Prediction of solid fluid phase equilibrium in gas processing at low temperature

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1st Trondheim Gas Technology Conference
21-22nd October 2009
Trondheim, Norway

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Outline

- Offshore natural gas liquefaction concepts
- Solid blocking risk and solid behavior prediction
- Conclusion

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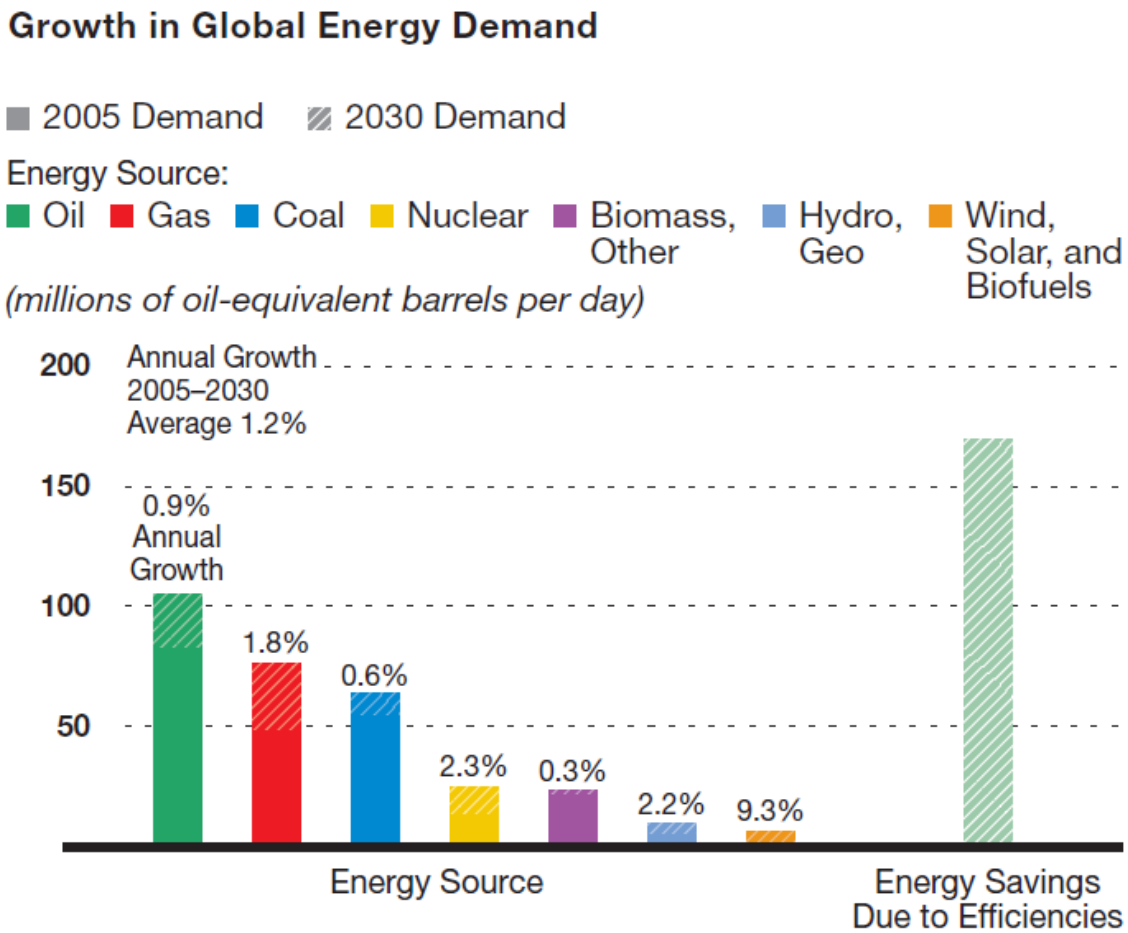
Offshore natural gas liquefaction concepts: Why?



