



**UNCONVENTIONAL RESERVOIR ENGINEERING PROJECT**  
**COLORADO SCHOOL OF MINES**



# Experimental Study on Adsorption and Filtration of Hydrocarbons in Tight Shale Samples

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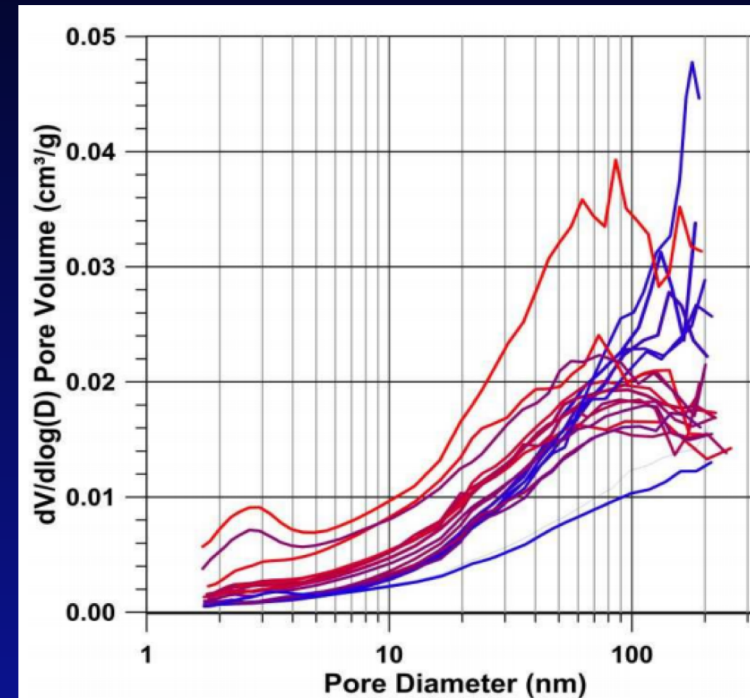
**UNCONVENTIONAL RESERVOIR ENGINEERING PROJECT**

Advisory Board Meeting, May 4, 2018, Golden, Colorado

# Problem Statement

- Portion of pores in Niobrara samples have comparable sizes with hydrocarbon molecules.

	Size (diameter), nm
Pore, Niobrara	1 -- >100
Paraffins	0.4 -- 1
Aromatics	1 -- 3



Pore Size Distribution of Niobrara Samples



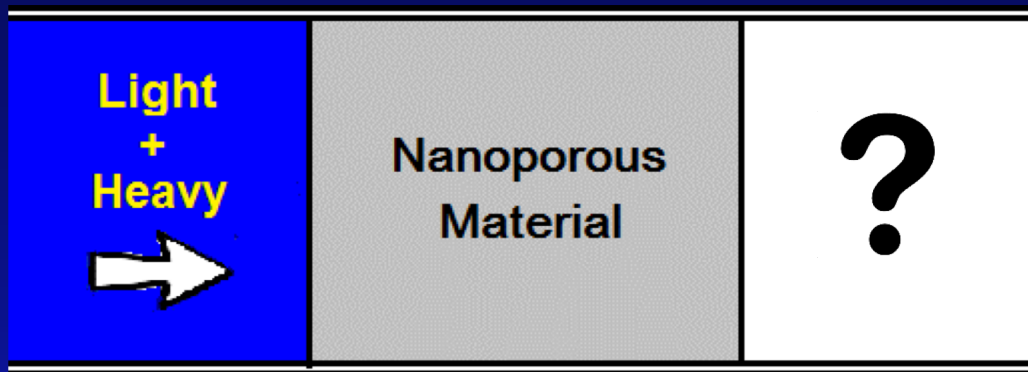
# Problem Statement

- Niobrara sample may potentially act as a semi-permeable membrane.

Hypothesis:

Light components can pass through.

Heavy components may be partially filtered (size exclusion ..?).

