

Effect of swelling treatment by organic solvent on the structure and pyrolysis performance of the direct coal liquefaction residue

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Supplementary Materials

Table S1 Analytical results of compounds from pyrolysis products of DCLR

No	RT/min	Compound	Molecular formula	Content/%
1	1.57	N-Acetyl-L-alanine	C ₅ H ₉ NO ₃	19.24
2	2.27	Tetrahydrofuran	C ₄ H ₈ O	3.23
3	3.64	Toluene	C ₇ H ₈	2.84
4	4.61	Furfural	C ₅ H ₄ O ₂	10.51
5	5.09	Ethylbenzene	C ₈ H ₁₀	1.44
6	5.4	n-Butyl ether	C ₈ H ₁₈ O	1.12
7	5.67	Cyclohexanone	C ₆ H ₁₀ O	4.28
8	5.95	Butanoic acid, 4-hydroxy	C ₄ H ₈ O ₃	0.68
9	7.49	Carbamic acid, methyl-, phenyl ester	C ₈ H ₉ NO ₂	0.87
10	8.11	2-Pyrrolidinone, 1-methyl-	C ₅ H ₉ NO	2.20
11	8.61	Allophanic acid, 4-benzoyl-,m-tolyl ester	C ₁₆ H ₁₄ N ₂ O ₄	0.84
12	8.96	Phenol, 3-methyl-	C ₇ H ₈ O	1.86
13	9.08	Oxalic acid, dodecyl 2-methylphenyl ester	C ₂₁ H ₃₂ O ₄	1.03
14	10	Phenol,2,4-dimethyl-	C ₈ H ₁₀ O	1.85
15	10.11	Naphthalene,1,2,3,4-tetrahydro-	C ₁₀ H ₁₂	1.95
16	10.3	Phenol, 4-ethyl-	C ₈ H ₁₀ O	0.68
17	10.51	Naphthalene	C ₁₀ H ₈	1.12
18	10.59	Dodecane	C ₁₂ H ₂₆	1.03
19	11.16	4-(2,5-Dihydro-3-methoxyphenyl) butylamine	C ₁₁ H ₁₉ NO	0.67
20	11.58	2-Phenyl-4-penten-2-ol	C ₁₁ H ₁₄ O	0.84

21	11.9	1-Tetradecen	C ₁₄ H ₂₈	0.71
22	12.01	Tridecane	C ₁₃ H ₂₈	1.03
23	12.35	Naphthalene, 1-methyl-	C ₁₁ H ₁₀	0.90
24	13.36	Tetradecane	C ₁₄ H ₃₀	1.09
25	14.64	Pentadecane	C ₁₅ H ₃₂	1.35
26	15.85	Hexadecane	C ₁₆ H ₃₄	2.43
27	16.48	[1,1'-Biphenyl]-4-carboxaldehyde	C ₁₃ H ₁₀ O	0.68
28	17	Heptadecane	C ₁₇ H ₃₆	1.63
29	18.09	Octadecane	C ₁₈ H ₃₈	1.34
30	19.13	Nonadecane	C ₁₉ H ₄₀	1.49
31	20.07	1-Nonadecene	C ₁₉ H ₃₈	0.81
32	20.12	Eicosane	C ₂₀ H ₄₂	1.89
33	20.82	Phenanthrene,3,6-dimethyl-	C ₁₆ H ₁₄	0.64
34	21.07	Heneicosane	C ₂₁ H ₄₄	2.90
35	21.56	Pyrene	C ₁₆ H ₁₀	0.73
36	21.98	Docosane	C ₂₂ H ₄₆	2.75
37	22.85	Tetracosane	C ₂₄ H ₅₀	3.03
38	23.69	Pentacosane	C ₂₅ H ₅₂	1.79
39	24	Friedelan-3-one	C ₃₀ H ₅₀ O	11.48
40	24.5	Hexacosane	C ₂₆ H ₅₄	3.06