- The growing demand for natural gas is 200% of oil and 150% of average energy growing demand

- Global LNG demand is expected to grow about 4% per year through 2030, according to Exxmobile's report

Source: Exxmobile 2008Summary Annual Report

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Offshore natural gas liquefaction concepts: FLNG

- Shell plans floating LNG platform in Australia: Prelude and Concerto Gasfields
  - 3.5 MTPA LNG
  - FEED had begun

Source: http://cn.reuters.com/article/companyNewsEng/idCNSYD36255920091012

- FLEX LNG
  - 1.7-2.0 MTPA LNG
  - Generic FEED completed 1Q 2009

Source: http://www.flexlng.com/publish_files/Presentation_Pareto_Oil_and_Offshore_Conference_September_2009.pdf

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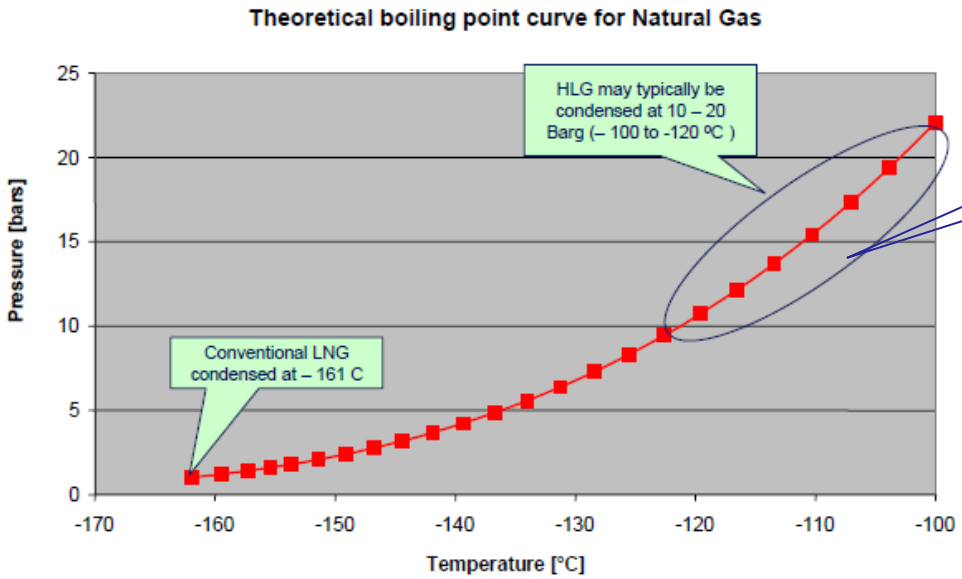
Offshore natural gas liquefaction concetps: HLG / PLNG



HLG product conditions

Aker Solutions
- Heavy Liquefied Gas (HLG)

Source: Pål Rushfeldt, 18.02.2005, HLG – Heavy Liquefied Gas

ExxonMobil
- Pressurized LNG

Source: Scott D. Papka, ect. Pressurized LNG: A New Technology for Gas Commercialization, The 15th International Offshore and Polar Engineering Conference, Seul, Korea, June 19-24, 2005

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Solid blocking risk in offshore gas processing

- CO_2, water, heavy hydrocarbons may form solid at low temperature and block passage
- Offshore requirement: compact, low weight, process reliability
- Floating-LNG: Offshore enviroment may deteriorate pre-processsing (CO_2 removal) and heavy hydrocarbon extraction
- HLG/PLNG: The tolerance of CO_2 and heavy hydrocarbon in the process should be evaluated to make processing simple

➢ It's important to predict the solid fluid phase equilibria to avoid solid blocking in process design

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Solid behavior prediction: Fundamental

- Fundamental: Phase equilibrium thermodynamics
- Minimization of a thermodynamic state function: This work, fix P and T, Minimize Gibbs energy
- Algorithm: PT flash and stability analysis developed by Michelsen etc[1].
- Implementation: Non-Equilibrium Simulator (NeqSim) developed by Solbraa[2].

[1] Michelsen, M.L. and J.M. Mollerup, *Thermodynamic models: fundamentals and computational aspects*.
[2] Solbraa, E., *Equilibrium and non-equilibrium thermodynamics of natural gas processing*.

