

APPENDICES



A

APPENDIX A Coal Characterisation: Conventional analyses

A.1 Description of standard methods used

ASTM D4326	:	Standard test method for major and minor elements in coal and coke ash by X-ray fluorescence. (ASTM, 1997)
CKS 561-1982	:	Specification for anthracitic and bituminous coals.
ISO 7404-2 (1985)	:	Methods for the petrographic analysis of bituminous coal and anthracite - Part 2: Preparation of coal samples (ISO, 1985).
ISO 7404-3 (1994)	:	Methods for the petrographic analysis of bituminous coal and anthracite - Part 3: Method of determining maceral group composition (ISO, 1994a).
ISO 7404-4 (1988)	:	Methods for the petrographic analysis of bituminous coal and anthracite - Part 4: Method of determining microlithotype-, carbominerite- and minerite composition (ISO, 1988).
ISO 7404-5 (1994)	:	Methods for the petrographic analysis of bituminous coal and anthracite - Part 5: Method of determining microscopically the reflectance of vitrinite (ISO, 1994b).
ISO 11760 (2005)	:	Classification of coals (ISO, 2005).
ISO 12902 (2001)	:	Solid mineral fuels - Determination of total carbon, hydrogen and nitrogen-instrumental methods (ISO, 2001).
ISO 19579 (2006)	:	Determination of total sulphur through IR spectroscopy (ISO, 2006)

SABS ISO 501 (2003)	:	Hard coal - Determination of the crucible swelling number (SANS, 2003).
SABS ISO 562 (1998)	:	Hard coal and coke: Determination of volatile matter (SANS, 1998).
SABS ISO 1171 (1997)	:	Solid mineral fuels: Determination of ash content (SANS, 1997).
SABS ISO 1928 (1995)	:	Determination of gross calorific value by the bomb calorimetric method, and calculation of net calorific value (SANS, 1995).
SANS 5925 (2007)	:	Moisture content of coal samples intended for general analysis (air-oven method) (SANS, 2007).
SANS 6072 (1984)	:	Yields of tar, water, gas, and coke residue from coal by low temperature distillation (SANS, 1984).
SANS 6073 (1984)	:	Coking properties of coal (Ruhr dilatometer test) (SANS, 2009).

A.2 XRD minerals-chemical structures and properties

Table A.1 Chemical formulas and properties of XRD minerals (Ralph & Chau, 2012).

Species	Chemical formula	X-ray diffraction pattern (By intensity (I/I₀))	Density (kg/m³)
<i>Anatase</i>	TiO ₂	3.51 (1), 1.891 (0.33), 2.379 (0.22)	3900
<i>Calcite</i>	CaCO ₃	3.035 (1), 2.095 (0.18), 2.285 (0.18)	2710
<i>Dolomite</i>	CaMg(CO ₃) ₂	2.883 (1), 1.785 (0.6), 2.191 (0.5)	2840
<i>Kaolinite</i>	Al ₂ Si ₂ O ₅ (OH) ₄	7.17 (1), 1.49 (0.9), 3.58 (0.8)	2600
<i>Magnetite</i>	Fe ³⁺ ₂ Fe ²⁺ O ₄	2.53 (1), 1.483 (0.85), 1.614 (0.85)	5150
<i>Muscovite</i>	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	3.32 (1), 9.95 (0.95), 2.57 (0.55)	2820
<i>Pyrite</i>	FeS ₂	1.633 (1), 2.709 (0.85), 2.423 (0.65)	5010
<i>Quartz</i>	SiO ₂	3.342 (1), 4.257 (0.22), 1.818 (0.14)	2620
<i>Rutile</i>	TiO ₂	3.245 (1), 1.687 (0.5), 2.489 (0.41)	4250
<i>Siderite</i>	Fe ²⁺ CO ₃	2.79 (1), 1.734 (0.8), 3.59 (0.6)	3960

A.3 Vitrinite reflectance and maceral scan analyses

The results obtained from both vitrinite random reflectance, as well as from maceral reflectance scan analyses are summarised respectively in Tables A.2 and A.3.

Table A.2 Results obtained from vitrinite random reflectance conducted on all four coals.

	<i>Coal INY</i>		<i>Coal UMZ</i>		<i>Coal G#5</i>		<i>Coal TSH</i>	
	Mean R_r	0.81	Mean R_r	0.81	Mean R_r	0.66	Mean R_r	1.23
	σ	0.09	σ	0.09	σ	0.05	σ	0.12
	Range %	0.5-1.0	Range %	0.5-1.0	Range %	0.5-0.7	Range %	1.0-1.6
<i>Rr%</i>	<i>Relative Frequency (%)</i>		<i>Relative Frequency (%)</i>		<i>Relative Frequency (%)</i>		<i>Relative Frequency (%)</i>	
0.5	Vitrinite	1.0	Vitrinite	10.0	Vitrinite	14.0	Vitrinite	4.0
0.6		13.0				68.0		
0.7		38.0				18.0		
0.8		31.0						
0.9		16.0						
1.0		1.0		1.0				
1.1								44.0
1.2								33.0
1.3								6.0
1.4								8.0
1.5								3.0
1.6								2.0
TOTAL		100.00		100.00		100.00		100.00

Table A.3 Results obtained from maceral scan analyses conducted on all four coals.

	<i>Coal INY</i>		<i>Coal UMZ</i>		<i>Coal G#5</i>		<i>Coal TSH</i>	
	Mean R_r	1.26	Mean R_r	1.27	Mean R_r	0.96	Mean R_r	1.46
	σ	0.53	σ	0.47	σ	0.57	σ	0.48
<i>Rr%</i>	<i>Relative Frequency (%)</i>		<i>Relative Frequency (%)</i>		<i>Relative Frequency (%)</i>		<i>Relative Frequency (%)</i>	
0.1	Liptinite	2.00	Liptinite	2.00	Liptinite	0.40	Liptinite	1.20
0.2						2.80		
0.3						2.80		
0.4						0.80		
0.5	Vitrinite	1.20	Vitrinite	10.00	Vitrinite	8.40		
0.6		6.40				31.40		
0.7		14.00				13.20		
0.8		12.40				5.20		
0.9	Inertinite	5.20	Inertinite	4.00	Inertinite	8.00		
1.0		3.60				0.80	Vitrinite	8.40
1.1		4.40				2.40		

Table A.3 Results obtained from maceral scan analyses conducted on all four coals (cont'd).

<i>Rr%</i>	<i>Relative Frequency (%)</i>		<i>Relative Frequency (%)</i>		<i>Relative Frequency (%)</i>		<i>Relative Frequency (%)</i>	
1.2	Inertinite	10.40	Inertinite	6.40	Inertinite	5.20	Vitrinite	14.80
1.3		1.60		4.00		2.80	9.20	
1.4		6.40		8.00		2.00	17.60	
1.5		5.60		4.80		2.80	Inertinite	6.40
1.6		5.60		5.60		1.20		2.40
1.7		5.20		5.20		1.40		3.20
1.8		4.00		6.80		1.20		2.00
1.9		4.00		3.60		0.40		2.40
2.0		1.60		2.40		0.80		2.00
2.1		3.60		0.40		1.20		1.20
2.2		0.80		1.60		0.40		0.40
2.3		0.40		0.80				1.20
2.4				0.40		0.80		
2.5						0.40		1.20
2.6				0.40		0.80		0.40
2.7						0.80		
2.8						0.40		
2.9		0.80				0.40		0.40
3.0						0.40		0.80
3.1		0.40						
3.2						0.40		
3.3								
3.4								0.40
3.5		0.40						0.40
3.6				0.80				
3.7				0.40				
TOTAL		100.00		100.00		100.00		100.00

A.4 Porosity calculations

According to Gregg and Sing (1982), porosity is defined as the ratio of the volume of open pores to the total volume of the solid (Hattingh, 2009). The incremental volume adsorbent (either CO₂ or N₂) adsorbed for each pore width has to be calculated in order to determine the volume of open pores, This is accomplished by the integral of the incremental adsorbed volume per pore diameter over the entire measured pore diameter range (Hattingh, 2009). From this the porosity can be subsequently calculated with the aid of Equation (A.1):

$$\varepsilon_0 = \rho_b \cdot \int \left(\frac{dV}{dD_{pore}} \right) dD_{pore} \quad \text{Equation (A.1)}$$

Appendix A: Conventional coal characterisation

The incremental adsorbed volume per pore diameter dV/dD_{pore} is determined from gas adsorption analyses (either CO₂ or N₂) and is given with respect to average pore diameter.



B

APPENDIX B

Coal Characterisation: Advanced analyses

B.1 ^{13}C NMR spectra obtained from CP-MAS DD analyses of all four coals

An overview of the results obtained from ^{13}C NMR CP-MAS dipolar dephasing experiments is presented for all four coals respectively in Figures B.1-B.4. Spectra for the inertinite-rich coals (INY and UMZ) are provided in Figures B.1 and B.2, respectively, while the results for the vitrinite-rich coals (G#5 and TSH) are given in Figure B.3 and B.4.

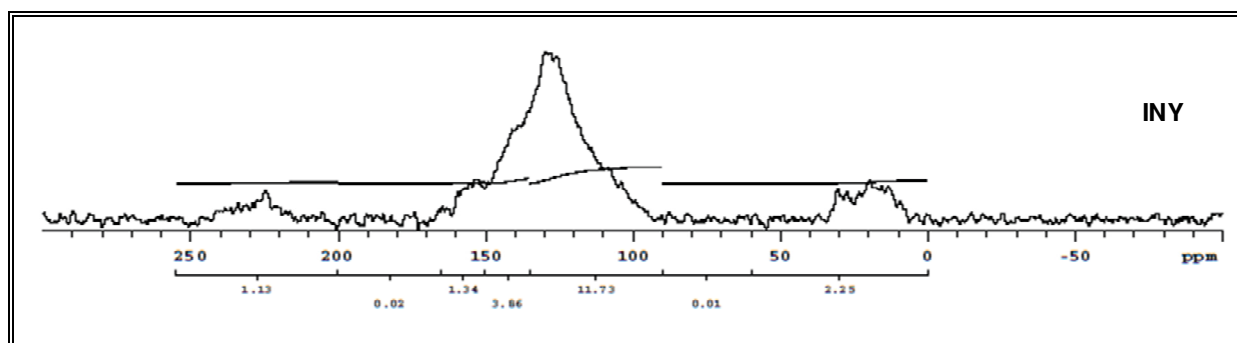


Figure B.1 CP-MAS DD spectra obtained for coal INY.

