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高含水油包水乳液的水合物储气性能研究

于 510640

Span80 / Tween80 $M_{Tween80}$ M_{Span80}=0.783 1 5 wt%

274.15 K 10:1 6 MPa 700 r/min 141.42 L /L

130 L /L

TE 82 A

Investigation on hydrate-based methane storage properties in water-in-oil emulsion with high water content

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Abstract: Water-in-oil emulsion is a newly emerging hydration enhancement material in recent years. It has good hydration and gas storage potential. However, in order to ensure the stability of emulsion, the water content of the water-in-oil emulsion usually does not exceed 50%. The gas storage capacity of hydrate is closely related to the water content. Therefore, high water content water-in-oil emulsion has more application prospects. In this study, a water-in-oil emulsion with water content of 55% was produced and the methane hydrate formation experiment was carried out by using the emulsion. The effects of the amount of emulsifier, initial pressure, stirring rate and cyclic capacity were investigated. The results show that the increase of water content will lead to the increase of emulsion droplet and the decrease of gas storage when the water content is more than 55%. The water content of the emulsion is 55% with 5 wt% (based on water content) of Span80 / Tween80 ($M_{Tween80}$ M_{Span80}=0.783 1) emulsion is the best emulsion for storing CH_4. The increase of initial pressure is beneficial to the improvement of hydrated gas storage performance. However, too high pressure will lead to the rapid formation of hydrate shell and thus reduce the overall gas storage capacity. The appropriate stirring rate is conducive to hydrate formation. The optimal emulsion hydration and gas storage conditions were temperature of 274.15K, gas-water volume ratio in the reactor of 10:1, methane initial pressure of 6 MPa, and stirring rate of 700 r/min. In this condition, the gas storage capacity was 141.42 L_{gas}/L_{water}; further four-cyclic gas storage experiment proved that the emulsion had good recyclability, which cyclic gas storage capacity is above 130 L_{gas}/L_{water}. The research results can provide technical supporting for natural gas storage and transportation and hydrocarbon-containing mixed gas separation.

Key words: methane; hydrate; emulsion; hydration rate; cyclic gas storage

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2018A030313245

1 m^3

170m^3 3-10 MPa 273.15K 了 [1]

[2-4] [5-7] [8-10]

[11-13] [14-17]

于 于

[18-20] [21-23]

[24-26] [27,28]

[29]] 273.35 K 700 r/min 700 nm 30%

了 Li [30] 30%

5 了 SDS +

Wang [31]

于 275 K

7 MPa 40% 122 L /L SDS PEG400 140 L /L

151 L /L 32] Azam [33] 于

158.2 kmol h^{-1} m^{-3} 59.1 L /(L min)

50%

50%

1

1.1

1 5.0

10^{-3} 8.7 10^{-7} 298.15 K 0.016

mg/L 243.54K Span80

Tween80 $M_{Tween80}$ M_{Span80}=0.783

1

Table 1 Experimental materials and reagents

	99.9%
80 Span80	
80 Tween80	
	18.25 M cm

1.2

1 100 mL

253~373K 40 MPa
Pt-100 ±0.1K
于 0-25 MPa ±0.25%
34970A THD-3030
±0.1 K

1

Fig. 1 Schematic diagram of static methane hydration experimental device

2 XT5405FSC
243~323K

2

Fig. 2 Schematic diagram of stirred methane hydration experimental device

1.3

Tween80

Span80

MPa

298.15K

1.4

1.4.1 水合储气量

1

$$C_V = \frac{n^H_{CH_4}(t)}{V_{H_2O}} \times 22400 \quad \text{mL/mol} \quad (\text{L} \quad /\text{L} \quad) \qquad 1$$

C_V L /L V_{H_2O} mL $n^H_{CH_4}(t)$ t

mol

t

$n^H_{CH_4}(t)$

$$n^H_{CH_4}(t) = [n^G_{CH_4}(0) + n^O_{CH_4}(0)] - [n^G_{CH_4}(t) + n^O_{CH_4}(t)] \qquad 2$$