Solid behavior prediction: Thermodynamic models

- Basic requirement: $f_i^l = f_i^v = f_i^s \quad i = 1, 2, \cdots, C$

- Vapor/Liquid phase:
  Soave-Redlich-Kwong (SRK) EOS + Van der Waals mixing rule

- Solid Phase: $f_i^{Solid} = P_i^{SatSolid} \varphi_i^{SatVapor} e^{\frac{V_i^{Solid}}{RT}(P - P_i^{SatSolid})}$

- Vapor pressure: Clausius-Claperyon Equation

$$\ln\left(\frac{P_2}{P_1}\right) = \left(\frac{\Delta h}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

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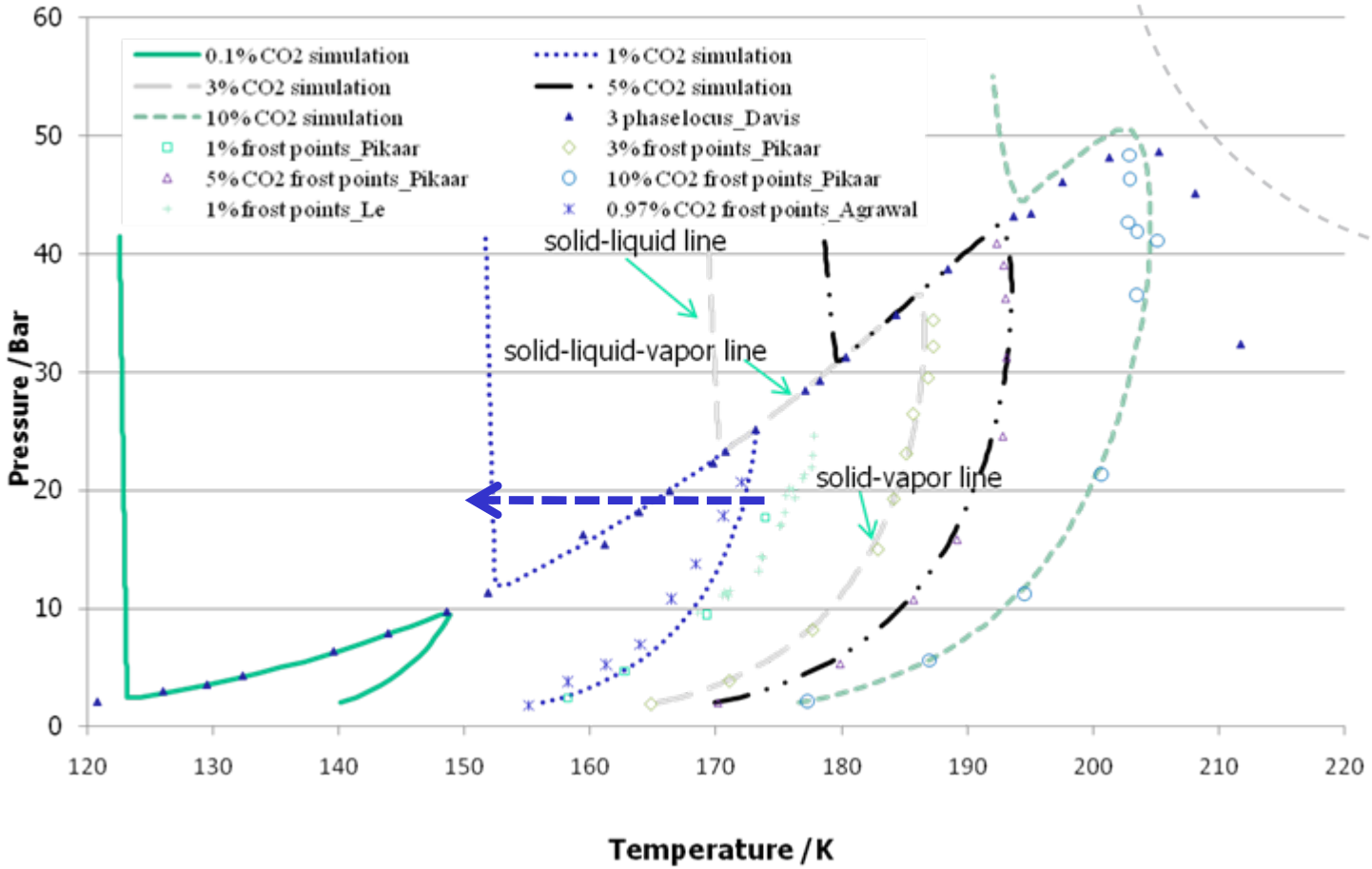
Solid behavior prediction: CO_2 + Methane PT diagram



