

UNCONVENTIONAL RESERVOIR ENGINEERING PROJECT Colorado School of Mines

CSN

Research Summary

Impact of Confinement on Propane Phase Behavior

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Outline

- Problem statement
- Motivation of the study
- Objectives
- Literature review
- Laboratory work

Propane PVT experiment at bulkPropane PVT experiment at confinementProducing condensed propane from nano-fluidic chips

- Analytical study
 - The Kelvin equation
 - Viscus flow equation
- Conclusion
- Ongoing and future studies



Problem Statement

- Condensation of petroleum retrograde gas especially around the wellbore in unconventional reservoir can decrease the well deliverability significantly.
- Unconventional reservoirs have abundant nano-pores in which phase behaviors of hydrocarbons deviate from the expected conventional behaviors i.e. condensation/ vaporization can happen at conditions different than those measured in PVT cells.
- When the condensate drop out begins, liquid and gas phase pressures are different by an amount controlled by the effect of confinement



Importance

- It is important to develop new relations to describe the phase transitions and interfacial dynamics of gascondensate systems under nano-scale confinement
- Better estimation of the dew point helps to predict of unconventional reservoir life and to improve production by minimizing the condensate dropout.



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Objectives

- Improve understanding of confined fluid phase behavior
- Improve numerical modeling of unconventional gascondensate reservoirs and provide better prediction capabilities



Wong et al. (1993) and Zegermann et al. (2009):

Confinement decrease critical temperature and increase critical density.

Page et al. (1993):

Pore size distribution, pore connections, pore structure and wettability of source rock components all can affect capillary condensation.

Lastoskie et al. (1994):

Kelvin type adsorption models overestimate condensation pressures at pore width bellow 7.5 nano-meter because of ignoring the fluid and pore wall interactions.



Literature Review

Danesh (1998):

In pores smaller than 10 nm, porous media has a significant effect on fluid phase behavior.

Ma et al. (2013):

All current equations of state such as van der Waals and Peng-Robinson only include interactions of fluid molecules together without considering the fluid molecule interactions with pore walls.

Shaina Kelly (2013):

Very small pore diameter applies some extra forces to fluid. This force (or pressure,) can be either disjoining (positive value, repulsive force) or conjoining (negative value, attractive force).



Literature Review

Li, et al. (2013):

In shale gas reservoirs due to confinement capillary condensation occurs at pressure below saturation vapor pressure. Also adsorption and desorption don't follow the same path due to hysteresis.

Lei Wang et al. (2014):

Hydrocarbon phase transition in nano-fluidic chips goes along the sequence imposed by the pore size, capillary force and surface energy.



Approach

Laboratory experiments:

- 1- Bulk PVT Experiments
- 2- Confined PVT Experiments inside nano-fluidic chips

Analytical modeling:

1- Using Peng-Robinson equation of state and Kelvin's equation to model hydrocarbon condensation pressure

2- Modify above model to predict the experimental results



Nano-Fluidic Chips

- Etching a silicon wafer with nano-channels
- Covering the channels with a piece of Pyrex slip to allow viewing inside the channels
- The Pyrex cover is bonded to the top of the silicon wafer by anodic bonding at high temperature (300- 500 °C) and high voltage (800- 1000 v).





Nano-Fluidic Chips

Connecting four coned ports to the four holes in the back of Silicon wafer using Super Glue





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Experiments



Experiments

1- Bulk PVT Experiments: to duplicate standard vapor pressures at different temperatures

- Pure propane gas
- Room temperature (68-72°F)
- 100 cc stainless steel high pressure pump
- No direct phase transition observation
- Pressurizing/ depressurizing
- Pressure versus volume plot, to detect point of phase transition







Experiments

2- Confined PVT Experiments

- Pure propane gas
- Room temperature (61-72°F)
- Direct observation of phase transition under microscope

Chip, nm	Condensation Temperature, °F	Observed Condensation Pressure, psi	Standard Vapor Pressure, psi (NIST)		
500	68.7	123.5	123		
50	69.6	123.8	124.2		
30	65.9	107.3	117.5		

Chip, nm	Vaporization Temperature, °F	Observed Vaporization Pressure, psi	Standard Vapor Pressure, psi (NIST)	
500	69.8	120	124.6	
50	69.8	123.5	124.6	
30	68.7	119.7	123	







Comments on the Observed Phase Behaviors

- In 500 nm chip condensation/vaporization happened in all channels at once, and at the same T and P.
- In 50 and 30 nm chips condensation happened in nano-channels first and then in order to get condensation in the larger channels, higher pressure was needed.
- In 50 and 30 nm chips vaporization happened in larger channels first and then in order to vaporize the condensation in nano-channels, lower pressure was needed.
- The existence of condensation in the nano-channels could effect the condensation pressure in the larger channels. Therefore we shouldn't expect to see the standard bulk condensation pressure in the larger channels (the lower pressure is expected)

The Kelvin Equation

$$\ln(\frac{p_{v}}{p_{v0}}) = -\frac{v^{l}\sigma}{RT}(\frac{1}{r_{1}} + \frac{1}{r_{2}})$$

- p_{v0} : Standard saturation pressure (bulk)
- p_v : Confined saturation pressure
- r₁: Width of pore
- r₂: Depth of pore

The Kelvin equation indicates that smaller channels cause more changes in the vapor pressure.