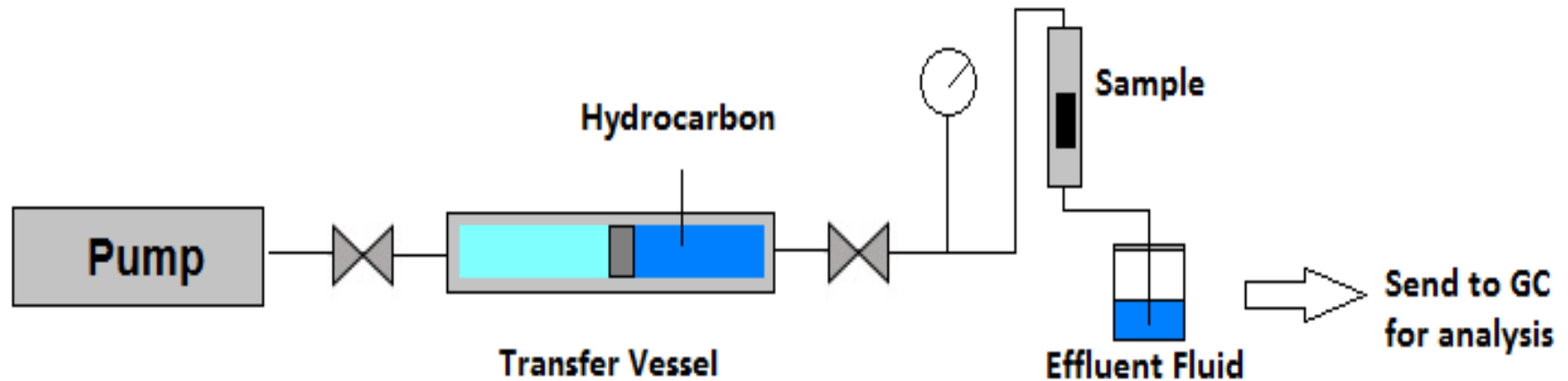


# Objective

- Through experiments, explore the hindrance effect of Niobrara sample on hydrocarbon transport.
- Investigate factors affecting the composition change of hydrocarbon mixtures flowing through Niobrara sample.
  - Adsorption
  - Hydrocarbon species
  - Pressure
  - Temperature
  - Mineralogy



# Experimental Setup



# Experimental Setup

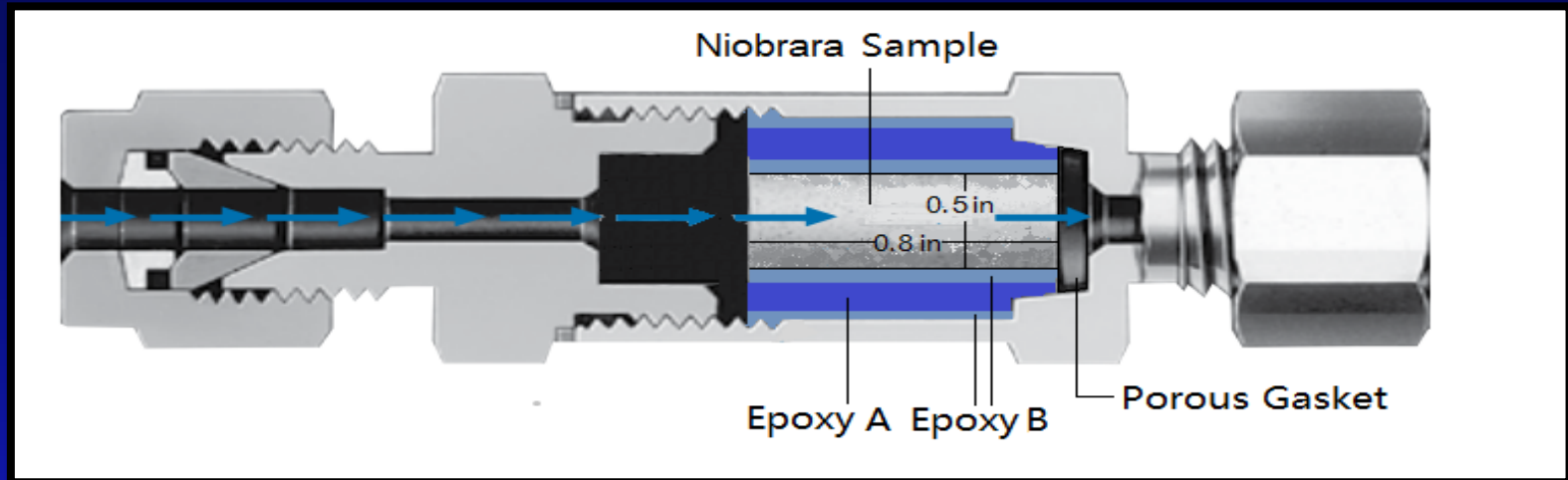
- **Gas Chromatograph**

Agilent 7890B

- **Mini Core Holder**

Modified from In-Line Filter

Working Pressure: 0-2500 psi



# Filtration Test

- Injection Fluid

Binary mixture of n-C<sub>10</sub> and n-C<sub>17</sub>

Component	Concentration, mol%
n-C <sub>10</sub>	79.616
n-C <sub>17</sub>	20.384

- Niobrara Sample

Sample	Length, in	Diameter, in	Pore Volume*, ml
A	0.6965	0.4885	0.171
B	0.717	0.4895	0.177

\*Pore volume is calculated based on an estimated porosity of 8%.

- Control Test

Control experiments are conducted without Niobrara sample (empty core holder).

