

## Supplementary Information

# Sub- and supercritical water conversion of organic-rich shale with low-maturity for oil and gas generation

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**Note:**

Detailed experimental data in Section 3.1 are shown in the Table S1-S4.

**Table S1.** Experiment conditions in Section 3.1.

Experiment Number	Reaction Temperature /°C	Reaction Pressure /MPa	Reaction Time /h	Particle Size Range / $\mu$ m	Water-shale Mass Ratio	Shale Mass /g	Water Mass /g
1	300	25	4	75-106	1	19.71	19.70
2	300	25	4	75-106	1	19.68	19.72
3	350	25	4	75-106	1	19.62	19.76
4	350	25	4	75-106	1	19.62	19.74
5	380	25	4	75-106	1	21.99	22.01
6	380	25	4	75-106	1	22.01	22.03
7	400	25	4	75-106	1	19.62	19.72
8	400	25	4	75-106	1	19.62	19.66
9	450	25	4	75-106	1	14.00	14.12
10	450	25	4	75-106	1	14.00	14.15
11	500	25	4	75-106	1	12.76	12.83
12	500	25	4	75-106	1	12.80	12.82
13	550	25	4	75-106	1	11.79	11.76
14	550	25	4	75-106	1	11.75	11.73
15	600	25	4	75-106	1	11.51	11.52
16	600	25	4	75-106	1	11.40	11.47
17	650	25	4	75-106	1	9.99	9.99
18	650	25	4	75-106	1	10.00	10.02

**Table S2.** Quantitative analysis of oil products and residues as well as TOC conversion efficiency and mass balance in Section 3.1.

Experiment Number	Oil Yield per Gram of Shale /mg	Oil Yield per Gram of TOC <sup>a</sup> /mg	Mass Fraction of Carbon in Oil /%	Organic Carbon in Oil per Gram of TOC /mg	Saturates /%	Aromatics /%	Resins /%	Asphaltenes /%	Shale Residual Mass /g	H/C of Shale Residual	TOC Conversion Efficiency <sup>b</sup>	Mass Balance <sup>c</sup>
1	15.05	99.64	73.8%	71.80	30.2%	38.3%	26.1%	5.4%	18.37	2.18	0.08	95%
2	14.34	94.93			31.5%	36.7%	26.7%	5.1%	17.56			91%
3	34.85	230.68	72.8%	161.74	12.4%	29.8%	27.1%	30.7%	17.22	1.72	0.17	92%
4	32.25	213.47			11.3%	30.6%	26.0%	32.1%	16.95			90%
5	52.27	346.05	78.5%	276.36	13.9%	36.2%	23.7%	26.3%	18.45	1.64	0.30	90%
6	54.07	357.94			12.5%	38.2%	24.5%	24.8%	18.68			91%
7	27.19	179.99	80.3%	140.96	22.3%	44.5%	17.0%	16.1%	17.54	1.62	0.18	93%
8	25.87	171.26			20.6%	43.5%	18.8%	17.1%	17.06			91%
9	14.99	99.25	42.2%	43.45	25.8%	39.7%	16.3%	18.2%	12.71	1.53	0.16	95%
10	16.10	106.60			24.2%	40.3%	15.6%	20.0%	12.44			93%
11	13.04	86.34	15.7%	13.10	42.1%	35.3%	16.2%	6.3%	11.44	1.23	0.18	95%
12	12.25	81.12			44.4%	33.4%	15.6%	6.6%	11.51			95%
13	8.96	59.33	25.6%	14.79	60.2%	26.8%	10.8%	2.2%	10.55	1.15	0.19	94%
14	8.50	56.30			58.2%	27.3%	11.6%	2.8%	9.93			90%
15	0.00	0.00	- <sup>d</sup>	-	-	-	-	-	9.71	1.03	0.20	90%
16	0.00	0.00	-	-	-	-	-	-	9.85			91%
17	0.00	0.00	-	-	-	-	-	-	8.17	0.88	0.31	91%
18	0.00	0.00	-	-	-	-	-	-	8.19			91%

<sup>a</sup>TOC is total organic carbon in oil shale.

