UNCONVENTIONAL RESERVOIR ENGINEERING PROJECT
COLORADO SCHOOL OF MINES

Experiments based modeling of the nanoconfinement effect on hydrocarbon phase behavior in nanopores

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Presentation Outline

- Motivation & literature review
- Review of previous experiments
- Modified flash calculation procedure
- Results of modeling
- Conclusion

Motivation

- Pore sizes of many shales are ~10 nm, phase behavior is affected by capillarity.
- Experimental studies on nanoscale phase behavior are very scarce.
- Existing phase behavior models only use a single pore size, effect of pore size distribution hasn't been investigated.

Literature Review

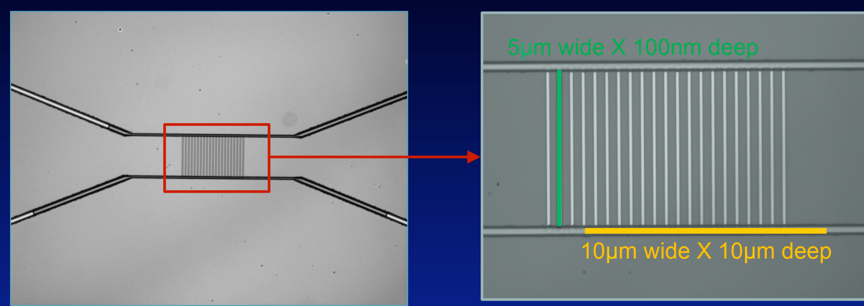
- Recently, compositional reservoir simulation has been improved by accounting for the capillary effect, critical properties shift, compaction effect, etc. in multi-component phase behavior calculation.

  Honarpour et al. 2012; Du et al. 2012; Firincioglu et al. 2012; Firincioglu et al. 2013; Wang et al. 2013; Jin et al. 2013; Zhang et al. 2013.

- Objectives of this study
  - Visualize the nanoconfinement effect with nanofluidic device, and model it with the modified flash calculation procedure
  - Investigate the effect of pore size distribution on flash vaporization with the verified flash calculation procedure

Experimental Setup

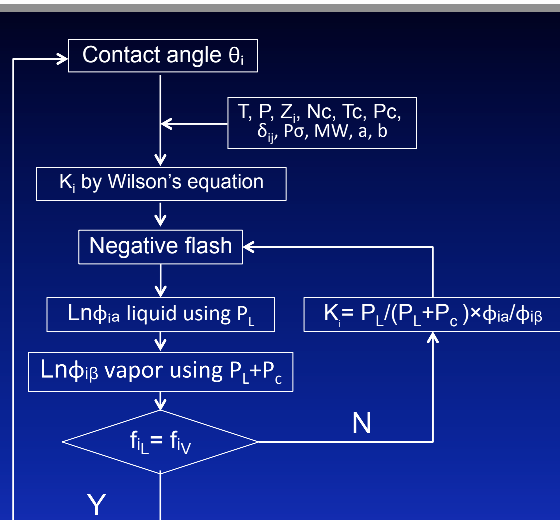
Silicon wafer + pyrex cover.



- a) n-pentane, b) Ternary mixture (15.47% iC_4-4.53% nC_4-80.00%C_8 molar fraction).
- 1atm@Golden, ~20 °C (68°F), observe vaporization by Δ~x °C.

Q. Wu, J. OK, Y. Sun, S.T. Retterer, K.B. Neeves, X. Yin, B. Bai, Y. Ma, 2013, Lab on a Chip.

Flash calculation procedure with capillary pressure



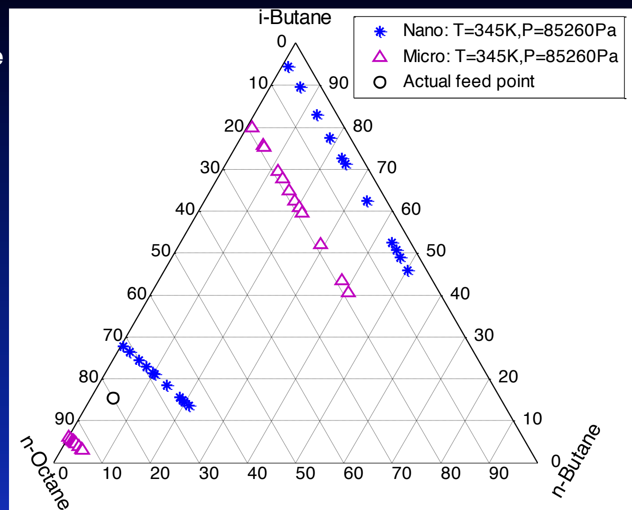
$$Pc = \frac{2(a+b) \cdot IFT \cdot \cos\theta}{a \cdot b}$$

Sigmund et al., 1973; Brusilovsky, 1992; Shapiro and Stenby 2001; Firincioglu et al, 2013.