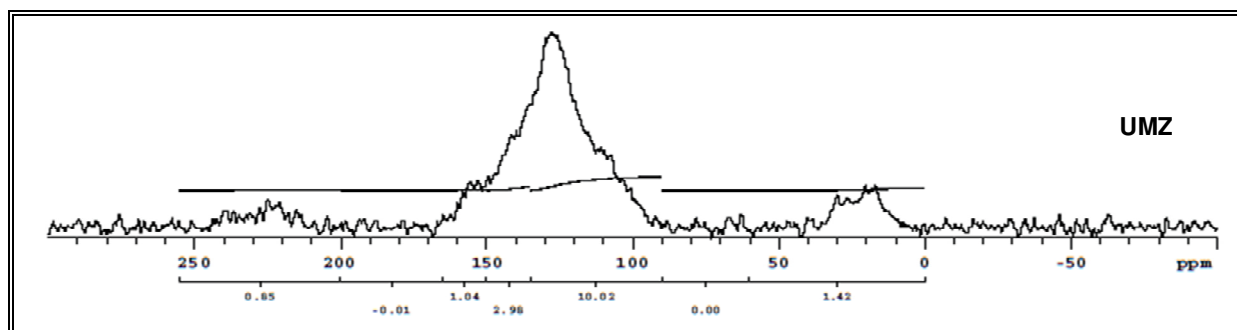


Figure B.2 CP-MAS DD spectra obtained for coal UMZ.

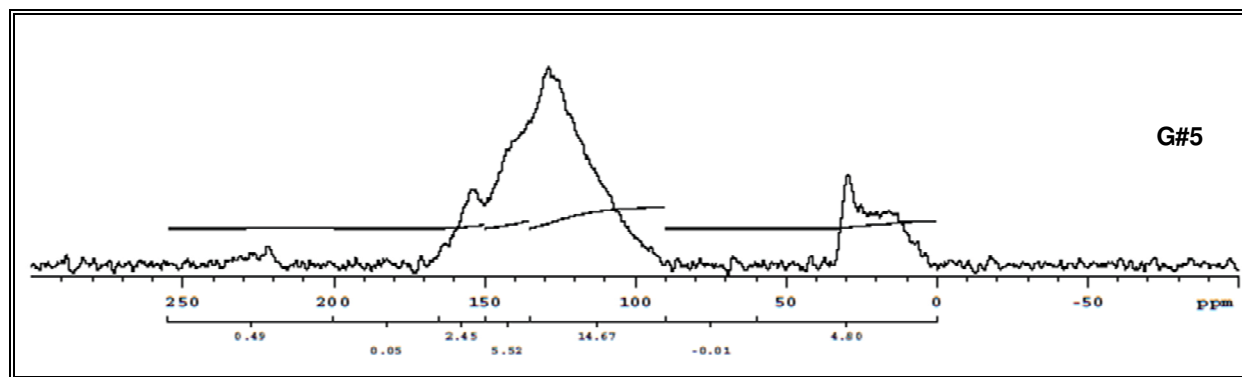


Figure B.3 CP-MAS DD spectra obtained for coal G#5.

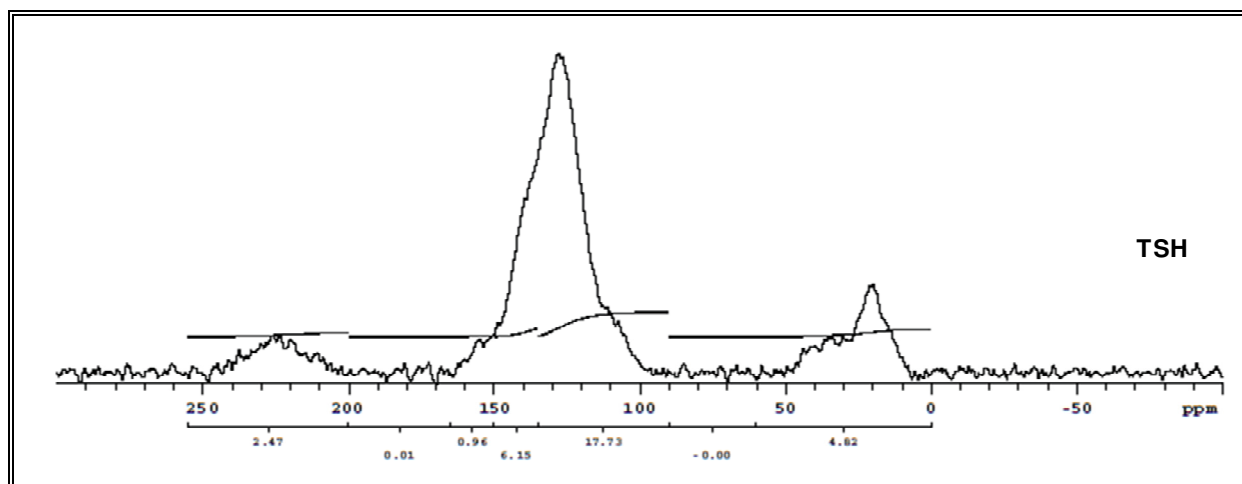


Figure B.4 CP-MAS DD spectra obtained for coal TSH.

B.2 XRD: Deconvolution results for amorphous carbon calculation

The amorphous fraction of carbon was determined according to the method outlined by Wu *et al.* (2008) and Wang *et al.* (2001). A descriptive account of the procedure has been provided for all the coals in Section 5.4.1.3. An overview of the deconvolution results obtained for all four coals is respectively given in Figures B.5 and B.6 (a-b.). Figure B.5 graphically depicts the results for the inertinite-rich coals (UMZ and INY), while for the vitrinite-rich coals the deconvolution procedure is illustrated graphically in Figure B.6. The results for coal G#5 have been included again in order to provide a comparison between the amorphous and crystalline components of the different coals.

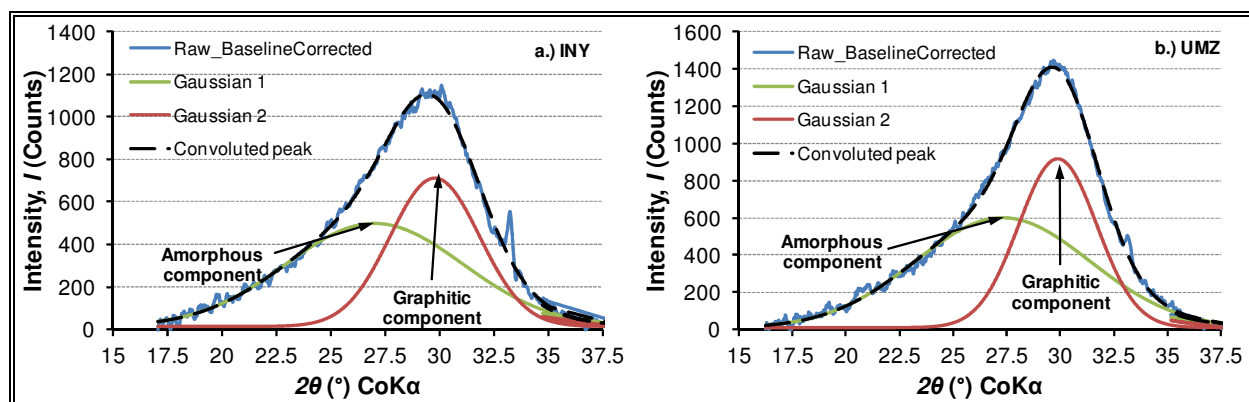


Figure B.5 Amorphous carbon deconvolution results for coal a.) INY and b.) UMZ.

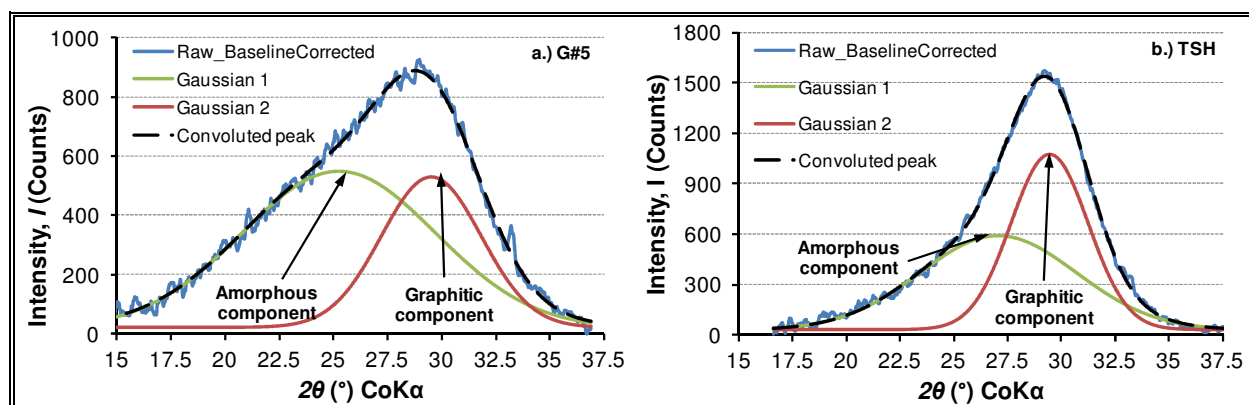


Figure B.6 Amorphous carbon deconvolution results for coal a.) G#5 and b.) TSH.