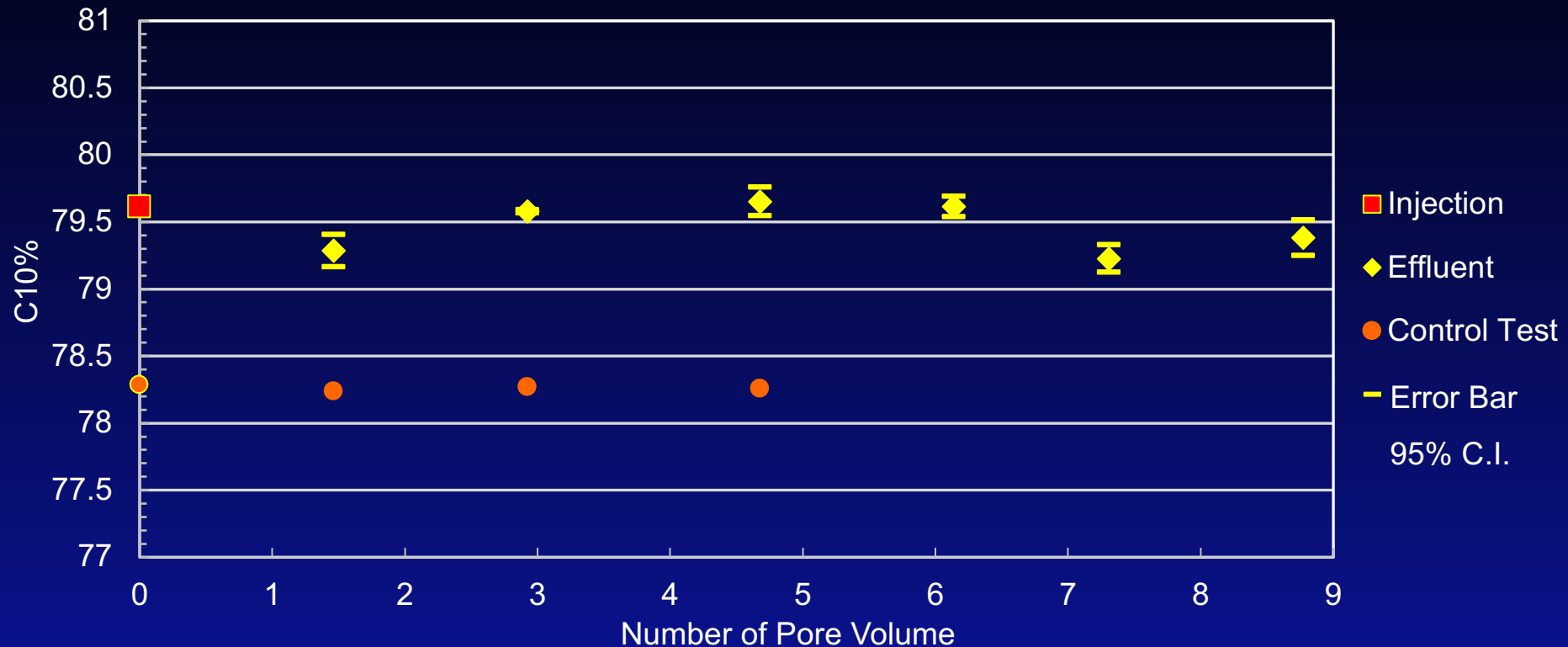
All the other subjects involved in the experiment are treated the same.

\*Initial fluid composition is different from injection fluid for filtration test.