Table S2 Analytical results of compounds from pyrolysis products of N-DCLR

No	RT/min	Compound	Molecular formula	Content/%
1	1.57	N-Acetyl-L-alanine	C ₅ H ₉ NO ₃	2.02
2	3.8	Formamide, N,N-dimethyl-	C ₃ H ₇ NO	0.76
3	4.61	Furfural	C ₅ H ₄ O ₂	1.82
4	5.67	Cyclohexanone	C ₆ H ₁₀ O	1.48
5	8.11	2-Pyrrolidinone, 1-methyl-	C ₅ H ₉ NO	80.89
6	8.98	2,5-Pyrrolidinedione,1-methyl-	C ₅ H ₇ NO ₂	1.22
7	10.11	Naphthalene,1,2,3,4-tetrahydro-	C ₁₀ H ₁₂	5.02
8	10.51	Naphthalene	C ₁₀ H ₈	2.21
9	15.85	Hexadecane	C ₁₆ H ₃₄	0.67
10	20.12	Eicosane	C ₂₀ H ₄₂	0.70
11	21.07	Heneicosane	C ₂₁ H ₄₄	0.70
12	21.98	Docosane	C ₂₂ H ₄₆	0.65
13	22.85	Tetracosane	C ₂₄ H ₅₀	0.71
14	23.69	Pentacosane	C ₂₅ H ₅₂	0.57
15	24.5	Hexacosane	C ₂₆ H ₅₄	0.58

Table S3 Analytical results of compounds from pyrolysis products of C-DCLR

No	RT/min	Compound	Molecular formula	Content/%
1	1.57	N-Acetyl-L-alanine	C ₅ H ₉ NO ₃	4.45
2	3.8	Formamide, N,N-dimethyl-	C ₃ H ₇ NO	2.61
3	4.61	Furfural	C ₅ H ₄ O ₂	6.75
4	5.67	Cyclohexanone	C ₆ H ₁₀ O	2.61
5	8.11	2-Pyrrolidinone, 1-methyl-	C ₅ H ₉ NO	37.22
6	8.98	2,5-Pyrrolidinedione, 1-methyl-	C ₅ H ₇ NO ₂	0.81
7	10.11	Naphthalene, 1,2,3,4-tetrahydro-	C ₁₀ H ₁₂	24.35
8	10.51	Naphthalene	C ₁₀ H ₈	10.02
9	13.2	1(2H)-Naphthalenone, 3,4-dihydro-	C ₁₀ H ₁₀ O	1.82
10	15.85	Hexadecane	C ₁₆ H ₃₄	0.79
11	17	Heptadecane	C ₁₇ H ₃₆	0.60
12	20.12	Eicosane	C ₂₀ H ₄₂	1.02
13	21.07	Heneicosane	C ₂₁ H ₄₄	1.08
14	21.98	Docosane	C ₂₂ H ₄₆	1.01
15	22.85	Tetracosane	C ₂₄ H ₅₀	1.11
16	23.69	Pentacosane	C ₂₅ H ₅₂	1.75
17	24.5	Hexacosane	C ₂₆ H ₅₄	0.97
18	24.72	Heptacosane	C ₂₇ H ₅₆	1.03

Table S4 Analytical results of compounds from pyrolysis products of D-DCLR

No	RT/min	Compound	Molecular formula	Content/%
1	1.57	N-Acetyl-L-alanine	C ₅ H ₉ NO ₃	2.46
2	4.61	Furfural	C ₅ H ₄ O ₂	5.29
3	5.67	Cyclohexanone	C ₆ H ₁₀ O	50.60
4	6.31	2-Cyclohexen-1-one	C ₆ H ₈ O	1.84
5	7.47	Phenol	C ₆ H ₆ O	1.37
6	8.11	2-Pyrrolidinone, 1-methyl-	C ₅ H ₉ NO	7.68
7	8.56	Phenol, 2-methyl-	C ₇ H ₈ O	0.78
8	8.98	2,5-Pyrrolidinedione, 1-methyl-	C ₅ H ₇ NO ₂	0.99
9	9.29	Benzofuran, 2-methyl-	C ₉ H ₈ O	0.69
10	10.11	Naphthalene, 1,2,3,4-tetrahydro-	C ₁₀ H ₁₂	11.80
11	10.51	Naphthalene	C ₁₀ H ₈	1.88
12	10.78	1H-Indene, 2,3-dihydro-2-methyl-	C ₁₀ H ₁₀ O	0.73
13	15.06	Dibenzofura	C ₁₂ H ₈ O	2.04
14	15.2	1,2,3,4-Tetrahydrodibenzofuran	C ₁₂ H ₁₂ O	1.98
15	15.85	Hexadecane	C ₁₆ H ₃₄	0.84
16	16.18	1,6-Pentalenedione, hexahydro-6a-(2-propynyl)-, cis-	C ₁₁ H ₁₂ O ₂	1.71
17	16.28	6H-Dibenzo[b,d]-pyran	C ₁₃ H ₁₀ O	0.59
18	17	Heptadecane	C ₁₇ H ₃₆	0.69
19	19.13	Nonadecane	C ₁₉ H ₄₀	0.60
20	20.12	Eicosane	C ₂₀ H ₄₂	0.85