B.3 XRD: Deconvolution results for aromaticity calculation

The fraction of aromatic carbon was determined according to the method outlined by Lu *et al.* (2001). A descriptive account of the procedure has been provided for all the coals in Section 5.4.1.3. An overview of the deconvolution results obtained for all four coals is respectively given in Figures B.7 and B.8 (a-b.). Figure B.7 graphically depicts the results for the inertinite-rich coals (UMZ and INY), while for the vitrinite-rich coals the deconvolution procedure is illustrated graphically in Figure B.8. The results for coal G#5 have been included again in order to provide a comparison between the amorphous and crystalline components of the different coals.

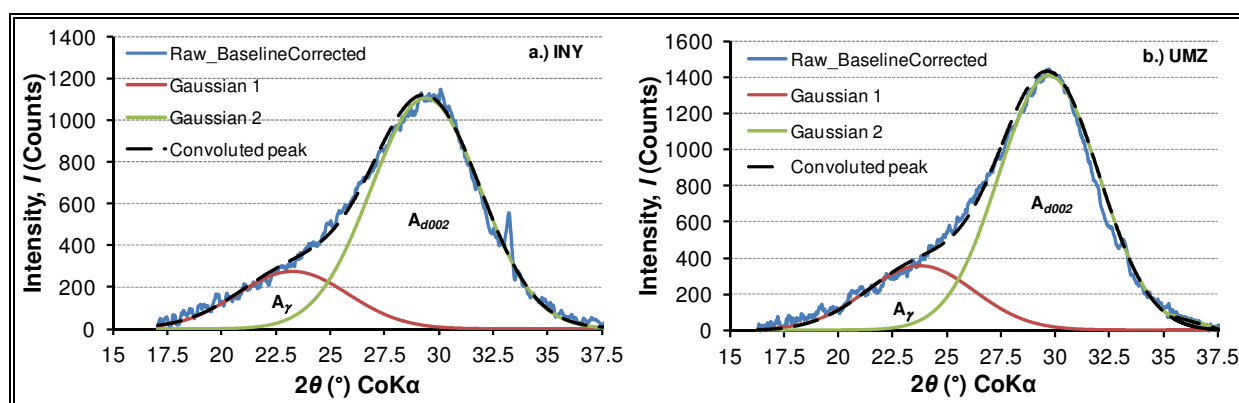


Figure B.7 Aromaticity deconvolution results for coal a.) INY and b.) UMZ.

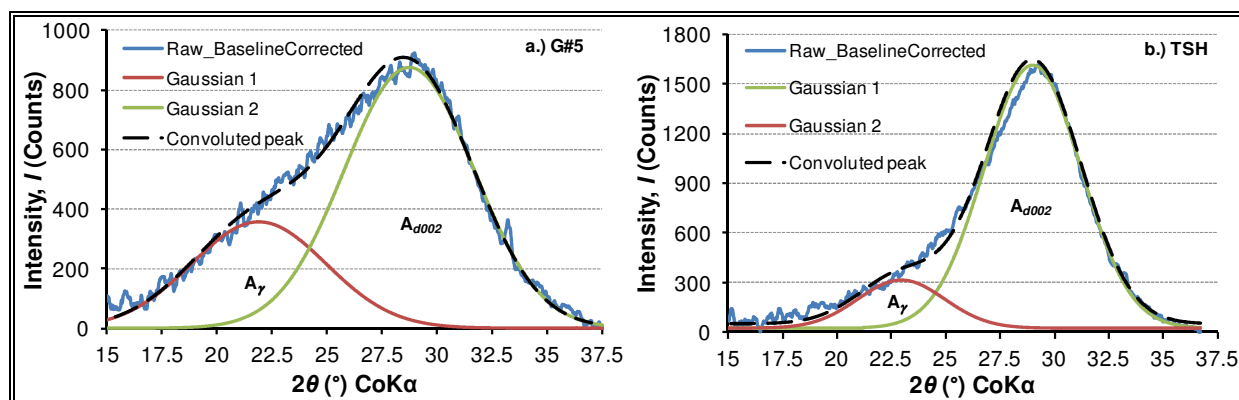


Figure B.8 Aromaticity deconvolution results for coal a.) G#5 and b.) TSH.

B.4 HRTEM processed images for coals UMZ, INY and G#5

Processed images are presented respectively in Figures B.9-B.11 for coals INY, UMZ and G#5.

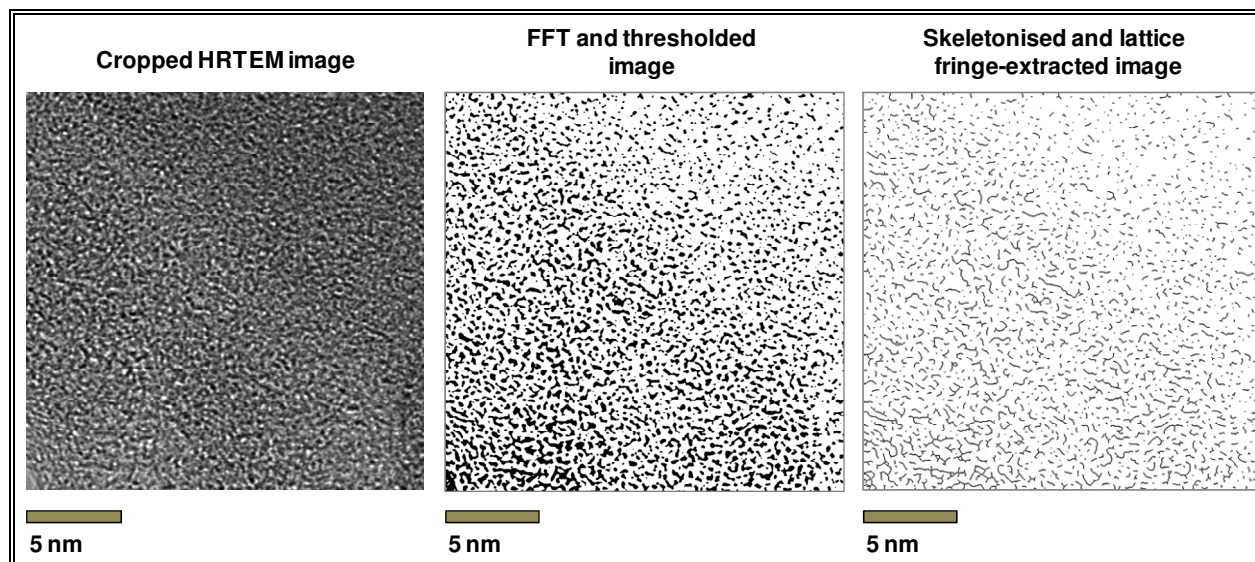


Figure B.9 Processed HRTEM images of coal INY (FFT threshold as well as skeletonised).

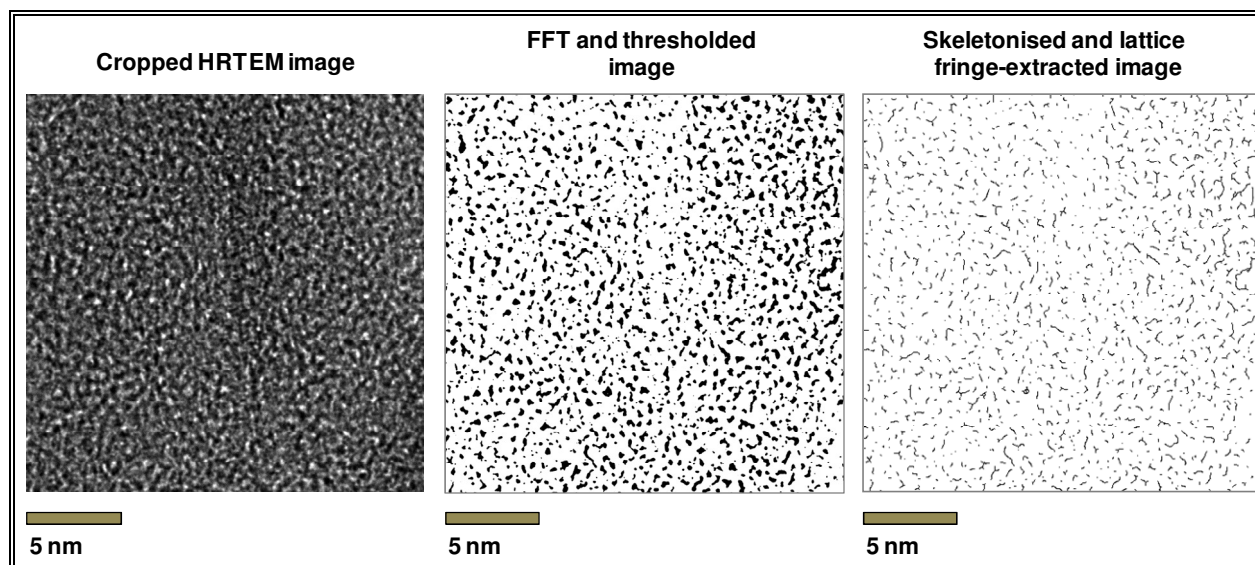


Figure B.10 Processed HRTEM images of coal UMZ (FFT threshold as well as skeletonised).