- Pitfall: Solid may melt during cooling down
- Pressure has little effect on S-L equilbrium

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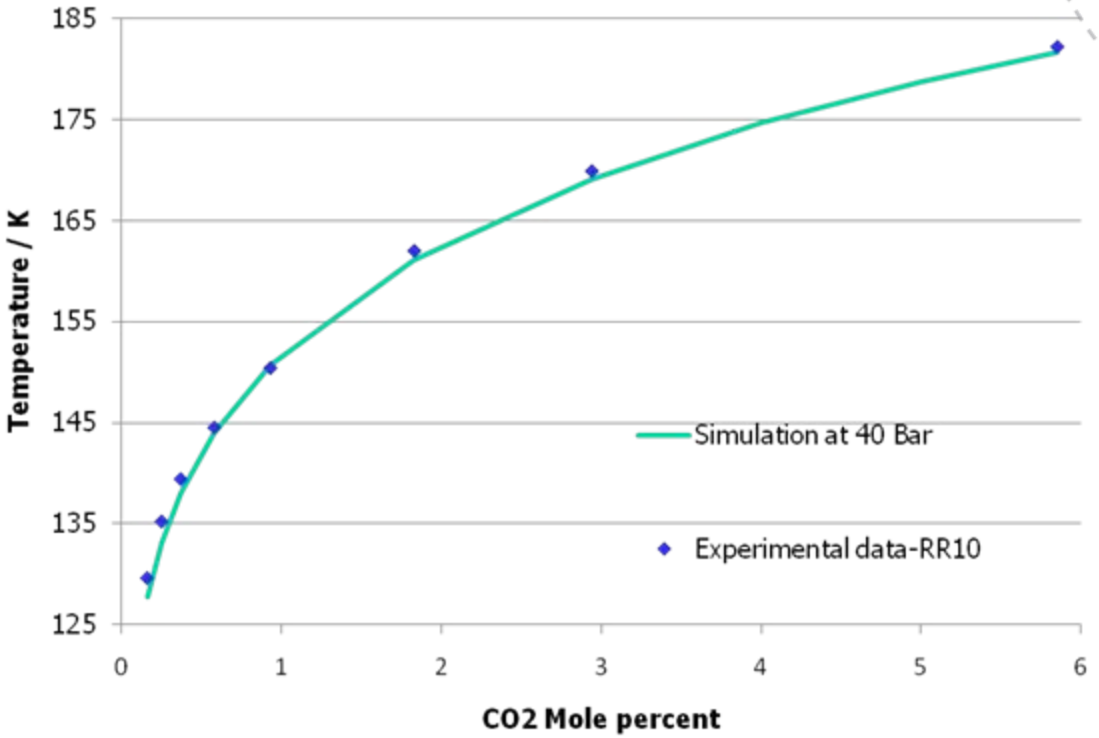
Solid behavior prediction: CO_2 solubility in liquid CH_4