Predicted phase behavior of the mixture

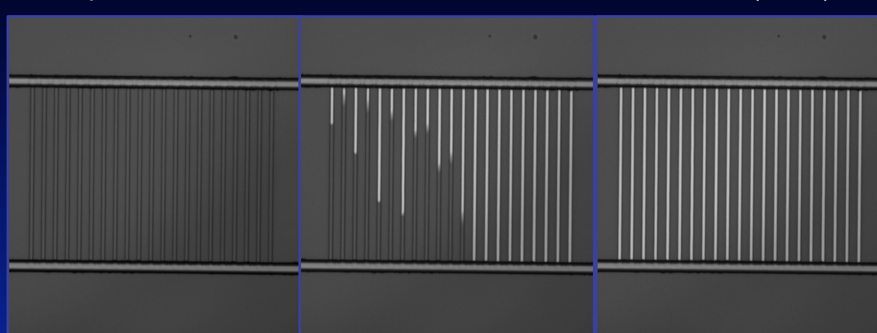
At 345K (161.3 °F), 1atm@ Golden, CO, the actual feed point:

- **2-phase state in micro-channels.**
- **Liquid state in nano-channels (5umx100nm).**
- **Based on the modeling, liquid is expected to first vaporize in the micro-channels and then flash into the nano-channels.**



Observation 1

Vaporization of C5 in nano & micro Channels at 20℃ (68°F).



3 consecutive images: Filled with Liquid, Partially Vaporized, Completely Vaporized.
Capture time lapse interval: 0.05s. $Tb_{pentane}$=97°F.

Vapor phase cannot be generated in nano-channels before the vaporization of liquid in micro-channels is complete, indicating a remarkable nanoconfinement effect. Afterwards, fluid in nano-channels vaporized very rapidly.

Observation 2

- Vaporization of nC4-iC4-nC8 in nano (5 µm X100 nm) & micro (50 µm X10 µm) Channels.

Photo taken at ~345K(161.3°F).

Air | Filled with Liquid | Vaporization in outlet

Tb_{octane}=257°F.

Fluid in micro-channel vaporized very slow at 345K. Preferential liberation of lighter components from the liquid phase to the gas phase in the micro-channels increases the apparent molecular weight of the remaining liquid, suppressing its bubble point.

Modeling of Experiments- Temperature Effect

The vaporization of the ternary mixture in the nanofluidic chip is treated as a flash calculation from 76.7 °F to 161.3°F at 1 atm@Golden.

Parameters	Before flash calculation			After flash calculation		
Temperature (°F)	76.7			161.3		
Liquid pressure (psia)	12.4psia			12.4psia		
Liquid(iC_4-nC_4-C_8, mol%)	0.155	0.045	0.800	0.049	0.019	0.932
Vapor(iC_4-nC_4-C_8, mol%)	0	0	0	0.644	0.168	0.188
Liquid fraction (vol%)	100.00			76.52		
Tb in micro-channel (°F)	**86.5**			**161.3**		
Tb in nano-channel (°F)	**194.2**			**267.5**		

Lighter components preferentially vaporizes, leaving a much heavier liquid behind; however, ∆Tb≈107°F doesn't change much, due to the IFT reduction resultant from temperature increase.

Modeling of Pressure Effect

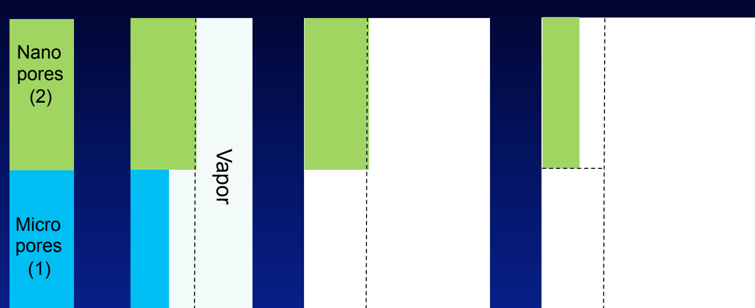
Vapor generation with liquid pressure dropping from 121.8 to 61.8psia at 161.3°F is modeled.

Parameters	Before flash calculation			After flash calculation		
Liquid pressure (psia)	121.8			61.8		
Temperature (°F)	161.3			161.3		
Liquid(iC_4-nC_4-C_8, mol%)	0.619	0.181	0.200	0.286	0.111	0.603
Vapor(iC_4-nC_4-C_8, mol%)	0	0	0	0.758	0.210	0.032
Liquid fraction (vol%)	100.00			10.44		
Pb in micro-channel (psia)	**121.8**			**61.8**		
Pb in nano-channel (psia)	**99.4**			**27.3**		

Vaporization in micro-channel significantly increases the pressure drawdown ∆Pb needed to vaporize the liquid in nano-channels, from 22.4 to 34.5 psia.