# Result & Discussion

## Effluent Fluid: Sample A



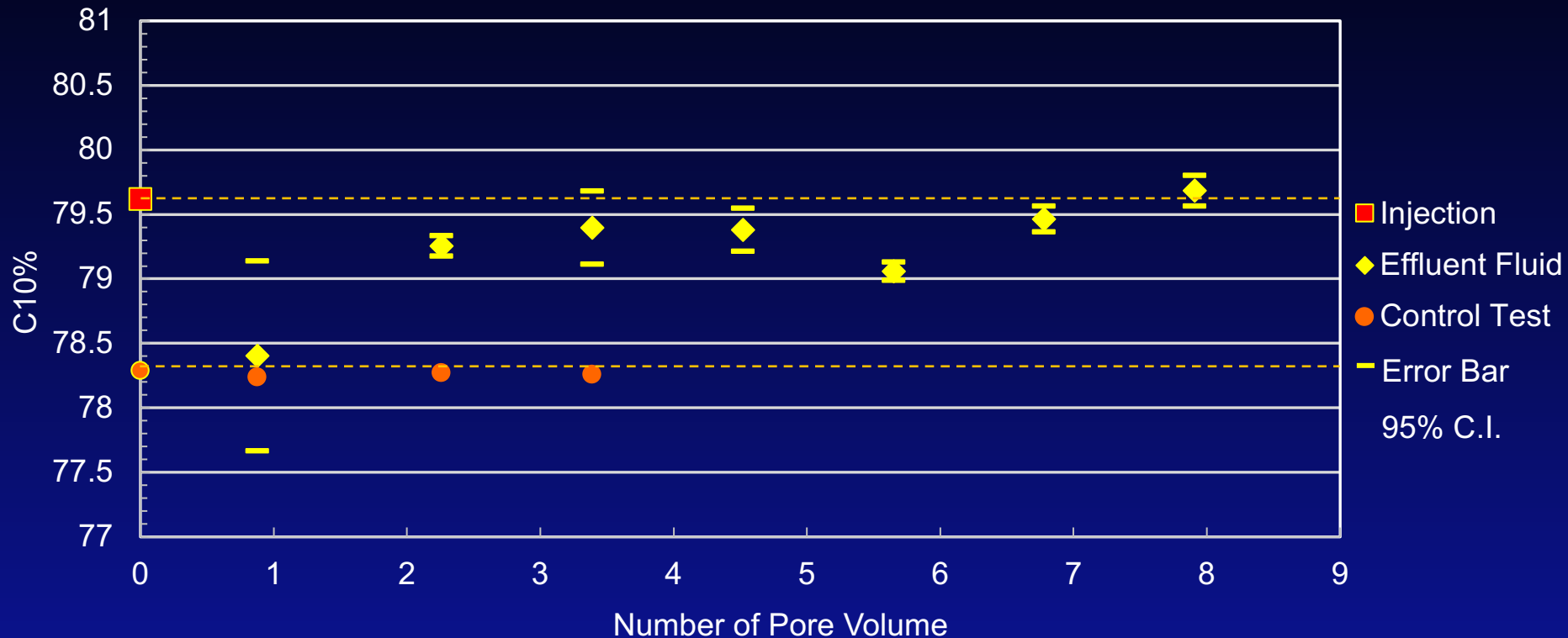
- Compared with the injection fluid, mole fraction of  $n\text{-C}_{10}$  in the effluent fluid is often on the lower side.
- Experimental results are reliable. No significant experimental error.





# Result & Discussion

## Effluent Fluid: Sample B



- Compared with the injection fluid, mole fraction of n-C<sub>10</sub> in the effluent fluid is often on the lower side.
- Experimental results are reliable. No significant experimental error.



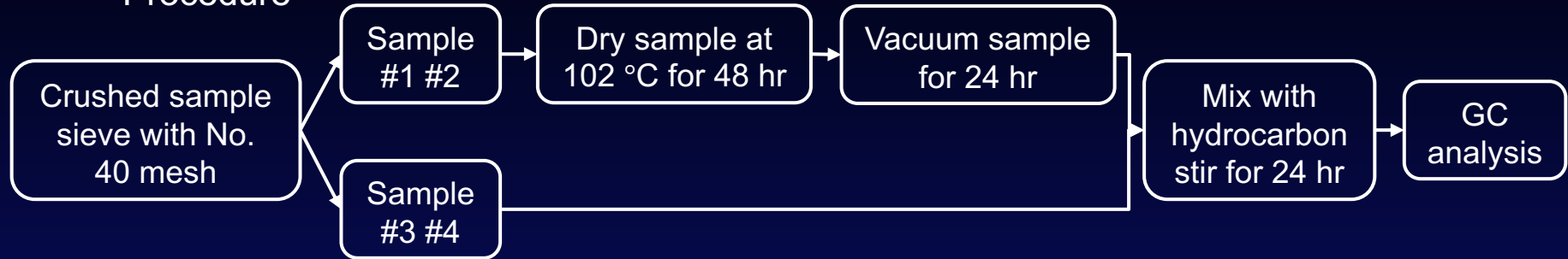
# Result & Discussion

- Hindrance effect (filtration) cannot be clearly detected.
- Adsorption effect of Niobrara sample on the mixture of n-C<sub>10</sub> and n-C<sub>17</sub> needs to be considered.
- n-C<sub>10</sub> and n-C<sub>17</sub> may also possess mobility difference through Niobrara sample.