$n^G_{CH_4}(0)$ $n^O_{CH_4}(0)$ 0 mol

0 $n^G_{CH_4}(t)$ $n^O_{CH_4}(t)$ t mol

0 t

$$n^G_{CH_4} = \frac{PV}{ZRT} \qquad 3$$

$n^G_{CH_4}$ P V T R

8.3145 J/(mol K) Z PR

$$x = \frac{P}{H} \qquad 4$$

x P MPa H MPa

x

$$x = \frac{n^O_{CH_4}}{n^O_{CH_4} + n_{oil}} \qquad 5$$

H [34]

$$\ln H = 38 - \frac{1966}{T} - 4.9\ln T \quad (7)$$

T K

1.4.2 水合储气速率

-

10 s 8 t 9

$$r = \frac{\mathrm{d}C_V}{\mathrm{d}t} \approx \frac{\Delta C_V}{\Delta t'} \left[\mathrm{L} \,/ (\mathrm{L} \cdot \mathrm{min})\right] \quad (8)$$

$$r_a = \frac{\Delta C_V}{\Delta t} \left[\mathrm{L} \,/ (\mathrm{L} \cdot \mathrm{min})\right] \quad (9)$$

$\Delta t'$

2

2.1

2 7 wt%

30% 40% 50%

55% 55%

3

50% 7 m

0 m 55% 1.31~9.42 m 4.56 m

0 m 50%

50% 55% 40 72

50%

50% 24h

60% 70%

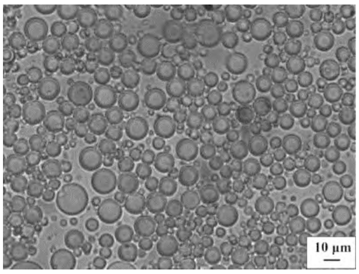
7.78~14.45 m

2 T=273.15 K P_0=7 MPa 7 wt%

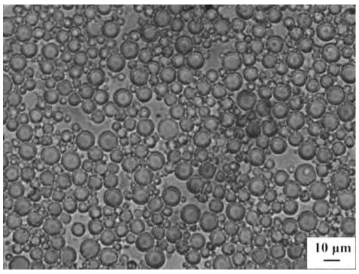
Table 2 Hydrate-based methane storage results of emulsions with different water-oil ratios

		mL	h	(L /L)	[L /(L h)]
1		50			
2	+7 wt%S80/T80	50			
3	30%	50			
4	40%	50			
5	50%	50			

6	55%	50	3.80	22.25	19.61
7	60%	50	0.19	17.26	49.56
8	70%	50	4.01	12.07	15.08

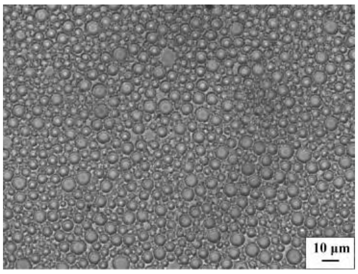


a 30/70 d_a=10.12 m



b 40/60 d_a=8.54 m

c 50/50 d_a=7.33 m



d 55/45 d_a=4.56 m

e 60/40 d_a=6.11 m

f 70/30 d_a= m /7.78~14.45 m)

3 7 wt% d_a

Fig. 3 Micromorphology of emulsions with different water-oil ratios

2.2

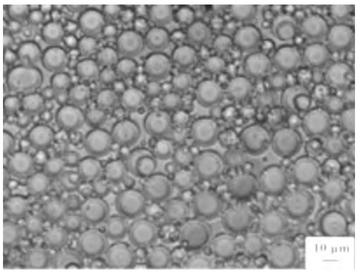
3 55/45 1 wt%~7 wt% 1 wt% 3 wt% 5 wt% 7 wt% 1.05 h 3.80 h 5 wt% 25.31 L /L 7 wt% 7 wt% 4 1 wt% 5 wt% 于 7 wt%

