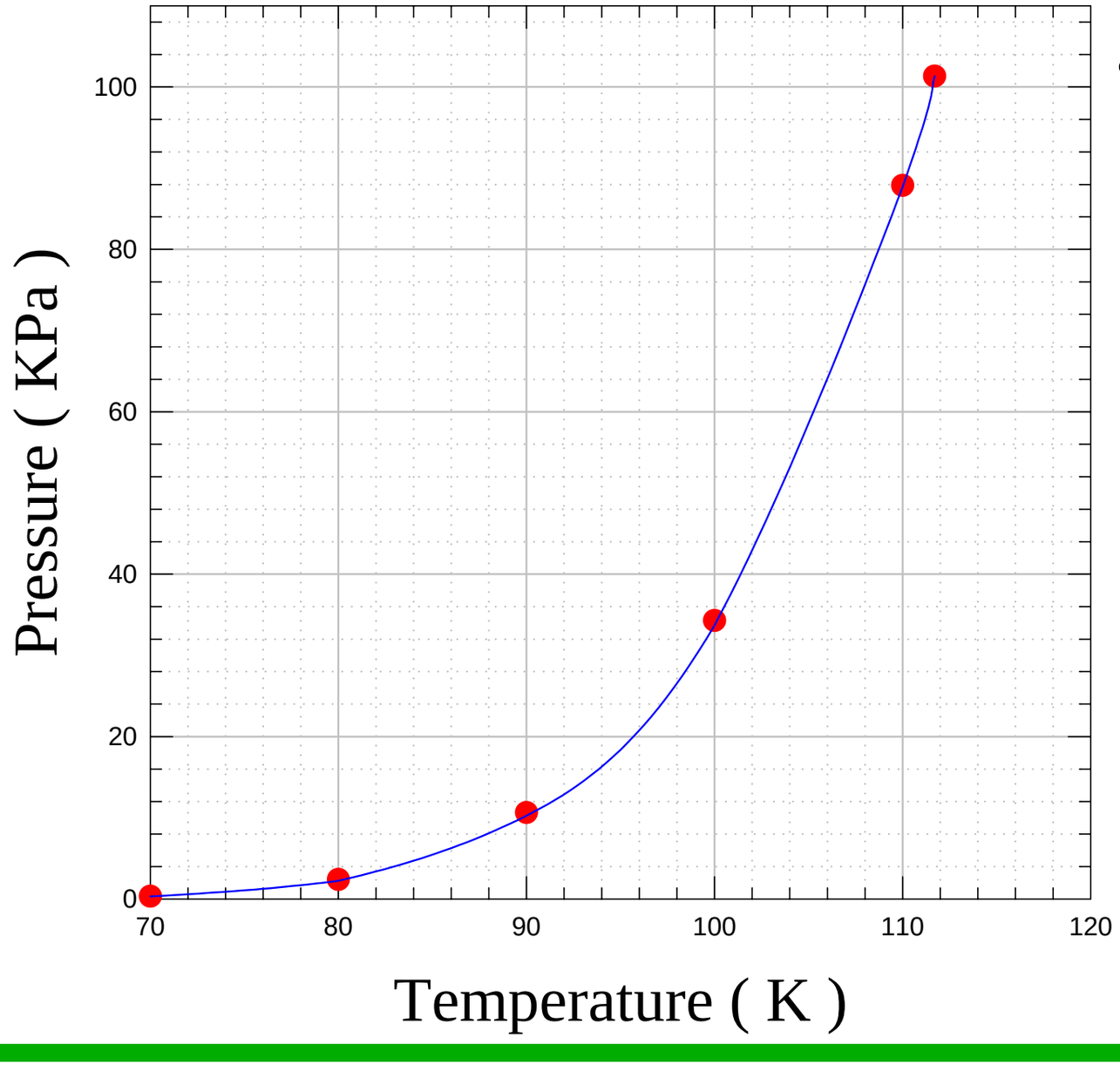
$^{13}CH_4$ Property Calculation Using PR

- We used Peng-Robinson equation of state for the modeling of methane isotope separation.

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

- Parameter ‘a’ and ‘b’ are functions of critical temperature and pressure.
- Alpha value is functions of reduced temperature and acentric factor.
- Acentric factor of $^{13}CH_4$ methane was adjusted to accurately estimate vapor pressure at a given temperature.

Comparison of $^{13}CH_4$ Vapor Pressure btn Correlation & PR Equation



- Acentric factor, ω was modified as 0.0108 to fit the correlated vapor pressure vs. temperature.