<sup>b</sup>TOC Conversion Efficiency is the sum of organic carbon in oil and gas products over total organic carbon in oil shale.

$$= \frac{\text{sum of masses of products of gas, oil and shale residual}}{\text{mass of shale fed}}$$

<sup>c</sup>Mass balance

*mass of shale fed*

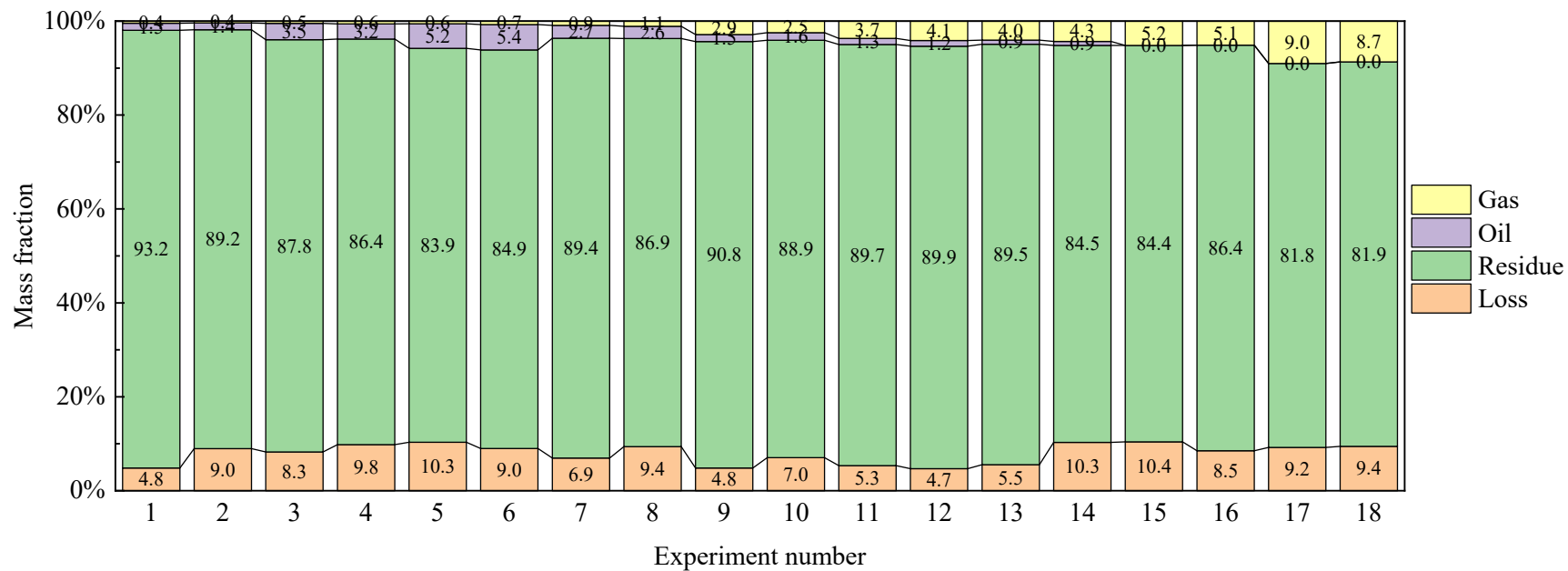
<sup>d</sup>- refers to no oil yield.