于

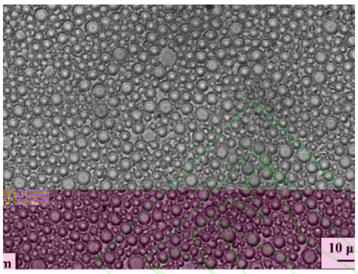
3 T=273.15 K P_0=7 MPa 55/45

Table 3 Hydrate-based methane storage results of emulsions with different emulsifier dosages

	wt%	mL	h	(L /L)	[L /(L h)]
1	1	50			
2	3	50			
3	5	50	1.05	25.31	25.13
4	7	50	3.80	22.25	19.61



a 1 wt% d_a=11.38 m　　b 3 wt% d_a=9.28 m



c 5 wt% d_a=5.33 m　　d 7 wt% d_a=4.56 m

4 55/45 d_a

Fig. 4 Micromorphology of emulsions with different emulsifier dosages

274.15 K 10:1

2.3

55% Span80/Tweeen80

5 wt% 1.45~8.82 5.33 6

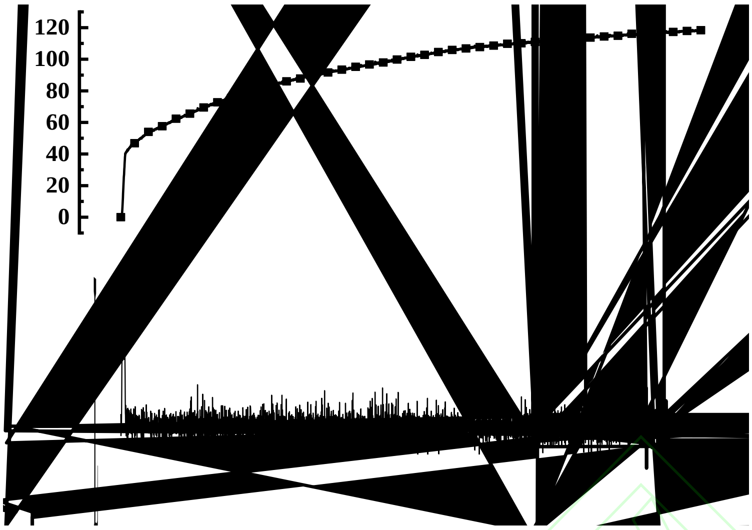
55% 5wt%

5 55% 5 wt%

274.15 K 10:1 900 r/min 6.08MPa

118.41 L /L

13.05 L /(L min)



5 6.08 MPa T=274.15 K

Fig. 5 Gas hydration kinetics of emulsions under 6.08 MPa

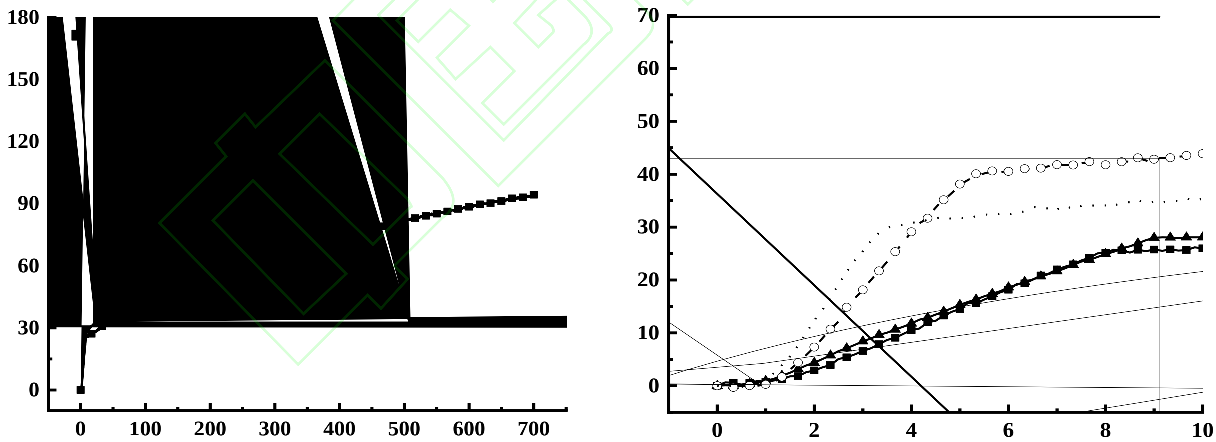
6 4.48~6.08 MPa

4.48 MPa 94.30 L /L 6.08 MPa

118.41 L /L 6.93 MPa 116.84 L /L

7.92 MPa 83.59 L /L

0.138 W/(m K)



a b

6 T=274.15 K 900 r/min

Fig. 6 C_V-t curves of emulsion under different pressure conditions

2.4

7 274.15 K 6 MPa 300~1100 r/min 300 r/min 700 r/min