21	21.07	Heneicosane	C ₂₁ H ₄₄	0.92
22	21.98	Docosane	C ₂₂ H ₄₆	0.93
23	22.85	Tetracosane	C ₂₄ H ₅₀	1.04
24	23.69	Pentacosane	C ₂₅ H ₅₂	0.85
25	24.5	Hexacosane	C ₂₆ H ₅₄	0.85

Table S5 Analytical results of compounds from pyrolysis products of A-DCLR

No	RT/min	Compound	Molecular formula	Content/%
1	1.57	N-Acetyl-L-alanine	C ₅ H ₉ NO ₃	5.23
2	1.76	Acetone	C ₃ H ₆ O	0.99
3	3.64	Toluene	C ₇ H ₈	27.42
4	3.8	Formamide, N,N-dimethyl-	C ₃ H ₇ NO	0.70
5	4.61	Furfural	C ₅ H ₄ O ₂	13.66
6	5.67	Cyclohexanone	C ₆ H ₁₀ O	11.91
7	8.11	2-Pyrrolidinone, 1-methyl-	C ₅ H ₉ NO	6.54
8	8.96	Phenol, 3-methyl-	C ₇ H ₈ O	1.19
9	10.11	Naphthalene, 1,2,3,4-tetrahydro-	C ₁₀ H ₁₂	17.67
10	10.51	Naphthalene	C ₁₀ H ₈	5.48
11	13.2	1(2H)-Naphthalenone, 3,4-dihydro-	C ₁₀ H ₁₀ O	0.80
12	15.85	Hexadecane	C ₁₆ H ₃₄	0.93
13	17	Heptadecane	C ₁₇ H ₃₆	0.68
14	19.13	Nonadecane	C ₁₉ H ₄₀	0.65
15	20.12	Eicosane	C ₂₀ H ₄₂	0.79
16	21.07	Heneicosane	C ₂₁ H ₄₄	1.07
17	21.98	Docosane	C ₂₂ H ₄₆	1.11
18	22.85	Tetracosane	C ₂₄ H ₅₀	1.30
19	23.69	Pentacosane	C ₂₅ H ₅₂	0.93
20	24.5	Hexacosane	C ₂₆ H ₅₄	0.96

Table S6 Analytical results of compounds from pyrolysis products of T-DCLR

No	RT/min	Compound	Molecular formula	Content/%
1	1.57	N-Acetyl-L-alanine	C ₅ H ₉ NO ₃	11.93
2	2.27	Tetrahydrofuran	C ₄ H ₈ O	0.84
3	3.64	Toluene	C ₇ H ₈	2.66
4	3.8	Formamide, N,N-dimethyl-	C ₃ H ₇ NO	0.85
5	4.61	Furfural	C ₅ H ₄ O ₂	24.38
6	5.67	Cyclohexanone	C ₆ H ₁₀ O	14.90
7	6.31	2-Cyclohexen-1-one	C ₆ H ₈	0.72
8	7.49	Carbamic acid, methyl-, phenyl ester	C ₈ H ₉ NO ₂	0.85
9	8.11	2-Pyrrolidinone, 1-methyl-	C ₅ H ₉ NO	6.64
10	9.08	Oxalic acid, dodecyl 2-methylphenyl ester	C ₂₁ H ₃₂ O ₄	0.73
11	10.11	Naphthalene, 1,2,3,4-tetrahydro-	C ₁₀ H ₁₂	12.21
12	10.51	Naphthalene	C ₁₀ H ₈	3.89
13	12.01	Tridecane	C ₁₃ H ₂₈	0.82
14	13.36	Tetradecane	C ₁₄ H ₃₀	0.69