Flash vaporization with a pore size distribution

Visual representation of flash vaporization



P_b = P1 > P2 Single phase liquid; composition $z1_0 = z2_0$

$P_v=P_L+P_{c1}$ (IFT+Pore 1) Single phase liquid in nano pores; composition $z2 = x1 > z2_0$

$P_v=P_L+P_{c2}$ (IFT+Pore 2) Liquid reaches bubble point in nano pores; composition $z2 = x1 > z2_0$

$P_v=P_L+P_{c2}$ (IFT +Pore 2) Liquid reaches bubble point in nano pores; composition $z2 = x1 > z2_0$

Vaporization stops when

a) All liquid vaporizes

or:

b) PL=0 (P_v-P_c)

Flash vaporization with a pore size distribution

Pore size distribution

Fluid composition – a model black oil

Apparent Mw = 64.6

- N_2 0.007
- CO_2 0.023
- C1 0.330
- C2 0.050
- C3 0.053
- iC4 0.060
- nC4 0.067
- iC5 0.070
- nC5 0.080
- nC6 0.110
- C13 0.150

T (Formation)=189 °F

Pb (no confinement)= 1836 psia

IFT @ Pb = 1.92 mN/m

Assumptions:

✓All pores are interconnected
✓All pores have access to the outside of porous media
✓Gas can leave the porous media
✓Liquid remains imbibed

Flash vaporization with a pore size distribution

Pore size distribution

Liquid in 50 nm pores is vaporized when **P_v = 1769 psia**
Vtotal / Vinit = **1.019**
IFT = **2.09 mN/m** Pc = **10.5 psia**
Gas specific gravity = **0.87**
Liquid apparent Mw = **65.3**

Liquid composition

- N_2 0.00664
- CO_2 0.02274
- C1 0.32252
- C2 0.04990
- C3 0.05331
- iC4 0.06059
- nC4 0.06775
- iC5 0.07094
- nC5 0.08112
- C6 0.11171
- C13 0.15277

Gas composition

- N_2 0.02618
- CO_2 0.03687
- C1 0.73142
- C2 0.05543
- C3 0.03613
- iC4 0.02839
- nC4 0.02702
- iC5 0.01941
- nC5 0.01968
- C6 0.01802
- C13 0.00145

Flash vaporization with a pore size distribution

Pore size distribution

> 50 nm
(0.011)

25 nm
(0.403)

10 nm
(0.299)

<7.5 nm
(0.287)

Liquid in 50 nm pores is vaporized when **P_v = 190 psia**
Vtotal / Vinit = **11.675**
IFT = **11.61 mN/m**   Pc = **117 psia**
Gas specific gravity = **1.16**
Liquid apparent Mw = **107.9**

Liquid composition		Gas composition	
N_2	0.00024	N_2	0.01186
CO_2	0.00325	CO_2	0.03719
C1	0.02759	C1	0.54732
C2	0.01328	C2	0.07639
C3	0.02974	C3	0.06971
iC4	0.05438	iC4	0.06404
nC4	0.07135	nC4	0.06387
iC5	0.10403	iC5	0.04554
nC5	0.12720	nC5	0.04608
C6	0.21066	C6	0.03766
C13	0.35826	C13	0.00033

Flash vaporization with a pore size distribution

Pore size distribution

> 50 nm
(0.011)

25 nm
(0.403)

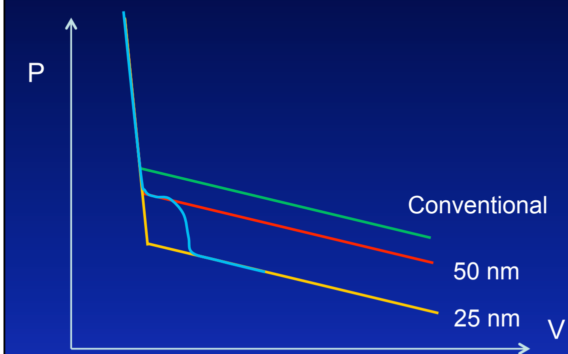
10 nm
(0.299)

<7.5 nm
(0.287)

After the liquid in 50 nm pores is completely vaporized, the capillary pressure to be generated in 10 nm pores is **P_c = 292 psia**, which is much higher that the vapor phase pressure **P_v = 190 psia**. thus the vaporization stops before the meniscus propagates into 10 nm pores.

Flash vaporization with a pore size distribution

Porous media with a pore size distribution – volume at different pressures (PV)



PV data from flash vaporization:

- PVT cell – green line
- If all pores are 50 nm – red line
- If all pores are 25 nm – yellow line
- If some pores are 50nm and some are 25nm, the data will first follow red line and then yellow line

Discussion

1. **A modified flash calculation model has successfully reproduced the vaporization sequence observed in the nanoconfinement experiments.**
2. **For mixtures, besides the pore size difference between the micro- and nano-channels, preferential liberation of the lighter components from the liquid to the vapor phase increases the apparent molecular weight of the residual liquid, which help suppress the vaporization of the residual liquid.**
3. **In the porous media with a pore size distribution, phase behavior of hydrocarbons will undergo different nanoconfinement magnitude as liquid phase recedes into smaller pores.**

Future work

1. Need sealing and connecting treatments on the chips for better control of a closed system in future experiments. (by Elham)
2. Model the vaporization processes of real reservoir fluids in the porous media with a pore size distribution that produce part of the gas or liquid (e.g. differential vaporization of condensate).

The End

Thank you & Questions