# Adsorption Test

- Procedure



- Binary mixture of n-C<sub>10</sub> and n-C<sub>17</sub>

Component	Concentration, mol%
n-C <sub>10</sub>	78.581
n-C <sub>17</sub>	21.419

- Hydrocarbon/Niobrara mass ratio

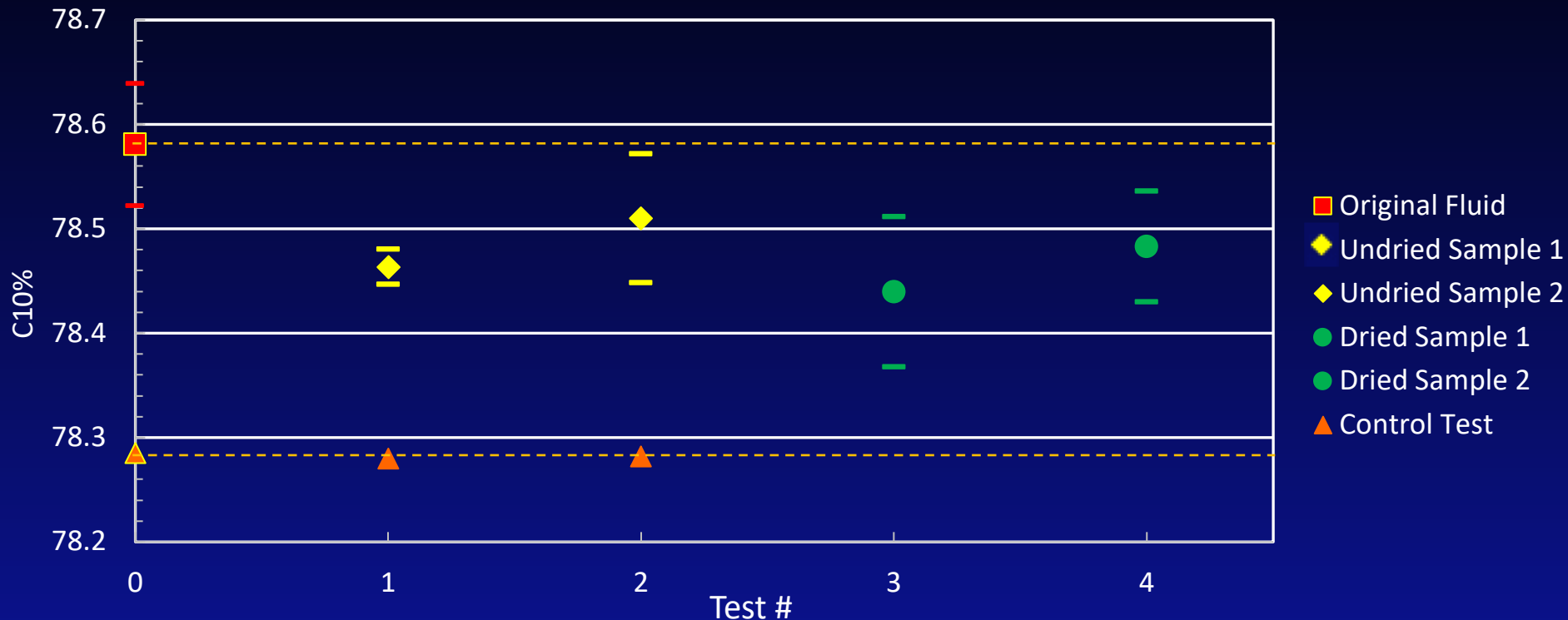
Sample #	1	2	3	4	Control Test*
Sample mass, g	2.71	2.72	2.75	2.76	--
HC mass, g	8.04	8.15	7.96	8.09	--
HC/Niobrara	2.97	2.99	2.9	2.93	∞

\*Control test is conducted without Niobrara sample. C10 and C17 mixture is stored in the same vial as adsorption test for 24 hr to check the experimental error caused by vaporization



# Result & Discussion

## Adsorption Test on Niobrara Sample



- Adsorption experiments suggest Niobrara sample adsorbs more  $n\text{-C}_{10}$  than  $n\text{-C}_{17}$ .
- Experimental error from vaporization can be neglected.

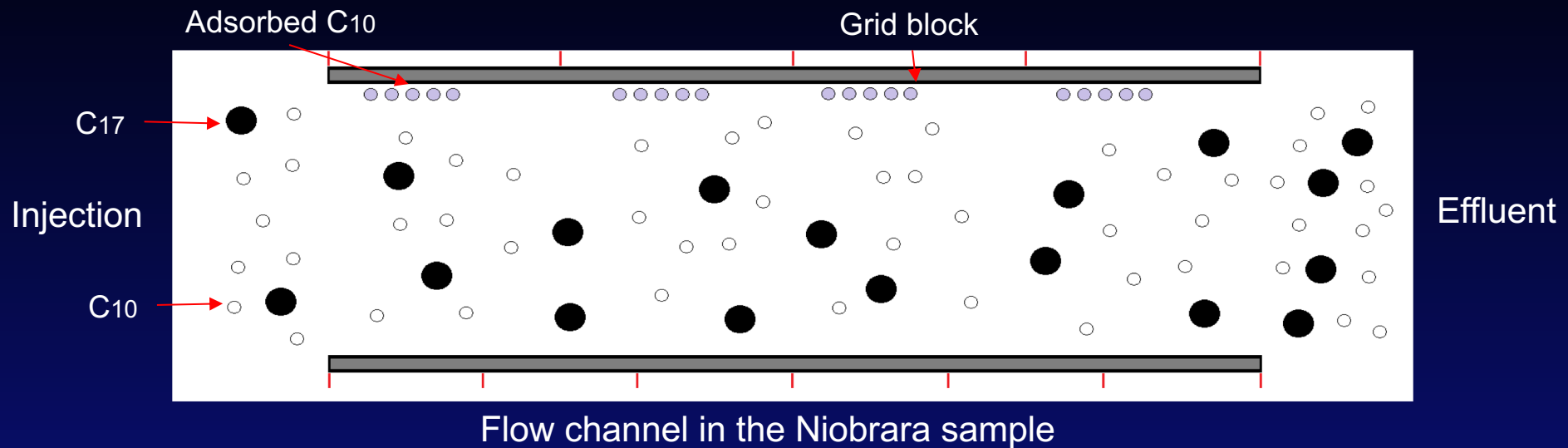


# Result & Discussion

- Adsorption effect of Niobrara sample on the mixture of n-C<sub>10</sub> and n-C<sub>17</sub> is non-negligible, and should be considered in the analysis of effluent composition.