15	14.64	Pentadecane	$C_{15}H_{32}$	0.89
16	15.85	Hexadecane	$C_{16}H_{34}$	1.76
17	17	Heptadecane	$C_{17}H_{36}$	1.11
18	18.09	Octadecane	$C_{18}H_{38}$	1.03
19	19.13	Nonadecane	$C_{19}H_{40}$	1.05
20	20.12	Eicosane	$C_{20}H_{42}$	1.79
21	21.07	Heneicosane	$C_{21}H_{44}$	1.87
22	21.98	Docosane	$C_{22}H_{46}$	1.83
23	22.85	Tetracosane	$C_{24}H_{50}$	1.98
24	23.69	Pentacosane	$C_{25}H_{52}$	1.63
25	24.5	Hexacosane	$C_{26}H_{54}$	1.73
26	24.89	Erucic acid	$C_{22}H_{42}O_2$	1.22

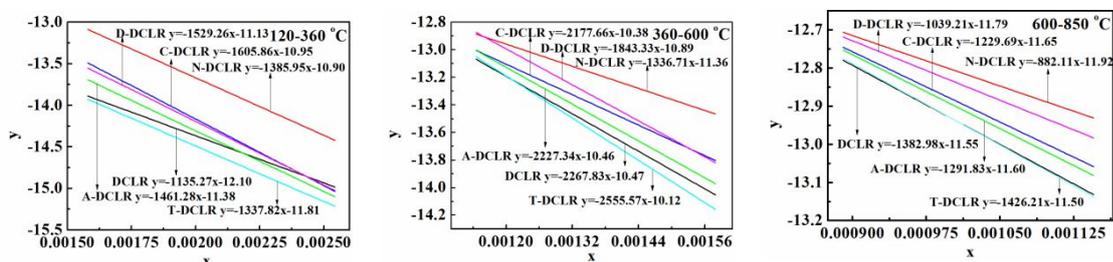


Figure S1(a) Fitting results of pyrolysis kinetics of residual samples (n=1)

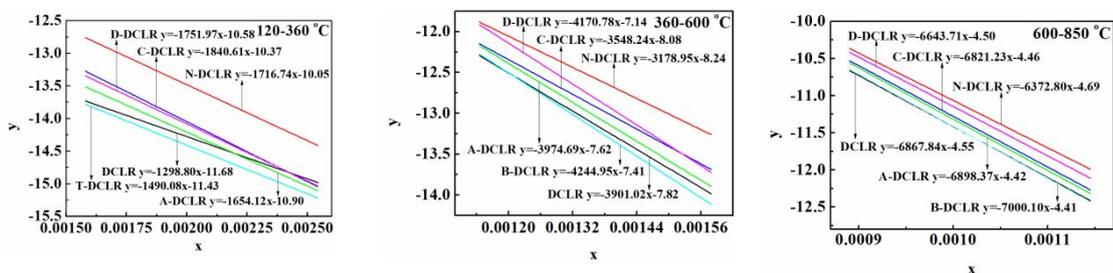


Figure S1(b) Fitting results of pyrolysis kinetics of residual samples (n=2)

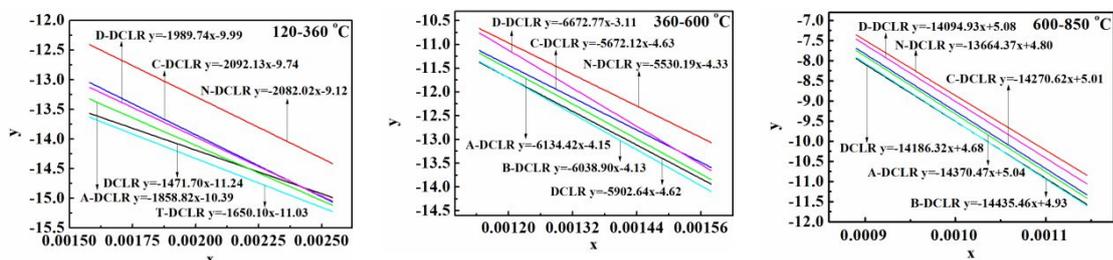


Figure S1(c) Fitting results of pyrolysis kinetics of residual samples (n=3)