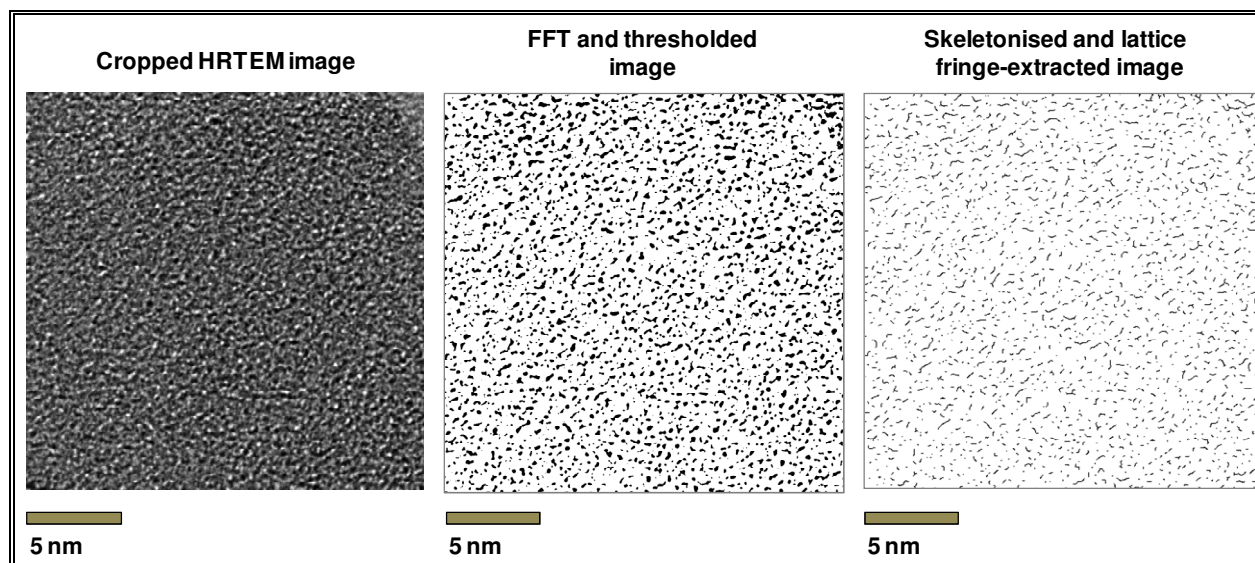


Figure B.11 Processed HRTEM images of coal G#5 (FFT threshold as well as skeletonised).

B.5 HRTEM size-range selected images for coals UMZ, INY and G#5

Fringes in selected length ranges were filtered from the original skeletonised images in order to highlight the subsequent length and orientation differences of fringes between the different coals. The range selected images are shown for coals INY, UMZ and G#5, respectively in Figures B.12-B.14. Fringes were categorized in a small, intermediate and large length range.

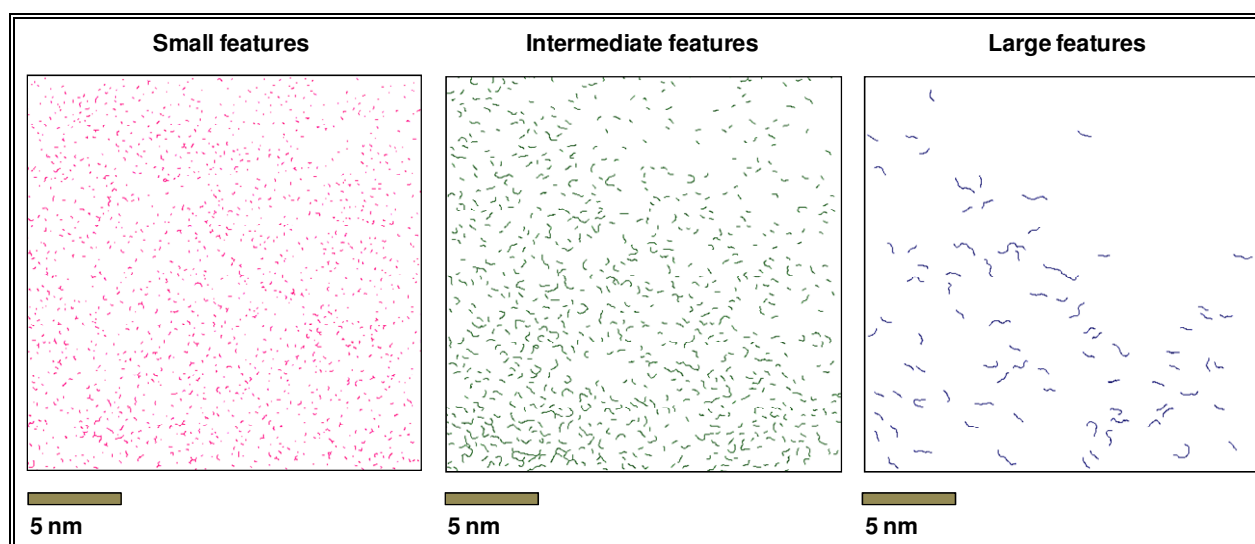


Figure B.12 Size range selected, skeletonised images of coal INY.

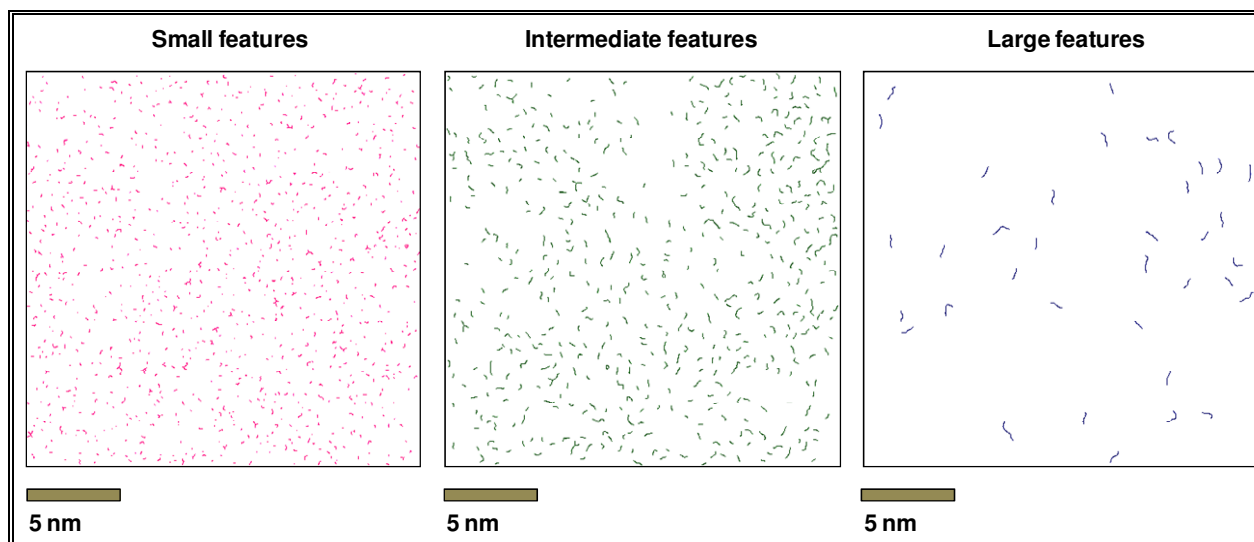


Figure B.13 Size range selected, skeletonised images of coal UMZ.

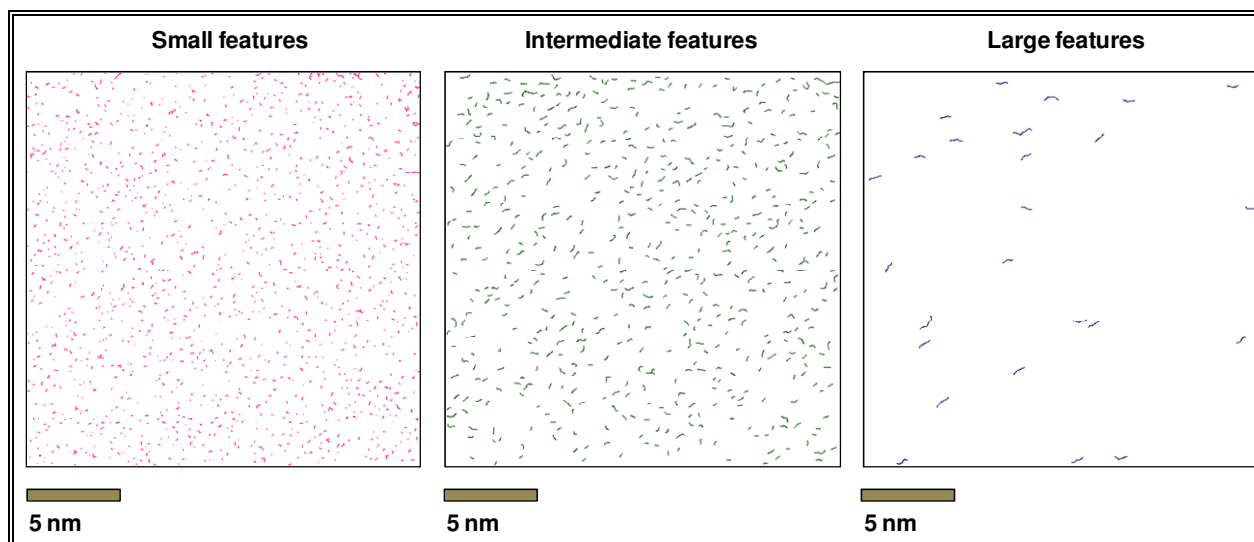


Figure B.14 Size range selected, skeletonised images of coal G#5.



C

APPENDIX C Product yield and -quality assessment

C.1 Influence of particle size on the yields of product obtained at 750 °C

A comparison between product yields observed at 750 °C for the two different particle size experiments (5 mm and 20 mm) is given in Table C.1, while a detailed discussion of the effect of particle size on product yield can be found in Section 6.5.2.3.

Table C.1 Effect of particle size on the product distribution during devolatilization at 750 °C.