# Simulation



## Input parameters:

- Time step
- Number of grid blocks
- **Velocity** of C<sub>10</sub> & C<sub>17</sub>
- Injected molar number of C<sub>10</sub> & C<sub>17</sub>
- **Adsorption capacity** of every grid block for C<sub>10</sub> & C<sub>17</sub>



## Output parameters:

- Composition of **effluent fluid** vs. time step
- Composition of **fluid inside rock** vs. time step

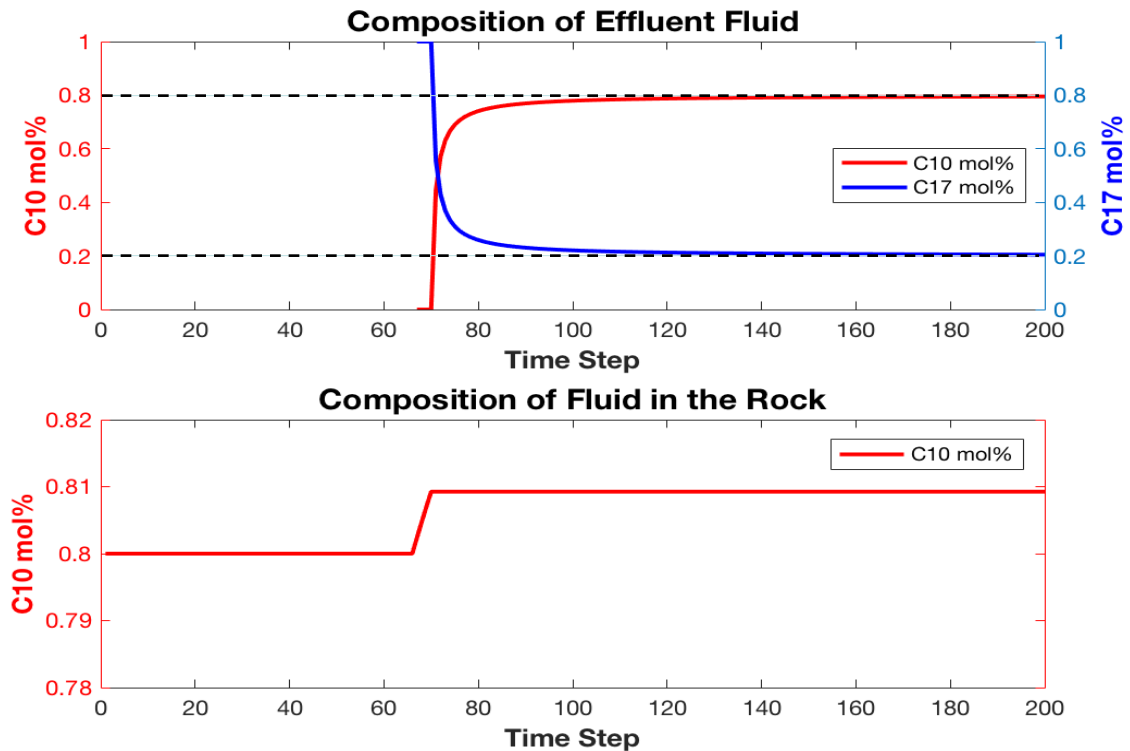


# Result & Discussion

## Case 1

- First, C<sub>17</sub> breaks through.
- Hereafter, C<sub>10</sub> comes out after filling all the adsorption spots.
- Gradually, effluent fluid composition approaches injection fluid.
- C<sub>10</sub> fraction of fluid left inside rock increases.

	n-C <sub>10</sub>	n-C <sub>17</sub>
Injected Molar Number, mol	80	20
Velocity, grid block/time step	3	2
Adsorption Capacity, mol/grid block	20	1
Number of Grid Block	120	