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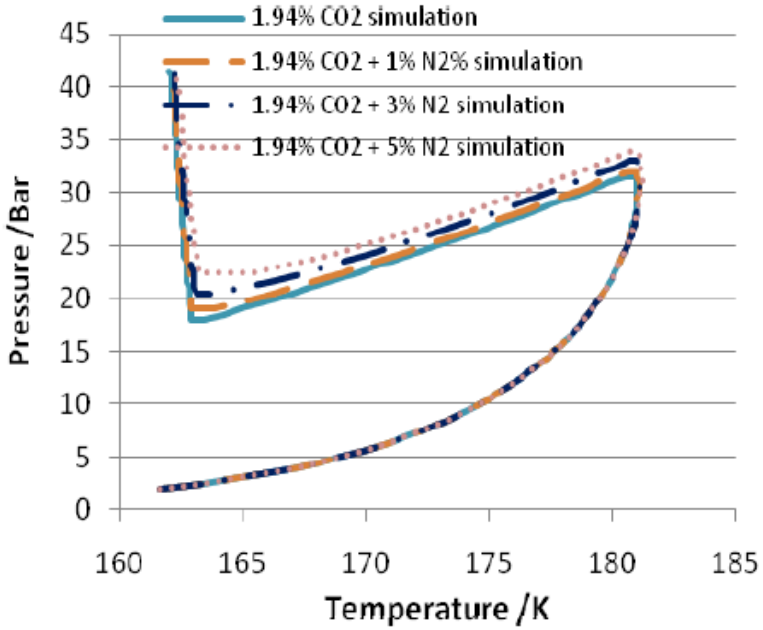
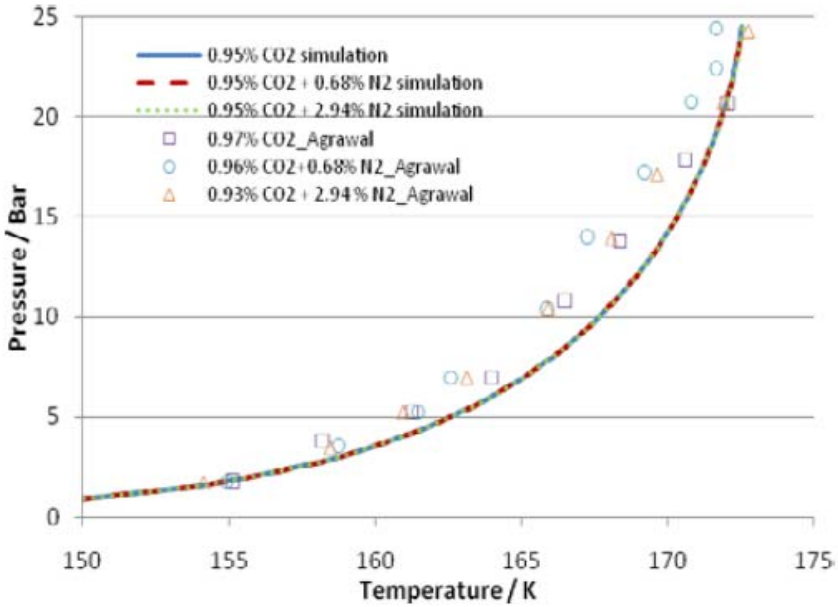
Solid behavior prediction: $CO_2 + CH_4 + N_2$





- The presence of nitrogen will depress the carbon dioxide solubility in liquid methane