Particle size	Products	Unit	Inertinite-rich coals		Vitrinite-rich coals	
			UMZ	INY	TSH	G#5
5 mm	Tar ^a	Wt. %	4.1 ± 0.35	5.5 ± 0.14	5.6 ± 0.37	7.4 ± 0.26
	Gas ^{a,b}	Wt. %	15.8 ± 1.30	14.5 ± 0.01	11.7 ± 0.10	18.1 ± 1.03
	Char ^a	Wt. %	80.1 ± 0.86	80.1 ± 0.63	82.7 ± 1.94	74.5 ± 0.11
	Total	Wt. %	100	100	100	100
20 mm	Tar ^a	Wt. %	4.0 ± 0.10	4.4 ± 0.44	5.4 ± 0.19	8.5 ± 0.67
	Gas ^{a,b}	Wt. %	16.6 ± 1.43	14.8 ± 0.20	12.7 ± 0.84	20.9 ± 1.58
	Char ^a	Wt. %	79.4 ± 0.22	80.9 ± 0.92	81.9 ± 1.23	70.6 ± 0.53
	Total	Wt. %	100	100	100	100

^a Values reported on a water and loss free basis. ^b Values estimated from species detected by gas chromatography.

C.2 Gas species evolution curves for 5 mm particles as determined from MS

A comparison between the gas evolution profiles from the 5 mm experiments (as measured by MS) is presented for both temperatures in Figures C.1 and C.2, respectively. A detailed discussion of the effect of temperature and particle size on gas evolution behaviour has been attended to in Section 6.5.3.1.

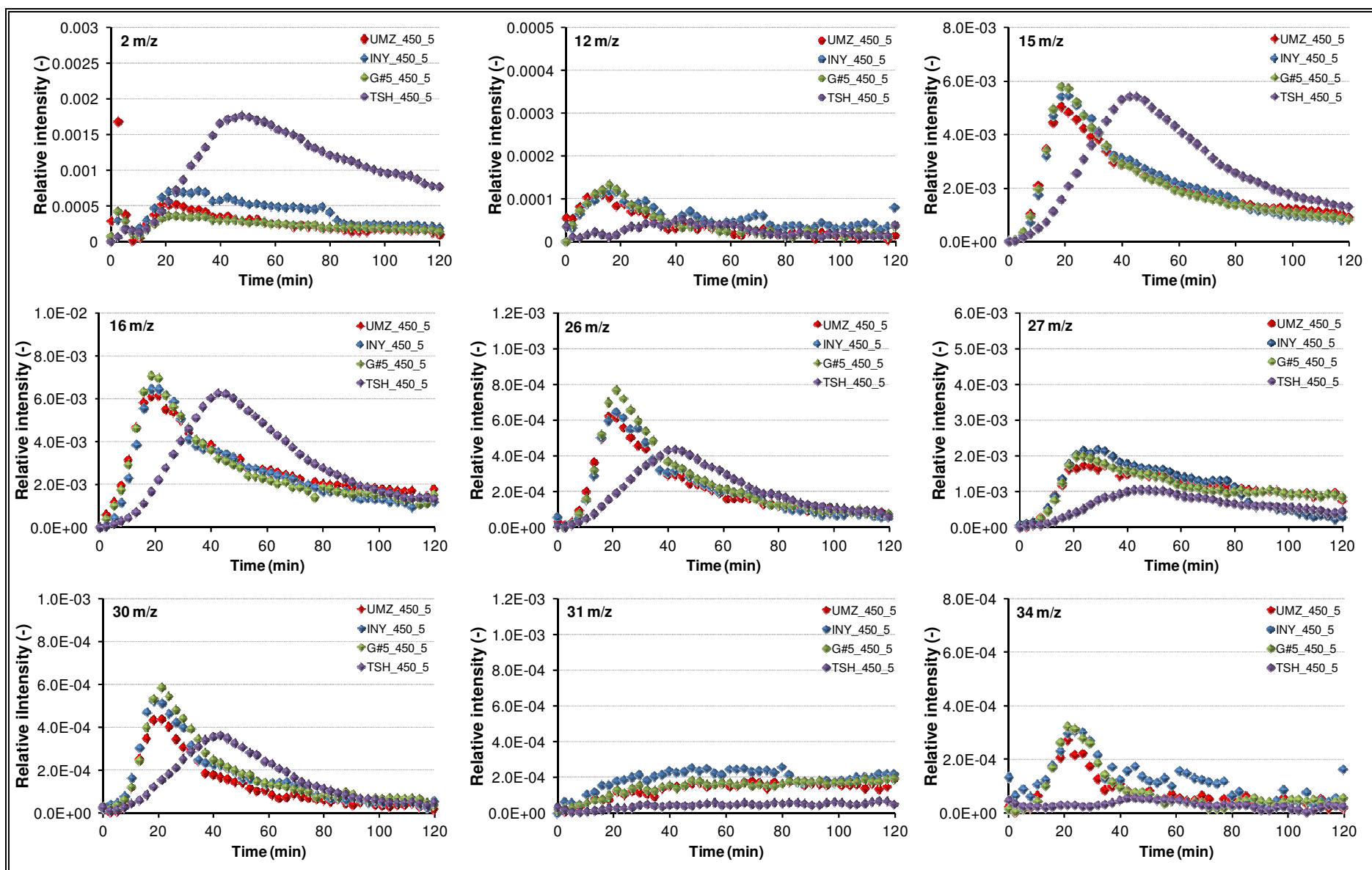


Figure C.1 Evolution curves of selected ion species obtained from 5 mm particles at 450°C.

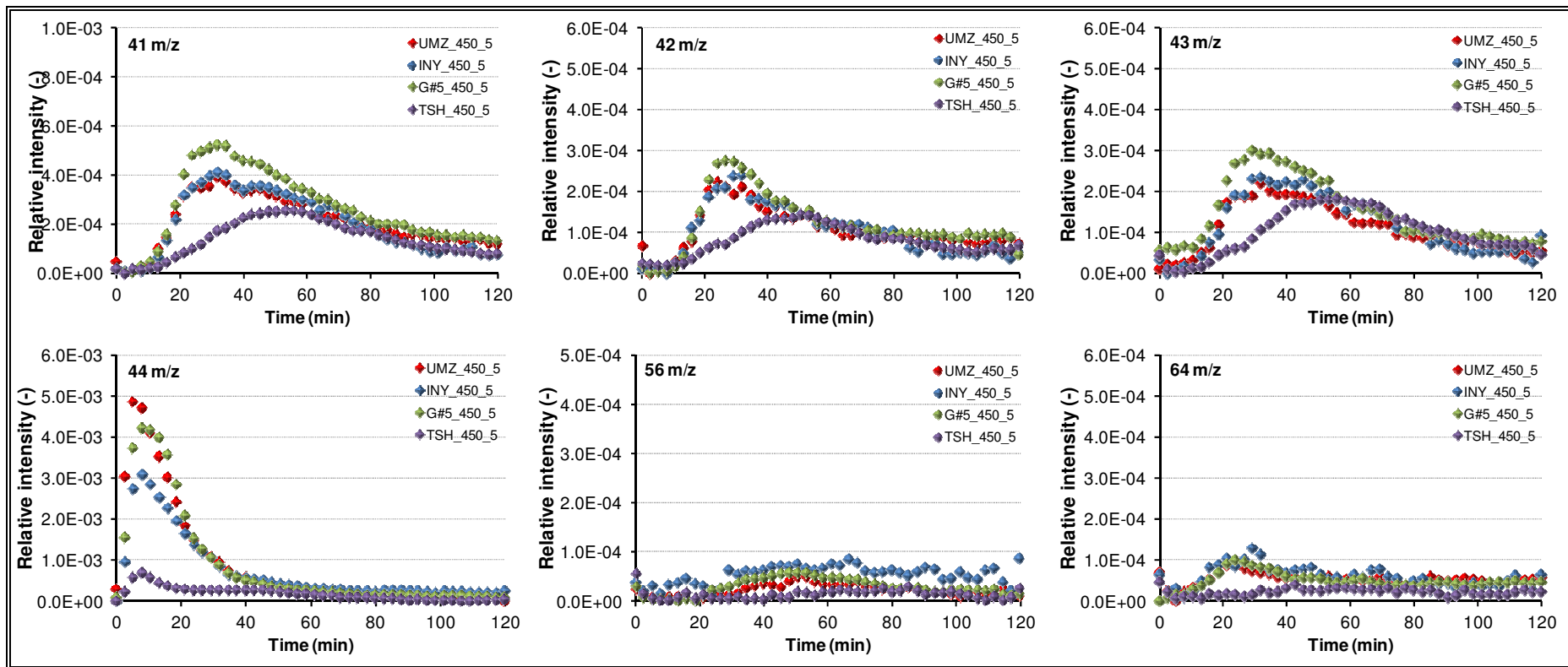


Figure C.1 Evolution curves of selected ion species obtained from 5 mm particles at 450 °C (continued).