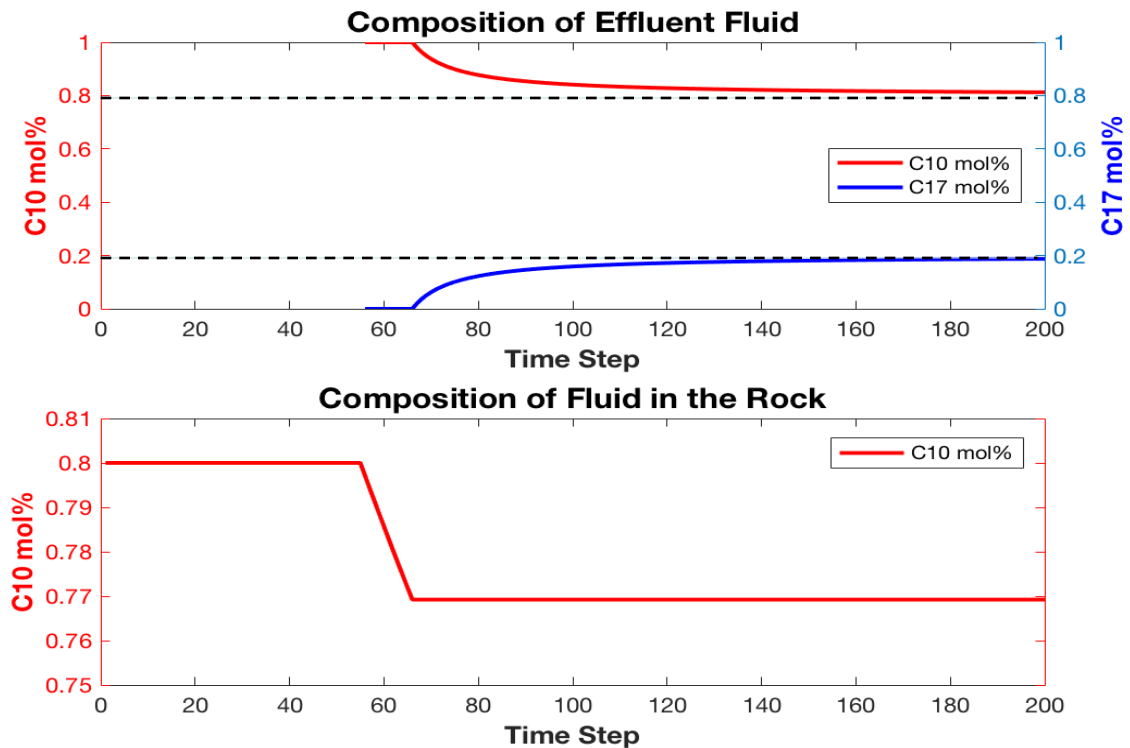


# Result & Discussion

## Case 2

- Reduce the adsorption capacity for C<sub>10</sub>, other parameters stay the same.
- Opposite initial trends, C<sub>10</sub> breaks through first, followed by C<sub>17</sub>.
- C<sub>10</sub> fraction of fluid left inside rock decreases.

	n-C <sub>10</sub>	n-C <sub>17</sub>
Injected Molar Number, mol	80	20
Velocity, grid block/time step	3	2
Adsorption Capacity, mol/grid block	10	1
Number of Grid Block	120	



