

# Supplementary material

## Effect of a HF-HF/HCl treatment of 26 coals on their composition and pyrolysis behavior

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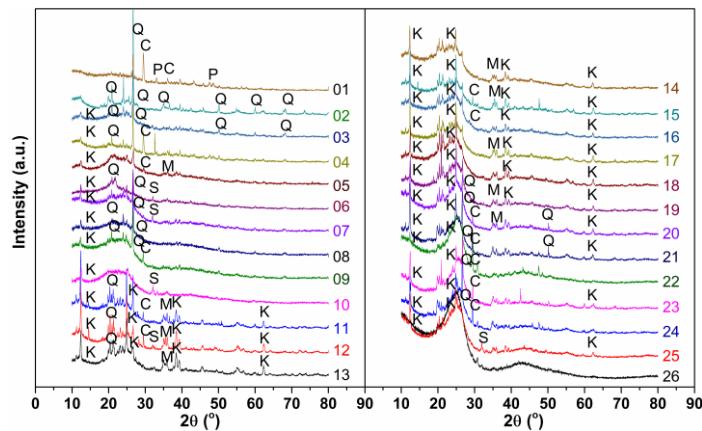


Figure S1. XRD of R-coals. K-Kaolinite; C-Calcium carbonate; P-Pyrite; S-Siderite; Q-Quartz; M-Magnetite

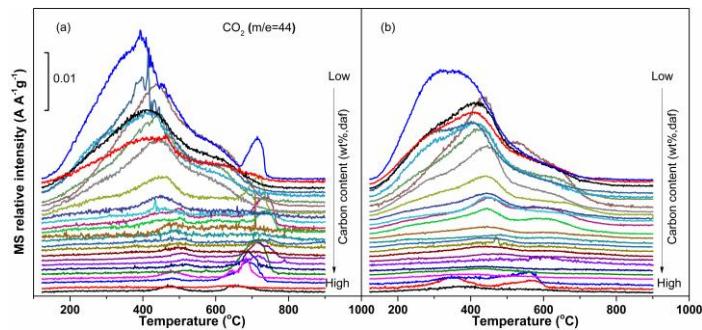


Figure S2. The MS signal of  $\text{CO}_2$  of R-coals (a) and D-coals (b)

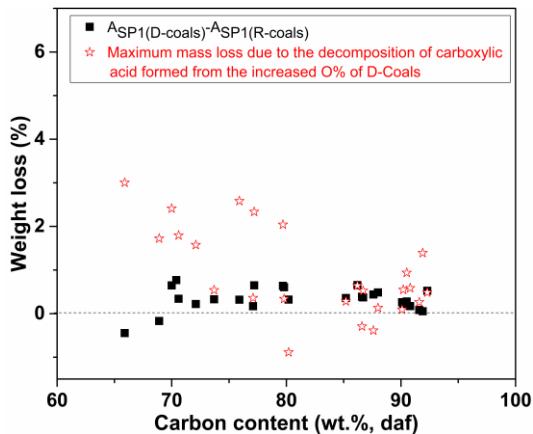


Figure S3. Comparison of the increased  $A_{sp1}$  by the acid treatment ( $A_{sp1(D\text{-coals})} - A_{sp1(R\text{-coals})}$ ) with the maximum mass loss due to the decomposition of carboxylic acid, assuming the increased O% in D-coals all form carboxylic acid.

Table S1. Temperature of removing crystal water from clay minerals in coal

Mineral species	Mineral name	Chemical formula	Decrystallization
			water temperature (°C)
Clay	Kaolinite	$Al_2Si_2O_5(OH)_4$	450 <sup>1, 2</sup>
	Illite	$K_{1.5}Al_4(Si_{6.5}Al_{1.5})O_{20}(O)_4$ (Na, Ca) <sub>0.33</sub> (Al,	200-600 <sup>3</sup>
	Montmorillonite	$Mg_2[Si_4O_{10}] (OH)_2 \cdot nH_2O$	600-700 <sup>4</sup>
	Chlorite	$(Mg Fe Al)_6(Al Si)_4O_{10}(OH)_8$	600-900 <sup>5</sup>
	Sericite	$K_{0.5-1} (Al, Fe, Mg)_2 (Si, Al)_4O_{10}(OH)_2 \cdot nH_2O$	750-820 <sup>4</sup>
	Analcite	$NaAlSi_2O_6 \cdot H_2O$	490-600 <sup>6</sup>
	Muscovite	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	450-700 <sup>1</sup>
	Clinoptilolite	$KNa_2Ca_2(Si_29Al_7)O_{72} \cdot 32H_2O$	230-350 <sup>7</sup>
	Heulandite	$CaAl_2Si_7O_{18} \cdot 6H_2O$	80-450 <sup>6</sup>

## References

- (1) Pretorius, P. G. Pyrolysis product evaluation and prediction of coals of different rank. North-West University (South Africa), Potchefstroom Campus **2016**.
- (2) Mayoral, M. C.; Izquierdo, M. T.; Andrés, J. M.; Rubio, B. Aluminosilicates transformations in combustion followed by DSC. *Thermochim. Acta* **2001**, 373, 173-180.
- (3) O'Gorman, J. V.; Walker Jr, P. L. Mineral matter characteristics of some American coals. *Fuel* **1971**, 50, 135-151.
- (4) Vassilev, S. V.; Baxter, D.; Vassileva, C. G. An overview of the behaviour of biomass during

- combustion: Part I. Phase-mineral transformations of organic and inorganic matter. *Fuel*. **2013**, *112*, 391-449.
- (5) Vassileva, C. G.; Vassilev, S. V. Behaviour of inorganic matter during heating of Bulgarian coals: 2. Subbituminous and bituminous coals. *Thermochim. Acta* **2006**, *87*, 1095-1116.
- (6) Milligan, W. O.; Weiser, H. B. The mechanism of the dehydration of zeolites. *Fuel Process. Technol.* **1937**, *41*, 1029-1040.
- (7) Knowlton, G. D.; Mckague, H. L.; White, T. R. Thermal study of types of water associated with clinoptilolite. *Clay Alay Miner* **1981**, *29*, 403-411.