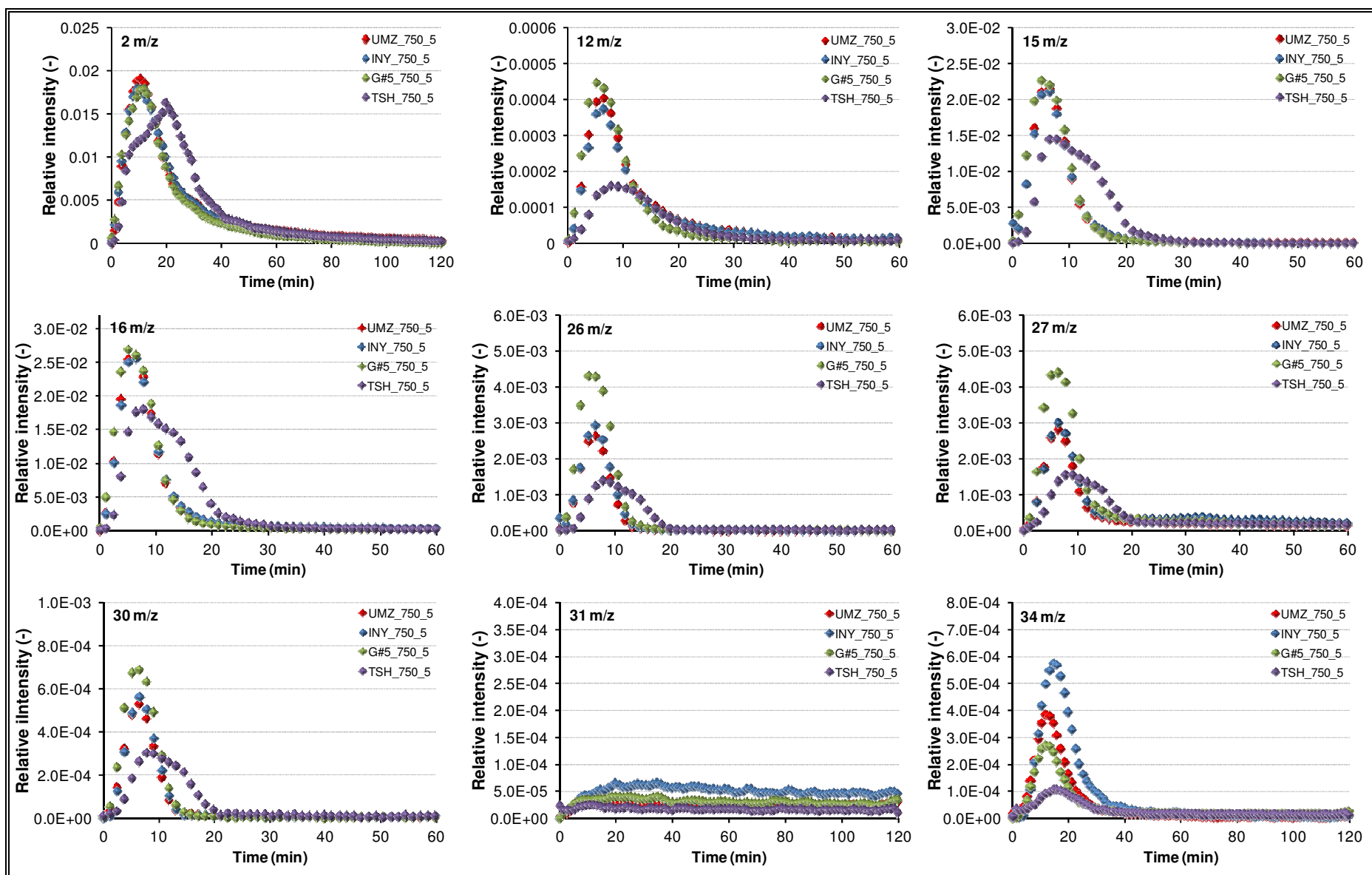


Figure C.2 Evolution curves of selected ion species obtained from 5 mm particles at 750°C.

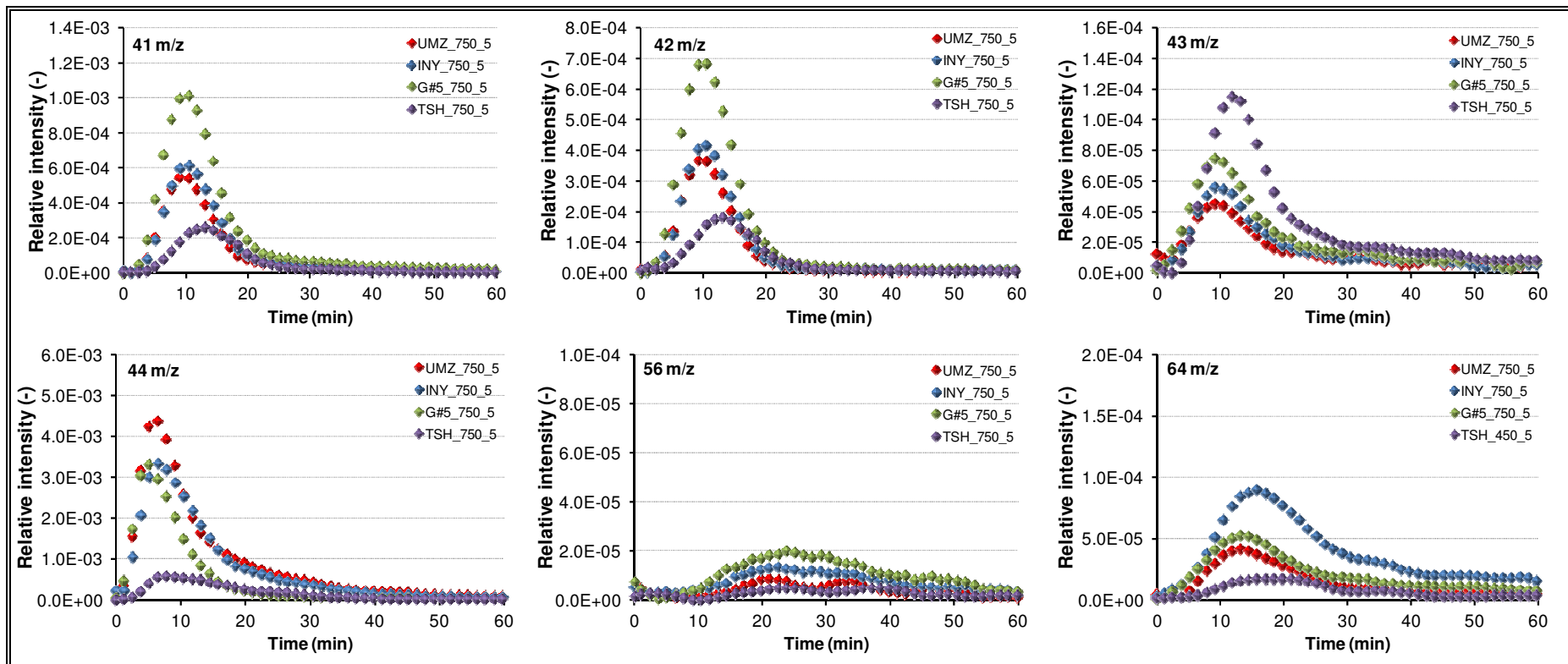


Figure C.2 Evolution curves of selected ion species obtained from 5 mm particles at 750 °C (continued).

C.3 Experimental reproducibility of gas evolution profiles determined by MS

Reproducibility measurements were conducted on all four coals during the qualitative evaluation of gaseous species evolution by mass spectrometry (MS). A comparison of the obtained reproducibility curves for the devolatilization of the 20 mm particles at 450°C is provided respectively in Figures C.3 to C.6 for coals UMZ, INY, G#5 and TSH. Only the evolution profiles of the following selected ions have been included for comparison: 2, 12, 15, 16, 26, 27, 31, 34, 36, 41, 42, 43, 44, 56 and 64 m/z. The selection of these ions have been based on observations made during previous investigations on devolatilization of coals and biomasses (Arenillas *et al.*, 1999; Tihay & Gillard, 2010) and representative molecular formulas for each mass can be found in Table 6.10 (Chapter 6). Gas evolution profiles for the 750°C and 5 mm experiments have not been included but showed similar levels of reproducibility.