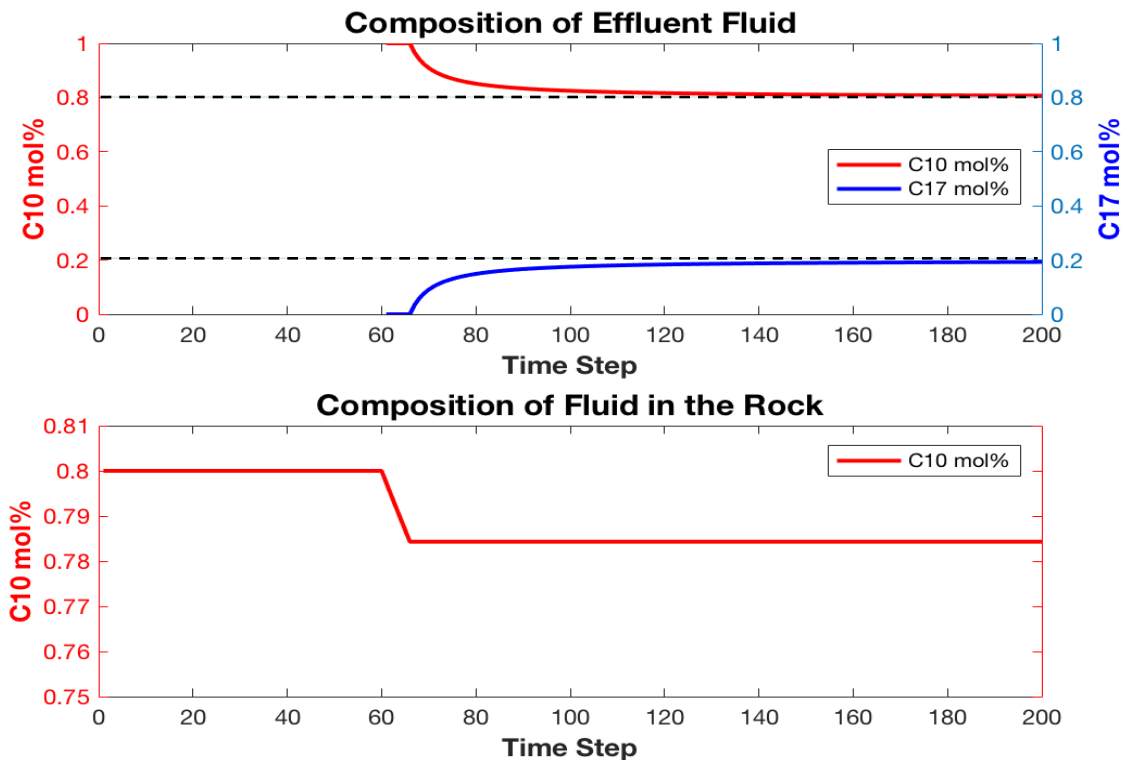


# Result & Discussion

## Case 3

- Increase the mobility of  $C_{10}$ , other parameters stay the same.
- Opposite initial trends,  $C_{10}$  breaks through first, followed by  $C_{17}$ .
- $C_{10}$  fraction of fluid left inside rock decreases.

	n-C <sub>10</sub>	n-C <sub>17</sub>
Injected Molar Number, mol	80	20
Velocity, grid block/time step	4	2
Adsorption Capacity, mol/grid block	20	1
Number of Grid Block	120	



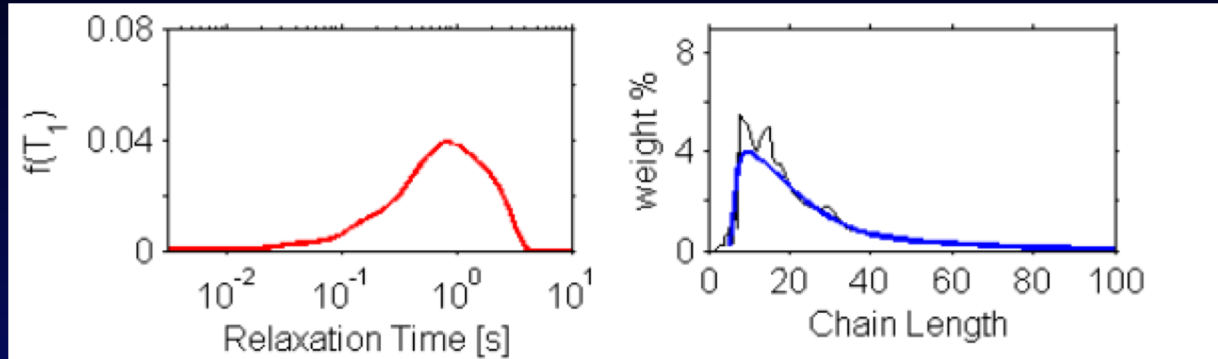
# Result & Discussion

- Built a simple (non-physical) model to evaluate the relative influences of adsorption vs. mobility difference.
- Model predicts that after reaching steady-state there is no difference between injected and produced composition.
- However, at early times, different sets of values of adsorption capacity and mobility difference can give opposite trends.



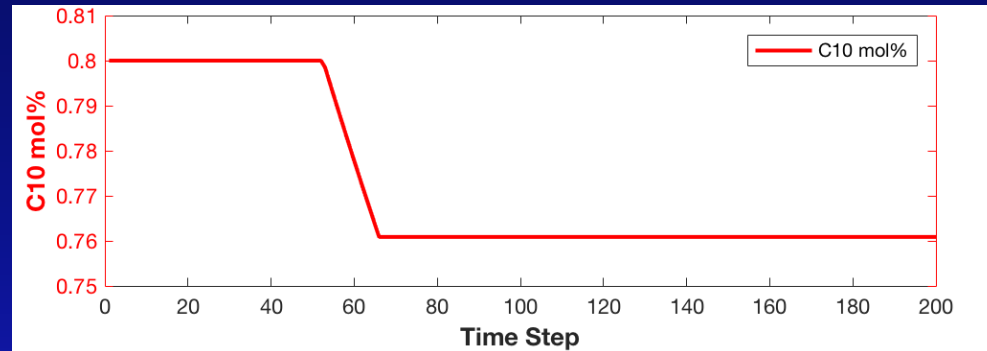
# Future Work

- Fluid composition measurement using NMR



Estimate of chain length distribution from NMR relaxation measurements for oil

- Determine the composition of fluid left inside Niobrara sample



Composition of fluid left inside Niobrara sample



# References

Cho, Y., Eker, E., Uzun, I. et al. 2016. Rock Characterization in Unconventional Reservoirs: A Comparative Study of bakken, Eagle Ford, and Niobrara Formations. Paper SPE 180239 presented at the SPE Low Perm Symposium, Denver, Colorado, 5-6 May. <https://doi.org/10.2118/180239-MS>

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Thank You  
Questions?