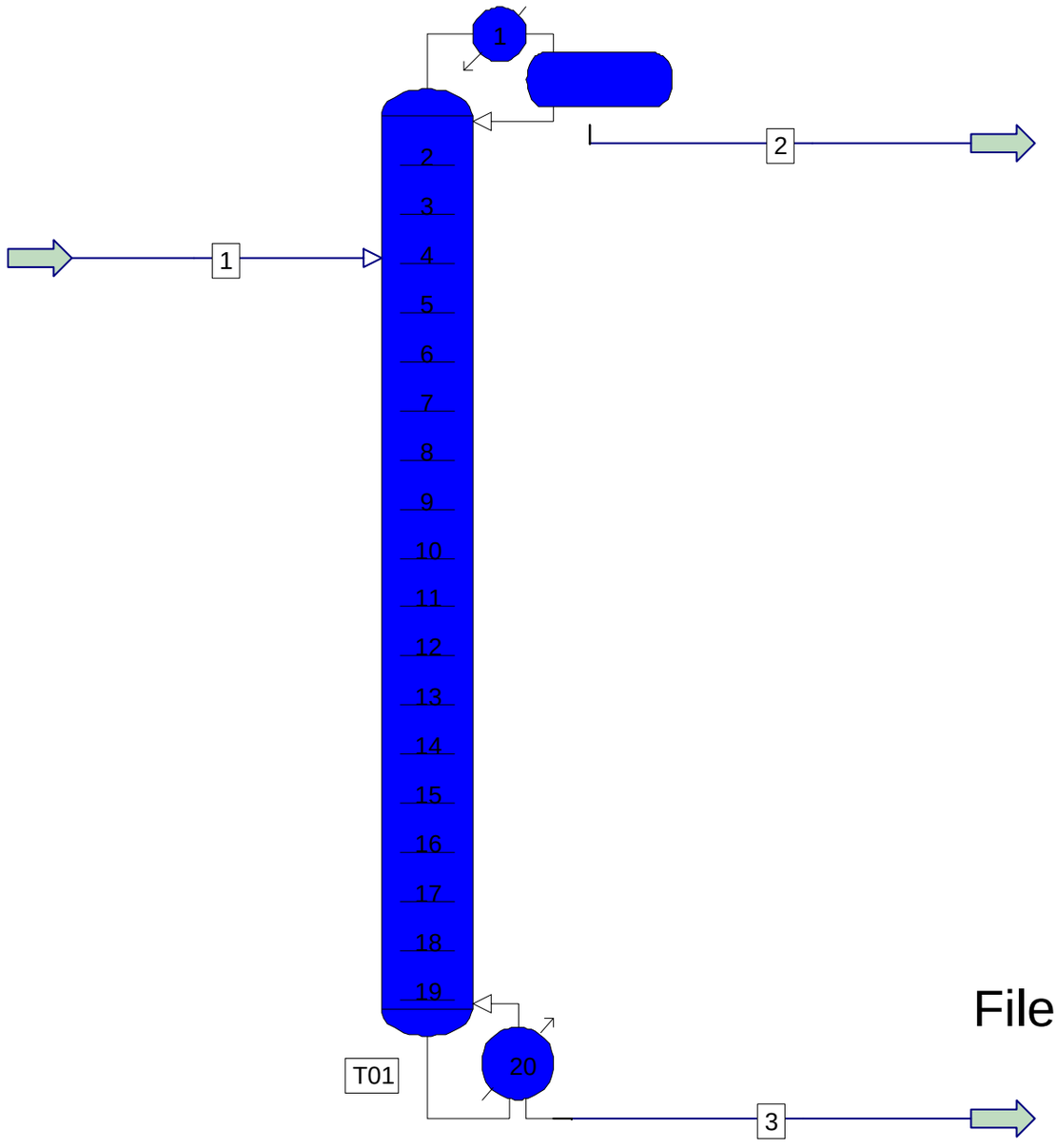
LNG Feed Composition: Supplied from KOGAS

Components	Mole Percent
Nitrogen	0.0700
$^{12}CH_4$ Methane	89.3574
$^{13}CH_4$ Methane	0.9026
Ethane	7.8100
Propane	1.3000
i-Butane	0.2400
n-Butane	0.3200
Temperature (^oC)	-155.0