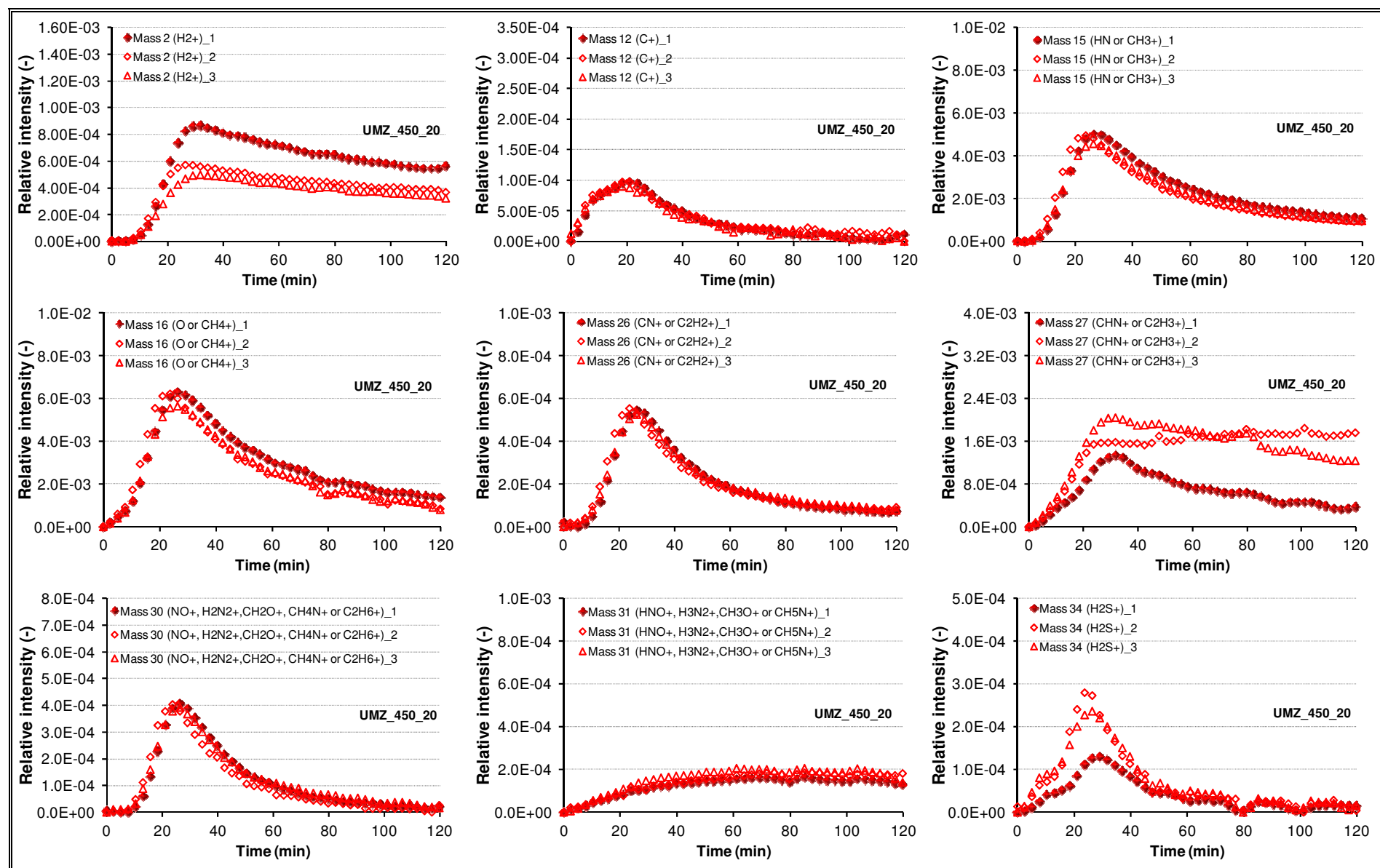


Figure C.3 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm UMZ coal at 450°C.

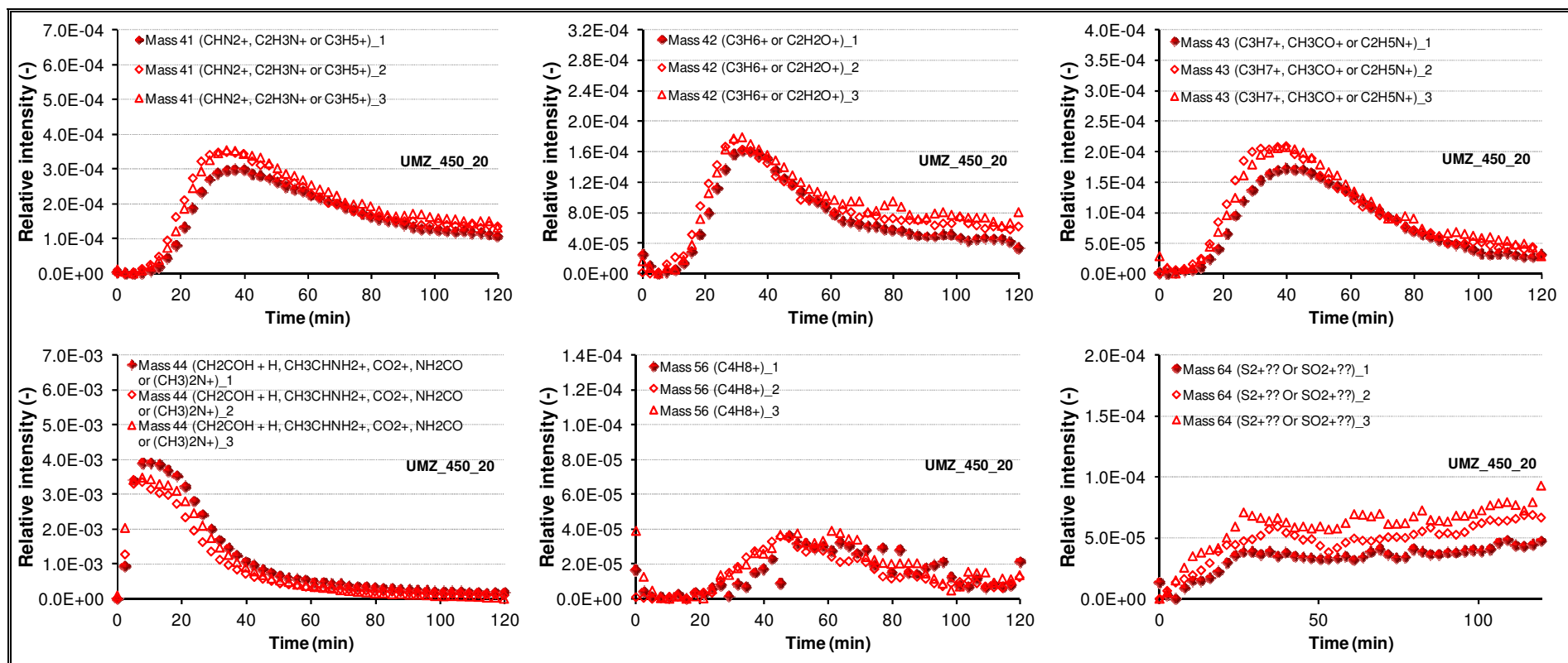


Figure C.3 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm UMZ coal at 450°C (continued).

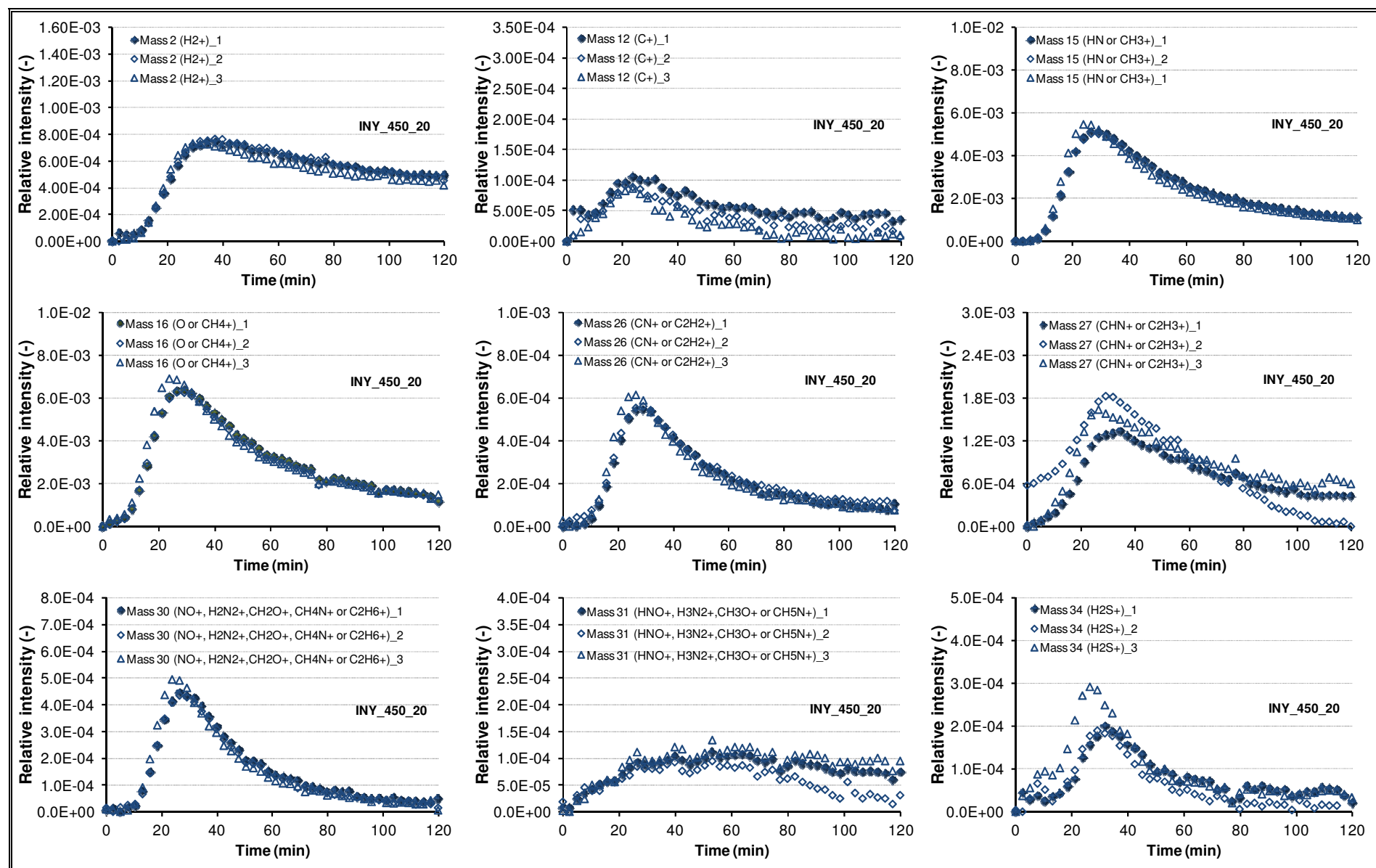


Figure C.4 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm INY coal at 450 °C.