**Table S3.** Quantitative analysis of gas products in Section 3.1.

Experiment Number	Gas Yield per Gram of Shale /ml	H <sub>2</sub> per Gram of Shale /mL	CO per Gram of Shale /mL	CH <sub>4</sub> per Gram of Shale /mL	CO <sub>2</sub> per Gram of Shale /mL	C <sub>2</sub> per Gram of Shale /mL	C <sub>3</sub> per Gram of Shale /mL	C <sub>4</sub> per Gram of Shale /mL	C <sub>5</sub> per Gram of Shale /mL	C <sub>6</sub> per Gram of Shale /mL	Organic Carbon in Gas per Gram of TOC <sup>a</sup> /mg	Gas Yield per Gram of Shale /mg
1	2.94	0.31	0.00	0.23	2.38	0.03	0.00	0.00	0.00	0.00	8.17	4.46
2	2.77	0.39	0.00	0.17	2.16	0.03	0.00	0.00	0.00	0.00		4.05
3	4.32	0.77	0.00	0.76	2.12	0.32	0.00	0.00	0.00	0.00	12.68	4.73
4	4.62	0.62	0.00	0.96	2.70	0.35	0.00	0.00	0.00	0.00		5.93
5	5.80	1.15	0.00	1.15	1.90	0.41	0.26	0.12	0.03	0.00	19.84	5.58
6	6.21	1.30	0.00	1.20	2.50	0.59	0.36	0.20	0.05	0.00		7.34
7	9.04	2.18	0.00	2.23	2.23	0.89	0.67	0.38	0.11	0.01	36.52	9.15
8	9.76	2.05	0.00	2.44	2.90	1.03	0.73	0.45	0.15	0.02		11.06
9	25.45	4.55	0.00	8.97	4.07	3.91	2.90	1.91	0.24	0.01	115.61	28.65
10	23.59	4.35	0.00	7.91	3.47	3.84	2.41	1.17	0.44	0.01		24.74
11	40.13	5.19	0.00	19.43	4.92	6.78	3.09	0.38	0.03	0.01	168.64	36.66
12	42.89	4.90	0.00	20.58	5.41	7.38	3.79	0.78	0.05	0.02		41.24
13	52.66	8.77	0.01	30.87	6.01	6.89	0.09	0.07	0.03	0.01	171.18	40.36
14	54.72	8.30	0.02	31.88	6.77	7.49	0.13	0.09	0.05	0.01		43.25
15	75.63	15.81	0.11	48.25	9.03	2.38	0.00	0.00	0.00	0.00	197.87	51.80
16	74.16	15.94	0.09	46.53	9.33	2.28	0.00	0.00	0.00	0.00		51.08
17	130.47	34.34	0.62	73.93	21.28	0.42	0.00	0.00	0.00	0.00	307.78	90.09
18	126.93	33.19	0.47	72.86	20.06	0.34	0.00	0.00	0.00	0.00		86.87

<sup>a</sup>TOC is total organic carbon in oil shale.

Fig. S1. Mass balance.



The mass loss could come from the evaporating of low boiling point hydrocarbons, solid residue loss during collecting and small amounts of organics dissolved in water.

**Table S4.** Test of low temperature distillation of shale by aluminum retort in N<sub>2</sub> atmosphere.

Experiment Number	Reaction Temperature /°C	Heating Rate °C/min	Duration at End Point of Heating /h	Reaction Pressure /atm	Atmosphere	Particle Size Range /µm	Shale Mass /g	Oil Yield per Gram of Shale /mg	Oil Yield per Gram of TOC <sup>a</sup> /mg	Average Oil Yield per Gram of TOC /mg
19	25-380	6	4	1	N <sub>2</sub>	75-106	29.99	25.13	166.36	171.46
20	25-380	6	4	1	N <sub>2</sub>	75-106	30.04	26.67	176.55	
21	25-520	6	0.3	1	N <sub>2</sub>	75-106	29.99	52.03	344.44	346.89
22	25-520	6	0.3	1	N <sub>2</sub>	75-106	30.01	52.77	349.34	

<sup>a</sup>TOC is total organic carbon in oil shale.

**Table S5.** Pyrolysis of shale in N<sub>2</sub> atmosphere.

Experiment Number	Reaction Temperature /°C	Reaction Pressure /MPa	Reaction Time /h	Particle Size Range /µm	Shale Mass /g	Oil Yield per Gram of Shale /mg	Oil Yield per Gram of TOC <sup>a</sup> /mg	Saturates /%	Aromatics /%	Resins /%	Asphaltenes /%
23	350	25	4	75-106	19.65	11.47	75.93	28.34	39.13	24.36	8.17
24	350	25	4	75-106	19.64	13.54	89.63	28.51	40.22	23.75	7.52
25	380	25	4	75-106	22.00	23.04	152.50	17.03	46.30	17.28	19.39
26	380	25	4	75-106	22.01	24.26	160.60	16.77	44.76	18.44	20.03
27	400	25	4	75-106	19.60	26.36	174.50	20.39	35.64	18.16	25.81
28	400	25	4	75-106	19.59	25.76	170.53	19.84	36.71	16.78	26.67
29	450	25	4	75-106	14.00	14.49	95.92	23.93	46.03	13.58	16.46
30	450	25	4	75-106	14.02	13.86	91.75	24.13	47.56	13.22	15.09

<sup>a</sup>TOC is total organic carbon in oil shale.