$^{13}CH_4$ Separation Procedure

- Separation of C2+ from LNG:
- Step 1: Concentration of $^{13}CH_4$ from 1% to 9.2376%
- Step 2: Concentration of $^{13}CH_4$ from 9.2376% to 35%
- Step 3: Concentration of $^{13}CH_4$ from 35% to 40%
- Step 4: Concentration of $^{13}CH_4$ from 40% to 60%
- Step 5: Concentration of $^{13}CH_4$ from 60% to 80%
- Step 6: Concentration of $^{13}CH_4$ from 80% to 90%

Demethanizer Simulation Using PRO/II



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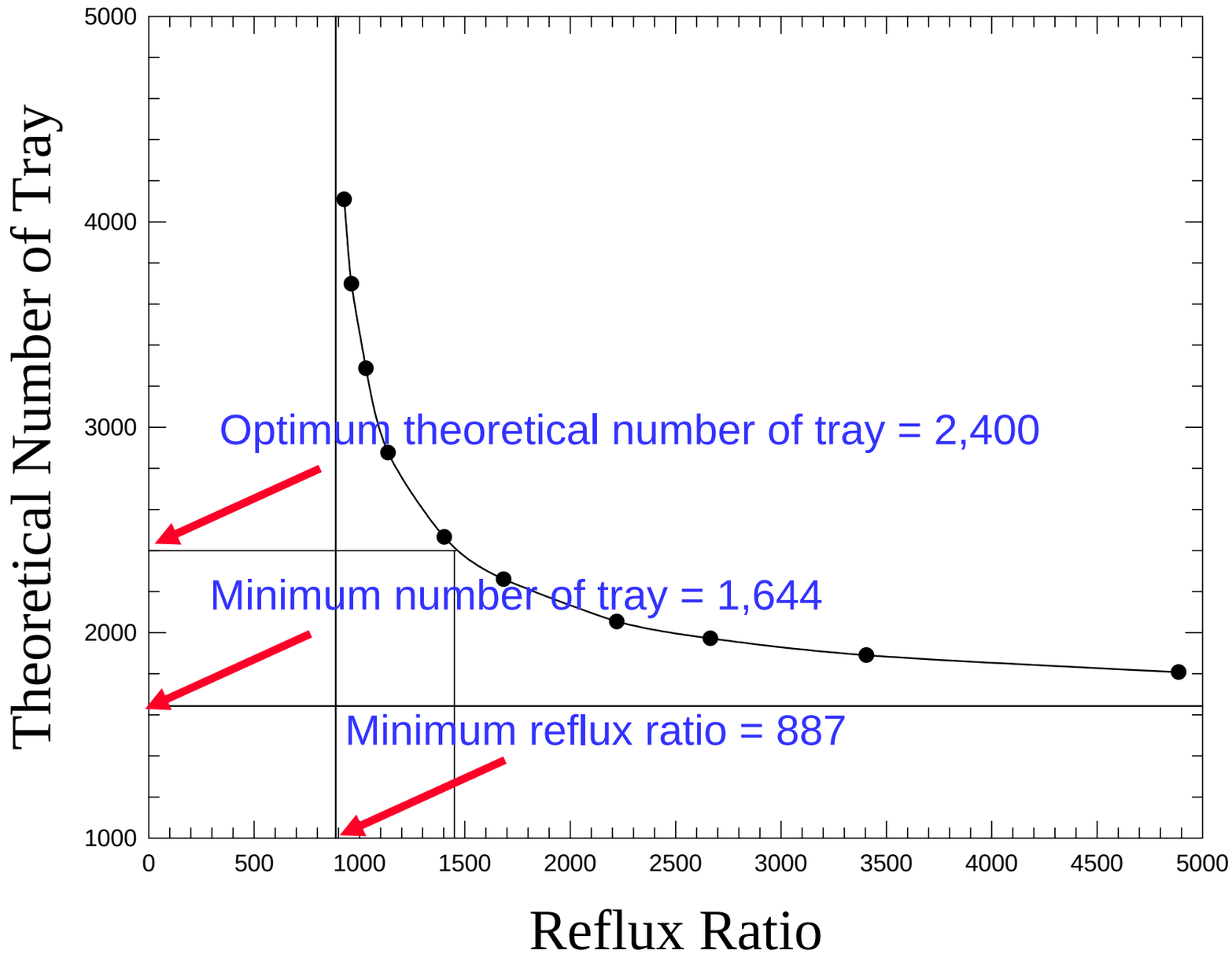
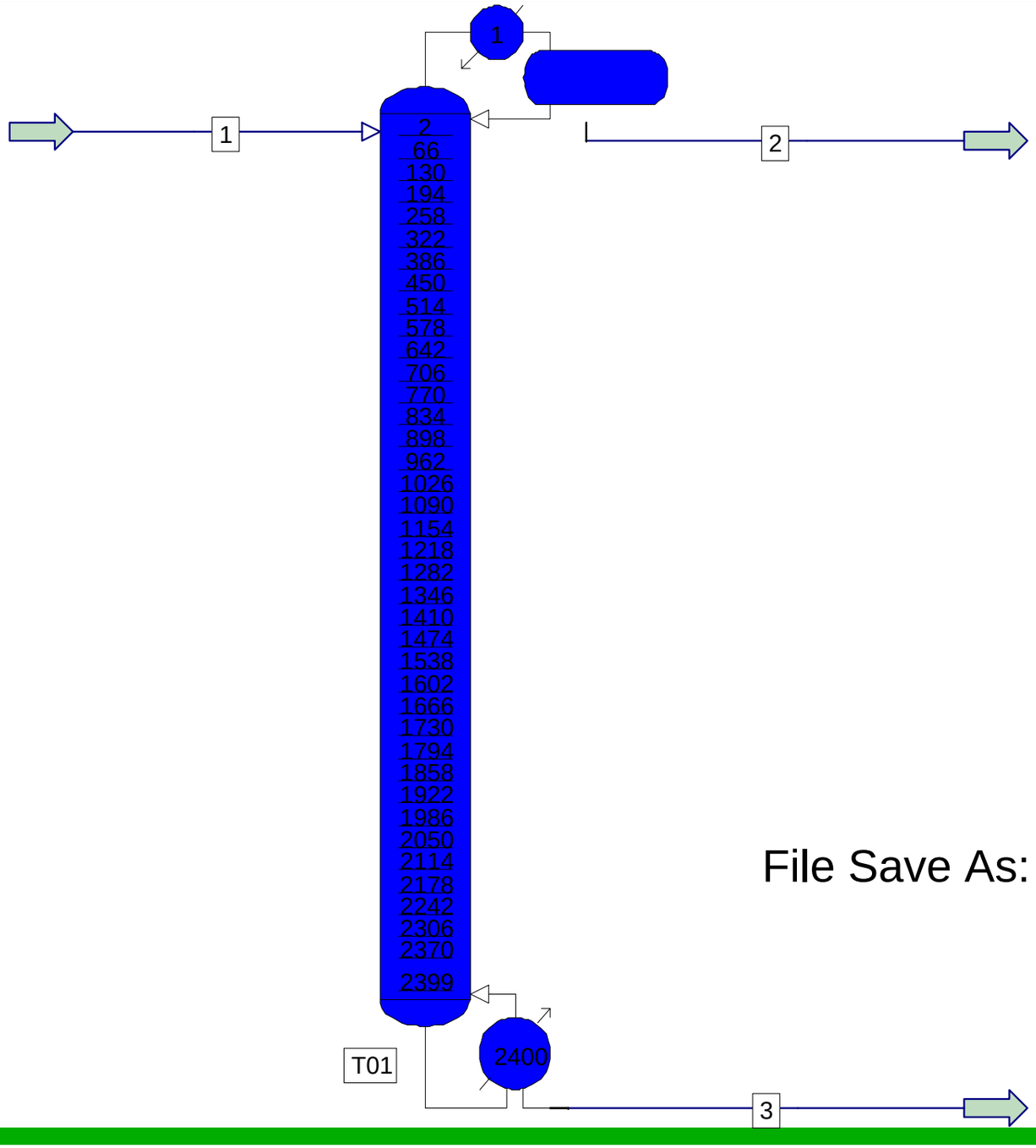
Shortcut Simulation