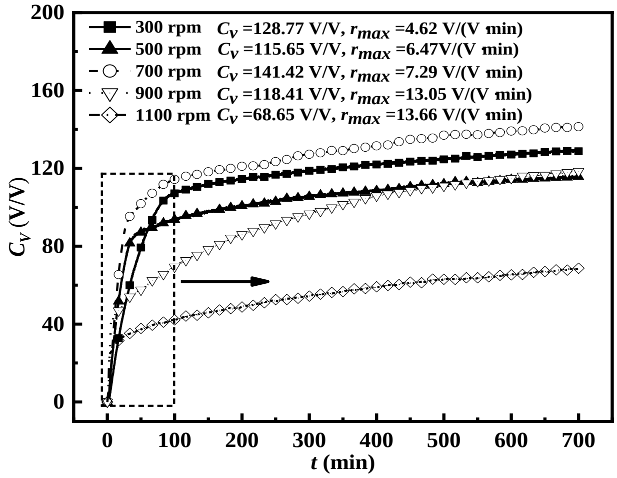
128.77 L /L 141.42 L /L 700~1100 r/min

1100 r/min 68.65 L /L

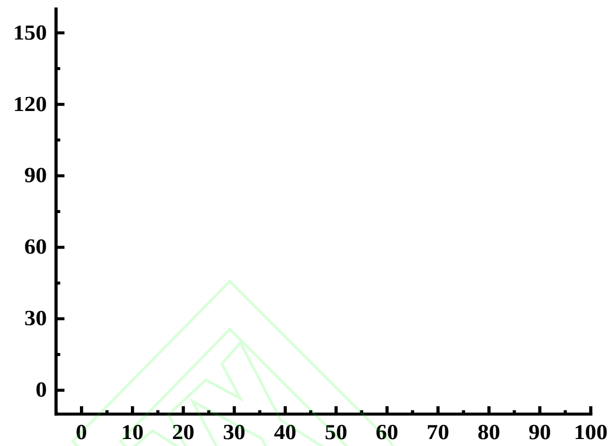
700 r/min

141.42 L /L 7.29 L /(L min) 33.66 min

95.32 L /L 67.40%



a



b

7 T=274.15 K P_0=6 MPa

Fig. 7 C_V-t curves of emulsion in different stirring rate systems

2.5

55% Span80/Tween80 5 wt% 274.15 K

6 MPa 10:1 700 r/min

8

133.33 L /L 141.74 L /L 134.95 L /L 137.71 L /L

5.84 L /(L

min) 8.30 L /(L min) 41 min 113.24 L

/L 82.23%

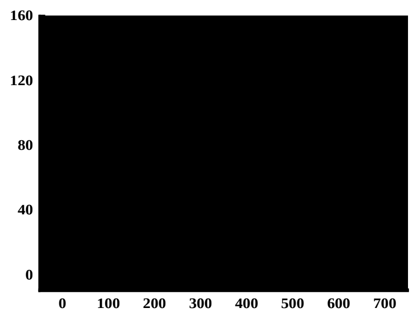
-

9

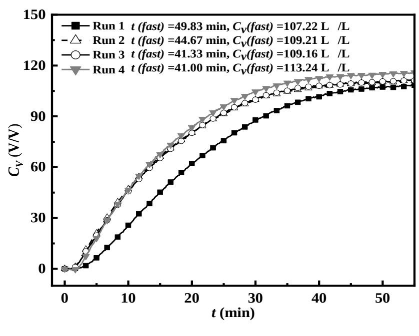
2~9 m 5 m

1~6 m 2 m

a



b



c

8 T=274.15 K P_0=6 MPa

Fig. 8 C_V-t curves of cycling hydrate based methane storage in emulsion

a d_a 5 m b d_a 2 m

9 d_a

Fig. 9 Comparison of the micro-morphology of the emulsion before and after experiment

3

了

于 55%
5wt% Span80/Tween80 5.33
6

274.15 K 10:1 6 MPa 700 r/min
141.42 L /L
130V/V 5.84 L /(L min) 8.30 L
/(L min) 5 2

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