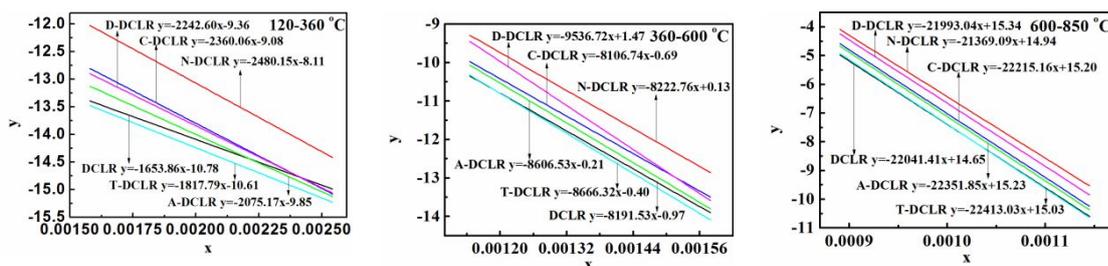


Figure S1(d) Fitting results of pyrolysis kinetics of residual samples (n=4)

Table S7(a) Pyrolysis kinetic parameters of the six residues in the temperature of 120-360 °C

T / °C	Samples	n	Regression equation	R ²	E/(kJ/mol)	A/min ⁻¹	2RT/E
120-360	DCLR	1	y = -1135.27x - 12.10	0.9769	9.439	0.063	0.211
		2	y = -1298.80x - 11.68	0.9855	10.798	0.110	0.185
		3	y = -1471.70x - 11.24	0.9903	12.236	0.193	0.163
		4	y = -1653.86x - 10.78	0.9925	13.750	0.344	0.145
	N-DCLR	1	y = -1385.95x - 10.90	0.7567	11.523	0.256	0.173
		2	y = -1716.74x - 10.05	0.8296	14.273	0.741	0.140
		3	y = -2082.02x - 9.12	0.8816	17.310	2.279	0.115
		4	y = -2480.15x - 8.11	0.9179	20.620	7.453	0.097
	C-DCLR	1	y = -1605.86x - 10.95	0.9174	13.351	0.282	0.149
		2	y = -1840.61x - 10.37	0.9430	15.303	0.577	0.130
		3	y = -2092.13x - 9.74	0.9616	17.394	1.232	0.115
		4	y = -2360.06x - 9.08	0.9747	19.622	2.689	0.102
	D-DCLR	1	y = -1529.26x - 11.13	0.9273	12.717	0.224	0.157
		2	y = -1751.97x - 10.58	0.9517	14.566	0.445	0.137
		3	y = -1989.74x - 9.99	0.9691	16.543	0.912	0.121
		4	y = -2242.60x - 9.36	0.9811	18.645	1.931	0.107
	A-DCLR	1	y = -1461.28x - 11.38	0.9295	12.149	0.167	0.164
		2	y = -1654.12x - 10.90	0.9502	13.752	0.305	0.145
		3	y = -1858.82x - 10.39	0.9654	15.454	0.571	0.129
		4	y = -2075.17x - 9.85	0.9764	17.253	1.095	0.116
T-DCLR	1	y = -1337.82x - 11.81	0.9376	11.123	0.099	0.179	
	2	y = -1490.08x - 11.43	0.9550	12.389	0.162	0.161	
	3	y = -1650.10x - 11.03	0.9683	13.719	0.267	0.145	
	4	y = -1817.79x - 10.61	0.9780	15.113	0.448	0.132	

Table S7(b) Pyrolysis kinetic parameters of six residues in the temperature of 360-600 °C

T / °C	Samples	n	Regression equation	R ²	E/(kJ/mol)	A/min ⁻¹	2RT/E
360-600	DCLR	1	y = -2267.83x - 10.47	0.9773	18.855	0.643	0.317
		2	y = -3901.02x - 7.82	0.9886	32.433	15.667	0.185
		3	y = -5902.64x - 4.62	0.9847	49.075	581.575	0.122
		4	y = -8191.53x - 0.97	0.9793	68.104	3.105 × 10 ⁴	0.088
	N-DCLR	1	y = -1336.71x - 11.36	0.9560	11.113	0.156	0.539
		2	y = -3178.95x - 8.24	0.9751	26.430	8.389	0.226
		3	y = -5530.19x - 4.33	0.9727	45.978	728.190	0.130
		4	y = -8222.76x + 0.13	0.9702	68.364	9.364 × 10 ⁴	0.088
	C-DCLR	1	y = -1843.33x - 10.89	0.9736	15.325	0.344	0.391
		2	y = -3548.24x - 8.08	0.9843	29.500	10.988	0.203
		3	y = -5672.12x - 4.63	0.9797	47.158	553.302	0.127
		4	y = -8106.74x - 0.69	0.9751	67.399	4.066 × 10 ⁴	0.089