**Note:**

Detailed experimental data in Section 3.2 are shown in the Table S6-S8.

**Table S6.** Experiment conditions in Section 3.2.

Experiment Number	Reaction Temperature /°C	Reaction Pressure /MPa	Reaction Time /h	Particle Size Range / $\mu\text{m}$	Water-TOC <sup>a</sup> Mass Ratio	Shale Mass /g	Water Mass /g	Mass Fraction of Carbon in Shale /%
Pretreated Shale <sup>b</sup> -1	380	25	4	75-106	6.5:1	24.20	21.98	12.7%
Pretreated Shale-2	380	25	4	75-106	6.5:1	24.21	22.03	
HCl-R-3	380	25	4	75-106	6.5:1	21.52	21.96	15.2%
HCl-R-4	380	25	4	75-106	6.5:1	21.51	22.03	
HF/HCl-R-5	380	25	4	75-106	6.5:1	5.81	21.95	56.3%
HF/HCl-R-6	380	25	4	75-106	6.5:1	5.77	22.05	
HNO <sub>3</sub> -R-7	380	25	4	75-106	6.5:1	4.70	21.96	69.5%
HNO <sub>3</sub> -R-8	380	25	4	75-106	6.5:1	4.74	21.85	
Pretreated Shale-9	650	25	4	75-106	6.5:1	11.05	10.06	12.7%
Pretreated Shale-10	650	25	4	75-106	6.5:1	11.11	10.12	
HCl-R-11	650	25	4	75-106	6.5:1	9.85	10.12	15.2%
HCl-R-12	650	25	4	75-106	6.5:1	9.80	10.04	
HF/HCl-R-13	650	25	4	75-106	6.5:1	2.65	10.07	56.3%
HF/HCl-R-14	650	25	4	75-106	6.5:1	2.75	10.32	
HNO <sub>3</sub> -R-15	650	25	4	75-106	6.5:1	2.22	10.32	69.5%
HNO <sub>3</sub> -R-16	650	25	4	75-106	6.5:1	2.20	10.07	

<sup>a</sup>TOC is total organic carbon in oil shale.

<sup>b</sup>Pretreated Shale refers to the shale undergone Soxhlet extraction with carbon disulfide.

**Table S7.** Quantitative analysis of oil products and residues in Section 3.2.

Experiment Number	Oil Yield per Gram of Shale /mg	Oil Yield per Gram of TOC <sup>a</sup> /mg	Mass Fraction of Carbon in Oil /%	Organic Carbon in Oil per Gram of TOC /mg	Saturates /%	Aromatics /%	Resins /%	Asphaltenes /%	Shale Residual Mass /g
Pretreated Shale <sup>b</sup> -1	32.56	256.78	78.6%	200.42	11.7%	30.8%	30.6%	26.9%	32.56
Pretreated Shale-2	32.11	253.21			12.9%	32.2%	28.9%	26.0%	32.11
HCl-R-3	31.23	205.61	77.5%	156.70	15.2%	42.6%	25.6%	16.5%	31.23
HCl-R-4	30.19	198.77			13.1%	41.3%	27.6%	17.9%	30.19
HF/HCl-R-5	133.05	236.48	78.1%	184.22	10.6%	38.9%	29.0%	21.5%	133.05
HF/HCl-R-6	132.36	235.27			11.9%	39.5%	27.8%	20.8%	132.36
HNO <sub>3</sub> -R-7	130.66	188.14	76.3%	145.02	11.9%	31.7%	32.3%	24.2%	130.66
HNO <sub>3</sub> -R-8	133.34	192.00			12.0%	33.5%	31.5%	23.0%	133.34
Pretreated Shale-9	0.00	0.00	- <sup>c</sup>	-	-	-	-	-	0.00
Pretreated Shale-10	0.00	0.00	-	-	-	-	-	-	0.00
HCl-R-11	0.00	0.00	-	-	-	-	-	-	0.00
HCl-R-12	0.00	0.00	-	-	-	-	-	-	0.00
HF/HCl-R-13	0.00	0.00	-	-	-	-	-	-	0.00
HF/HCl-R-14	0.00	0.00	-	-	-	-	-	-	0.00
HNO <sub>3</sub> -R-15	0.00	0.00	-	-	-	-	-	-	0.00
HNO <sub>3</sub> -R-16	0.00	0.00	-	-	-	-	-	-	0.00