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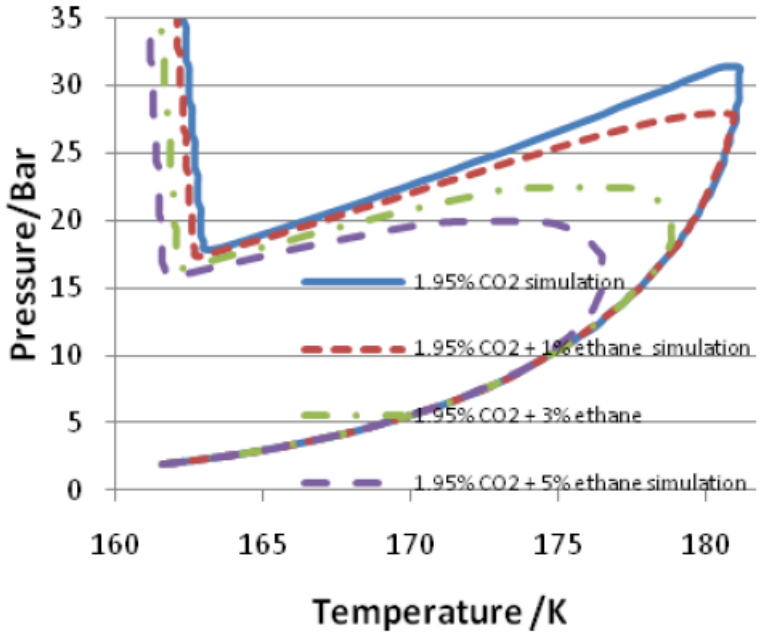
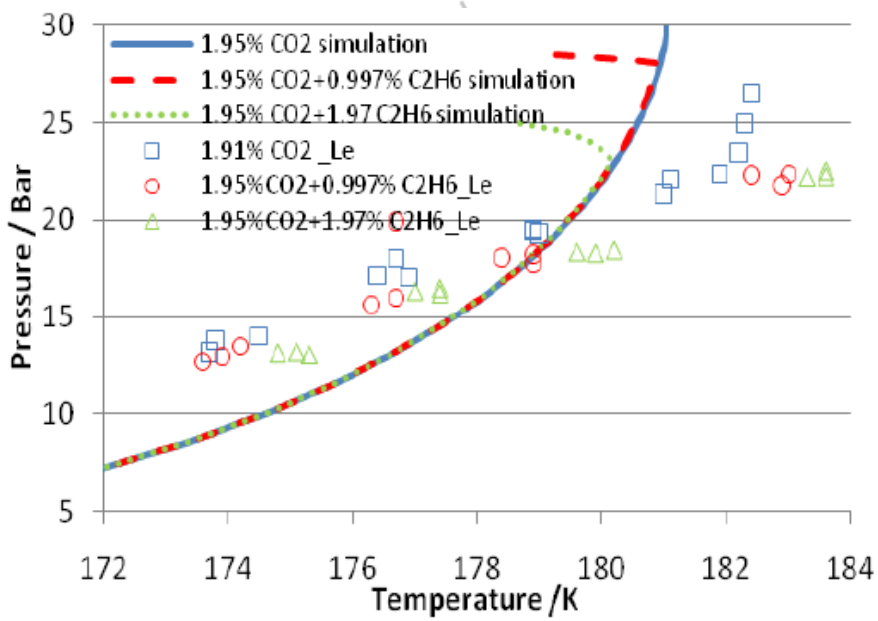
Solid behavior prediction: $CO_2 + CH_4 + C_2H_6$





- The presence of ethane will enhance the carbon dioxide solubility in liquid methane

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Solid behavior prediction: Multi-component system

CO_2, C_6H_6 solid formation in multi-component system

Product condition			Status			Composition (mole basis %)					
	P(Bar)	T(K)	Phases	Phase fraction	Density ($kg \cdot m^3$)	CH_4	C_2H_6	C_3H_8	C_6H_6	CO_2	N_2
Feed	90	300	gas	100%	87	80	5	3	0.1	6	5.9
LNG	1	110	Gas	22.32%	2.12	76.49	0.01	-	-	-	23.50
			Liquid	71.61%	476	87.60	6.98	4.19	0.02	0.3	0.91
			Solid1	5.98%	1509	-	-	-	-	100	-
			Solid2	0.09%	1010	-	-	-	100	-	-
HLG	12	150	Gas	14.89%	21.7	77.99	0.13	-	-	0.1	21.78
			Liquid	79.91%	416	85.59	6.23	3.75	0.1	1.01	3.32
			Solid1	5.18%	1414	-	-	-	-	100	-
			Solid2	0.02%	988	-	-	-	100	-	-
HLG	20	165	Gas	23.41%	34.9	83.71	0.33	0.02	-	0.47	15.47
			Liquid	72.69%	397	83.10	6.77	4.12	0.14	2.74	3.13
			Solid	3.90%	1370	-	-	-	-	100	-

- At 110 K and 150 K, carbon dioxide and benzene form solids together
- At 165 K, only carbon dioxide forms solid
- The solubility of carbon dioxide and benzene increase as T rises
- The pretreatment in HLG may be simpler than LNG

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Conclusion

- Solid blocking risk is one of the key issues in offshore natural gas liqufaction concepts
- This work predicts solid phase behavior in natural gas mixture at low temperature
- Thermodynamic models could be further evaluated, and systematic experiments should be carried out for offshore natural gas liquefaction design

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Thank You for your attention!

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