Assumptions of Kelvin equation:

- Pure component
- Equilibrium between gas and liquid phase
- Ideal gas
- Incompressible liquid and

$$p_v - p_{v0} \Box \quad \sigma(\frac{1}{r_1} + \frac{1}{r_2})$$

Pressurizing	Chip Depth, nm	Chip Width, nm	IFT, N/m	Condensation Temperature, °F	v, l/mol	Standard Vapor Pressure, psi (NIST)	Confined Vapor Pressure by Kelvin Eq, psi	Confined Vapor Pressure by Experiment, psi
	500	25000	0.008	68.7	0.088	123	122.9	123.5
	50	2500	0.007	69.6	0.088	125	123.6	123.8
	30	3000	0.008	65.9	0.088	117.5	115.3	107.3

Depressurizing	Chip Depth, nm	Chip Width, nm	IFT, N/m	Vaporization Temperature, °F	v, l/mol	Standard Vapor Pressure, psi (NIST)	Confined Vapor Pressure by Kelvin Eq, psi	Confined Vapor Pressure by Experiment, psi
	500	25000	0.007	69.8	0.088	124.6	124.4	120
	50	2500	0.007	69.8	0.088	124.6	123.2	123.5
	30	3000	0.008	68.7	0.088	123	120.8	119.7

The Modified Kelvin Equation

Kelvin equation with only two assumptions: pure component at equilibrum

$$\frac{p^{\nu}}{p_{\nu 0}} = \exp\left[\frac{T_c}{T.P_c}(p_{\nu 0} - p^{\nu}) + \frac{1}{RT}(\frac{A}{2}p^{l^2} + Bp^l - \frac{A}{2}p_{\nu 0}^{2} - Bp_{\nu 0})\right]$$

Chip Depth, nm	Chip Width, nm	Condensation Temperature, °F	v, m3/mol	IFT, N/m	Standard Vapor Pressure, psi	Confined Vapor Pressure by Experiment, psi	Confined Vapor Pressure by Kelvin Eq, psi	Confined Vapor Pressure by Modified Kelvin Eq, psi
500	25000	69	8.83E-05	0.007544	122.58	123.5	122.46	122.5
50	2500	70	8.84E-05	0.007483	124.2	123.8	122.84	123.1
30	3000	66	8.79E-05	0.007736	117.64	107.3	115.4	115.9

The modified Kelvin equation gives confined vapor pressure :

More close to observed values compare to original Kelvin Eq

The Modified Kelvin Equation

- Modified Kelvin equation may be more representative of reality since has less assumption
- In general the difference between Kelvin equation and its modified version may not be considered in the practical applications.

Confined vapor pressure, psi								
r1, nm	r2, nm	Original Kelvin	Modified Kelvin	Delta p, psi				
500	25000	122.46	122.50	0.04				
50	2500	122.84	123.12	0.29				
30	3000	115.40	115.89	0.49				
20	1000	114.32	114.97	0.65				
10	1000	111.17	112.43	1.26				
5	1000	105.11	107.46	2.35				



Producing the Condensed Propane from Chips

Methods:

- Vacuum at -1 atm for 1 day: condensation didn't move at all
- 300 °F (149°C) oven for 12 days: only micro-channels cleaned up
- Injecting high pressure nitrogen (1500- 2000 psi) for 1 minute: chips broke but condensation didn't move at all
- 600 °F heating stage: most of the condensations removed





Diffusion of Condensed Propane from Chips to Air



- During the heating process there is no actual flow inside the nano-channels
- Condensations get out of the channels by diffusion that takes long time 21

Diffusion of Condensed Propane from Chips to Air



- Diffusion only in X direction
- Room temperature
- The higher capillary pressure inside the channel, the longer the diffusion process takes
- The longer the channel length, the longer the diffusion process takes
- Depth and width of channel don't affect the diffusion time

Capillary Pressure versus Displacing Pressure



- Wetting fluid is held inside the channel by the capillary pressure
- Non-wetting fluid needs an external force to overcome the capillary force and enter to the channel: displacement pressure
- Capillary pressure between N2 and propane: 214 psi at 70 °F
- Nitrogen injection pressure: 1500- 2000 psi
- 2000 psi > 214 psi but propane didn't move any

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Conclusion

- Propane tends to condense at lower pressure in the nano-channels (confinement) than the bigger channels (bulk)
- Liquid propane tends to vaporize at lower pressure in the nano-channels (confinement) than the bigger channels (bulk)
- Displacing the condensed propane inside nanochannels with high pressure nitrogen is not possible (chips will break at that high pressure)

On Going and Future Studies

- Repeating the PVT experiments in 500 nm, 50 nm and 30 nm chips to validate the already observed condensation /vaporization pressures
- 2. Find other types of forces inside the confinement besides capillary such as van der Waals forces
- Investigate the magnitude of van der Waals forces inside the confinement and study their effects on phase behavior
- Including the shifts in critical properties to the modified Kelvin's equation

Thank You