Rigorous Simulation Example: PRO/II



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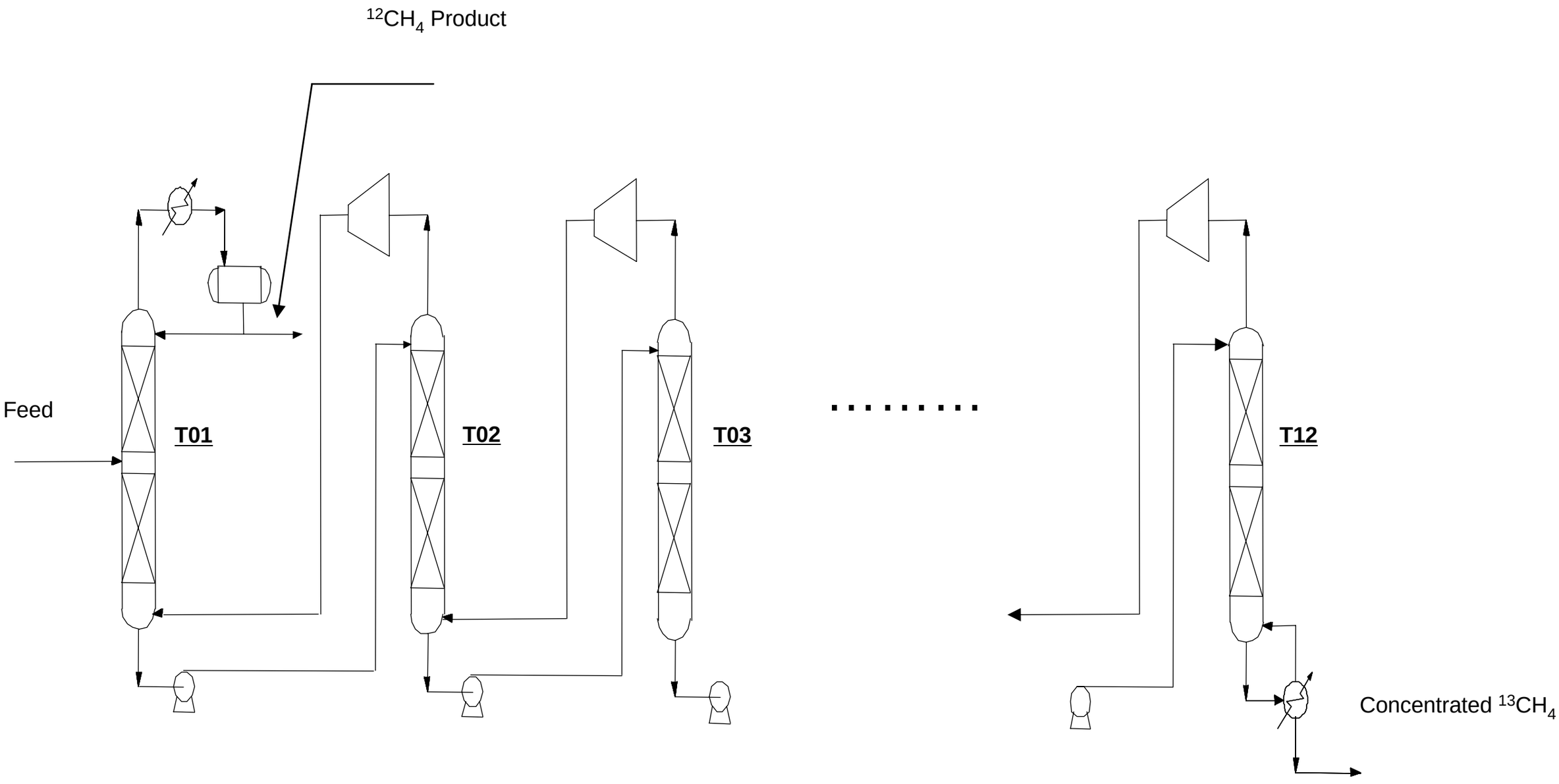
$^{13}CH_4$ Separation Step: 200 stages for each column



Case Study Results for a DeC1 & Cryogenic Distillation Columns

	Role	Minimum Trays	Minimum Reflux Ratio	Theoretical Trays
Step 1	Demethanizer	-	-	20
Step 2	1%→9.2376%	1,417	253.0	2,000
Step 3	9.2376%→35%	1,872	905.5	2,600
Step 4	35%→40%	1,644	887.0	2,400
Step 5	40%→60%	1,578	831.4	2,400
Step 6	60%→80%	1,688	739.0	2,400
Step 7	80%→90%	1,852	646.0	2,400

Relation of a distillation column operating time and top $^{13}CH_4$ impurities

	Top $^{13}CH_4$ Impurities	Operating Time
Step 7	0.5 mole%	11 hours
Step 6	1.0 mole%	31 hours
Step 5	2.0 mole%	59 hours
Step 4	5.0 mole%	24 hours
Step 3	5.0 mole%	926 hours
Step 2	15.0 mole%	5,158 hours
Step 1	-	6,209 hours

Conclusions

- $^{13}CH_4$ isotope separation process using a cryogenic distillation was simulated with PRO/II with PROVISION version 6.01. The modified Peng-Robinson modeling equation with a newly adjusted acentric factor was suitable to simulate the separation between methane isotope.
- It was concluded that 2,400 theoretical stages and six step procedures were required to obtain a 90 mole% of $^{13}CH_4$ methane product.