<sup>a</sup>TOC is total organic carbon in oil shale.

<sup>b</sup>Pretreated Shale refers to the shale undergone Soxhlet extraction with carbon disulfide.

<sup>c</sup>- refers to no oil yielded.



**Table S8.** Quantitative analysis of gas products and TOC conversion efficiency in Section 3.2.

Experiment Number	Gas Yield per Gram of TOC <sup>a</sup> /ml	H <sub>2</sub> per Gram of TOC /mL	CO per Gram of TOC /mL	CH <sub>4</sub> per Gram of TOC /mL	CO <sub>2</sub> per Gram of TOC /mL	C <sub>2</sub> per Gram of TOC /mL	C <sub>3</sub> per Gram of TOC /mL	C <sub>4</sub> per Gram of TOC /mL	C <sub>5</sub> per Gram of TOC /mL	C <sub>6</sub> per Gram of TOC /mL	Organic Carbon in Gas per Gram of TOC /mg	TOC Conversion Efficiency <sup>b</sup>
Pretreated Shale <sup>c</sup> -1	35.46	8.62	0.00	8.02	11.70	3.35	2.41	1.15	0.21	0.01	0.02	0.22
Pretreated Shale-2	34.37	8.87	0.00	8.30	11.04	3.12	1.87	0.95	0.21	0.01		
HCl-R-3	36.56	12.76	0.00	9.60	6.15	4.07	2.59	1.08	0.31	0.00	0.02	0.18
HCl-R-4	37.95	11.41	0.00	10.42	7.35	4.14	2.65	1.60	0.40	0.00		
HF/HCl-R-5	23.38	7.55	0.02	6.37	5.42	2.76	0.89	0.33	0.04	0.00	0.01	0.20
HF/HCl-R-6	21.67	7.39	0.02	6.18	4.49	2.39	0.84	0.31	0.05	0.00		
HNO <sub>3</sub> -R-7	35.36	4.43	0.34	6.83	18.32	2.10	2.14	0.96	0.22	0.01	0.02	0.17
HNO <sub>3</sub> -R-8	31.91	3.64	0.30	5.97	16.40	3.00	1.51	0.88	0.20	0.01		
Pretreated Shale-9	742.63	224.87	4.46	383.88	127.83	1.58	0.00	0.00	0.00	0.00	0.25	0.25
Pretreated Shale-10	751.52	227.82	3.26	387.88	130.93	1.62	0.00	0.00	0.00	0.00		
HCl-R-11	821.57	257.43	6.18	403.94	152.78	1.24	0.00	0.00	0.00	0.00	0.28	0.28
HCl-R-12	833.15	259.42	6.93	409.85	155.40	1.54	0.00	0.00	0.00	0.00		
HF/HCl-R-13	779.63	203.33	5.67	389.19	179.87	1.57	0.00	0.00	0.00	0.00	0.28	0.28
HF/HCl-R-14	768.30	200.82	4.33	385.25	176.30	1.60	0.00	0.00	0.00	0.00		
HNO <sub>3</sub> -R-15	713.38	184.93	6.13	356.88	163.70	1.75	0.00	0.00	0.00	0.00	0.26	0.26
HNO <sub>3</sub> -R-16	703.69	180.97	6.93	352.69	161.68	1.42	0.00	0.00	0.00	0.00		

<sup>a</sup>TOC is total organic carbon in oil shale.

<sup>b</sup>TOC Conversion Efficiency is the sum of organic carbon in oil and gas products over total organic carbon in oil shale.

<sup>c</sup>Pretreated Shale refers to the shale undergone Soxhlet extraction with carbon disulfide.