D-DCLR	1	$y = -2177.66x - 10.38$	0.9567	18.105	0.676	0.331
	2	$y = -4170.78x - 7.14$	0.9830	34.676	33.064	0.173
	3	$y = -6672.77x - 3.11$	0.9836	55.477	2.976×10^3	0.108
	4	$y = -9536.72x + 1.47$	0.9810	79.288	4.148×10^5	0.075
A-DCLR	1	$y = -2227.34x - 10.46$	0.9718	18.518	0.638	0.323
	2	$y = -3974.69x - 7.62$	0.9853	33.046	19.498	0.181
	3	$y = -6134.42x - 4.15$	0.9820	51.002	967.056	0.117
	4	$y = -8606.53x - 0.21$	0.9773	71.555	6.976×10^4	0.084
T-DCLR	1	$y = -2555.57x - 10.12$	0.9733	21.247	1.029	0.282
	2	$y = -4244.95x - 7.41$	0.9873	35.293	25.689	0.170
	3	$y = -6038.90x - 4.13$	0.9849	50.207	971.229	0.119
	4	$y = -8666.32x - 0.40$	0.9799	72.052	5.809×10^4	0.083

Table S7(c) Pyrolysis kinetic parameters of six residues in the temperature of 600-850 °C

T / °C	Samples	n	Regression equation	R ²	E/(kJ/mol)	A/min ⁻¹	2RT/E
600-850	DCLR	1	$y = -1382.98x - 11.55$	0.9991	11.498	0.133	0.868
		2	$y = -6867.84x - 4.55$	0.9838	57.099	725.739	0.175
		3	$y = -14186.32x + 4.68$	0.9800	117.945	1.529×10^7	0.085
		4	$y = -22041.41x + 14.65$	0.9801	183.252	5.078×10^{11}	0.054
	N-DCLR	1	$y = -882.11x - 11.92$	0.9919	7.334	0.059	1.360
		2	$y = -6372.80x - 4.69$	0.9772	52.983	585.449	0.188
		3	$y = -13664.37x + 4.80$	0.9762	113.606	1.660×10^7	0.088
		4	$y = -21369.09x + 14.94$	0.9772	177.663	6.579×10^{11}	0.056
	C-DCLR	1	$y = -1229.69x - 11.65$	0.9968	10.224	0.107	0.976
		2	$y = -6821.23x - 4.46$	0.9792	56.712	788.695	0.176
		3	$y = -14270.62x + 5.01$	0.9765	118.646	2.139×10^7	0.084
		4	$y = -22215.16x + 15.20$	0.9770	184.697	8.870×10^{11}	0.054
	D-DCLR	1	$y = -1039.21x - 11.79$	0.9969	8.640	0.079	1.155
		2	$y = -6643.71x - 4.50$	0.9717	55.236	738.050	0.181
		3	$y = -14094.93x + 5.08$	0.9707	117.185	2.266×10^7	0.085
		4	$y = -21993.04x + 15.34$	0.9718	182.850	1.010×10^{12}	0.055
	A-DCLR	1	$y = -1291.83x - 11.60$	0.9963	10.740	0.118	0.929
		2	$y = -6898.37x - 4.42$	0.9780	57.353	830.166	0.174
		3	$y = -14370.47x + 5.04$	0.9751	119.476	2.220×10^7	0.084
		4	$y = -22351.85x + 15.23$	0.9756	185.833	9.196×10^{11}	0.054
T-DCLR	1	$y = -1426.21x - 11.50$	0.9979	11.858	0.144	0.841	
	2	$y = -7000.10x - 4.41$	0.9799	58.199	850.875	0.171	
	3	$y = -14435.46x + 4.93$	0.9762	120.016	1.998×10^7	0.083	
	4	$y = -22413.03x + 15.03$	0.9764	186.342	7.550×10^{11}	0.054	