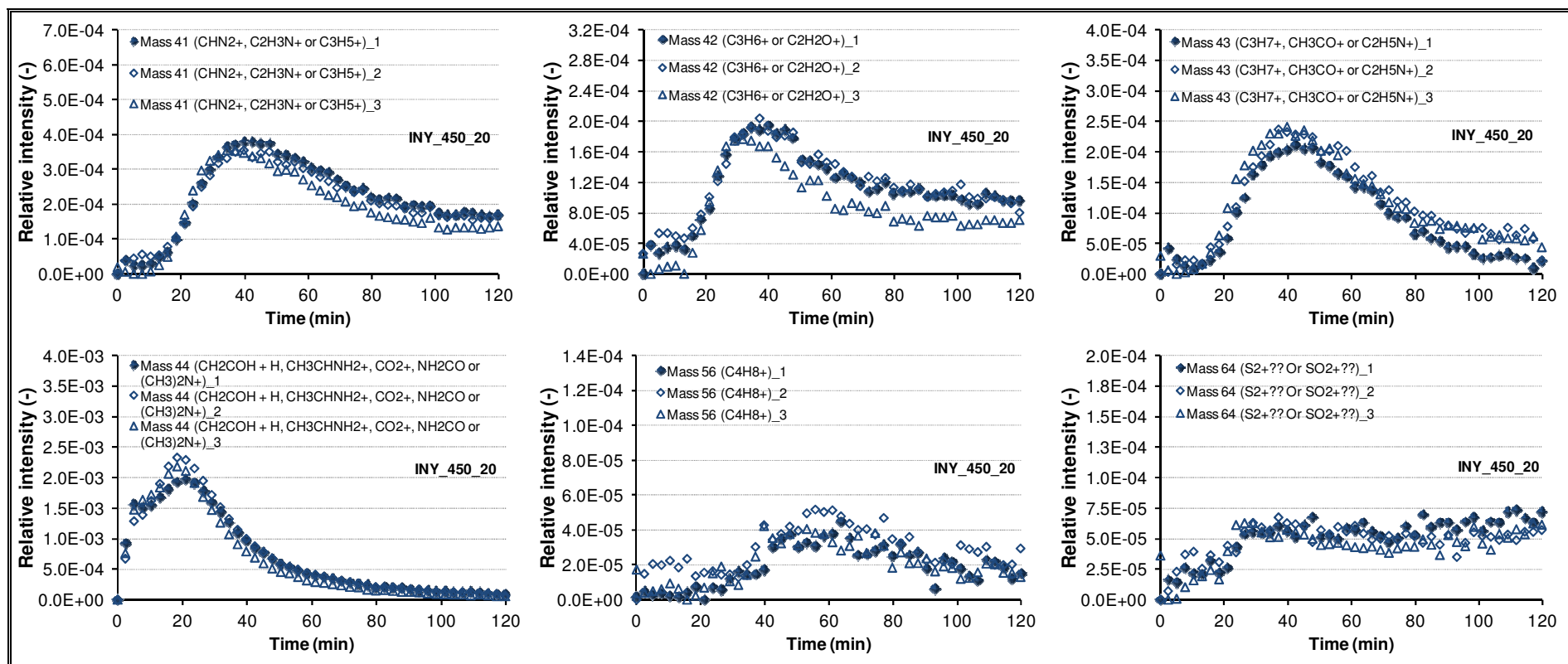


Figure C.4 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm INY coal at 450°C (continued).

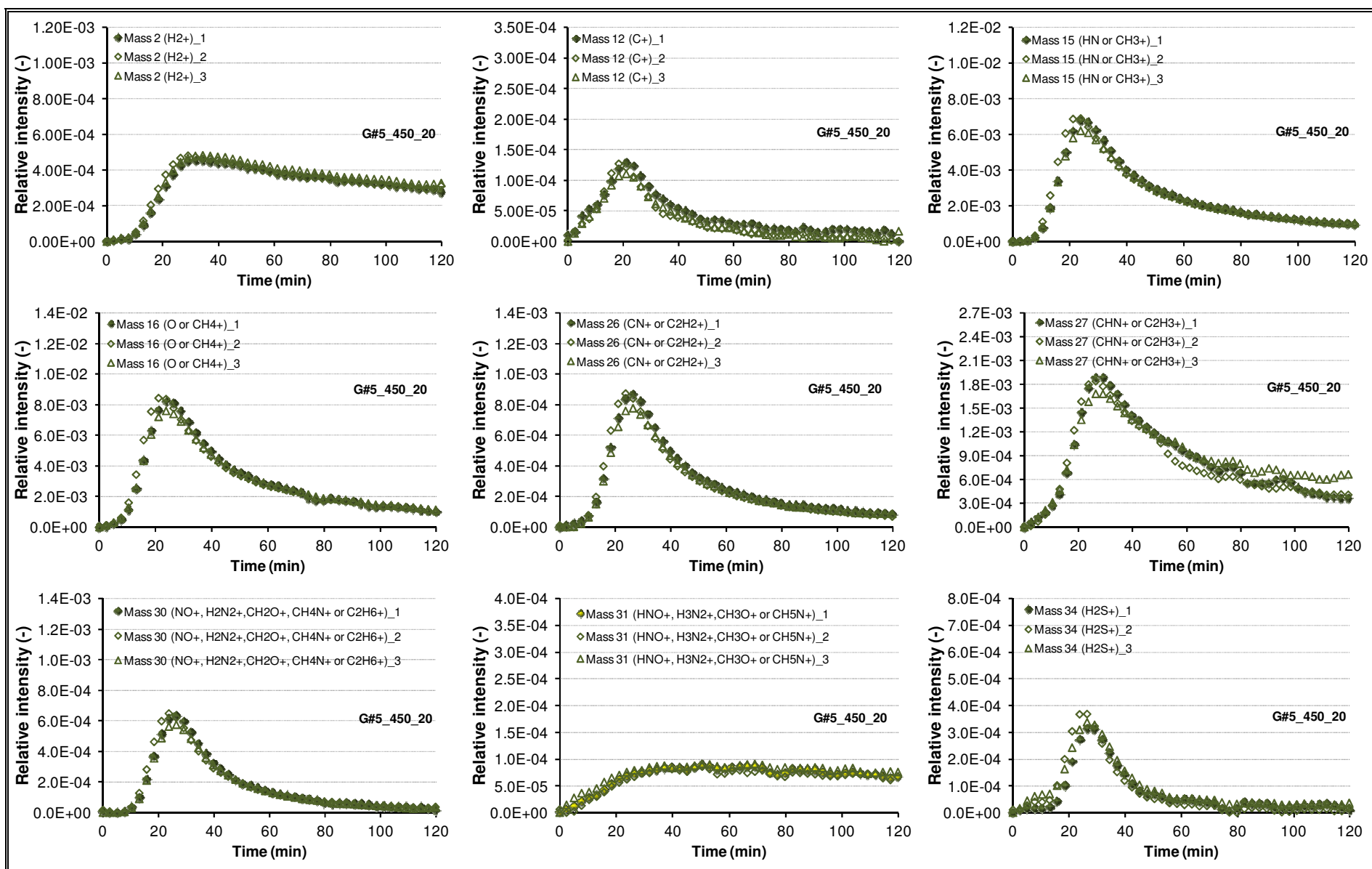


Figure C.5 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm G#5 coal at 450 °C.

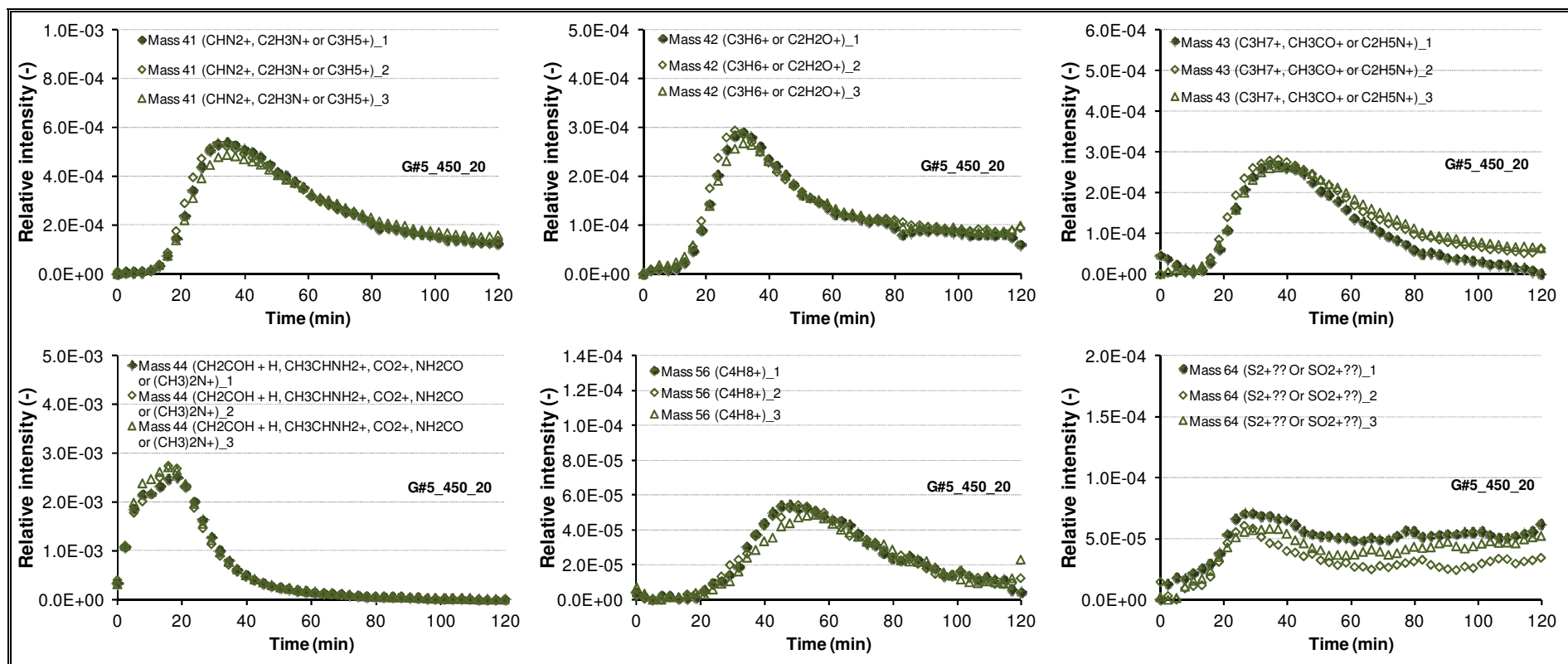


Figure C.5 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm G#5 coal at 450°C (continued).

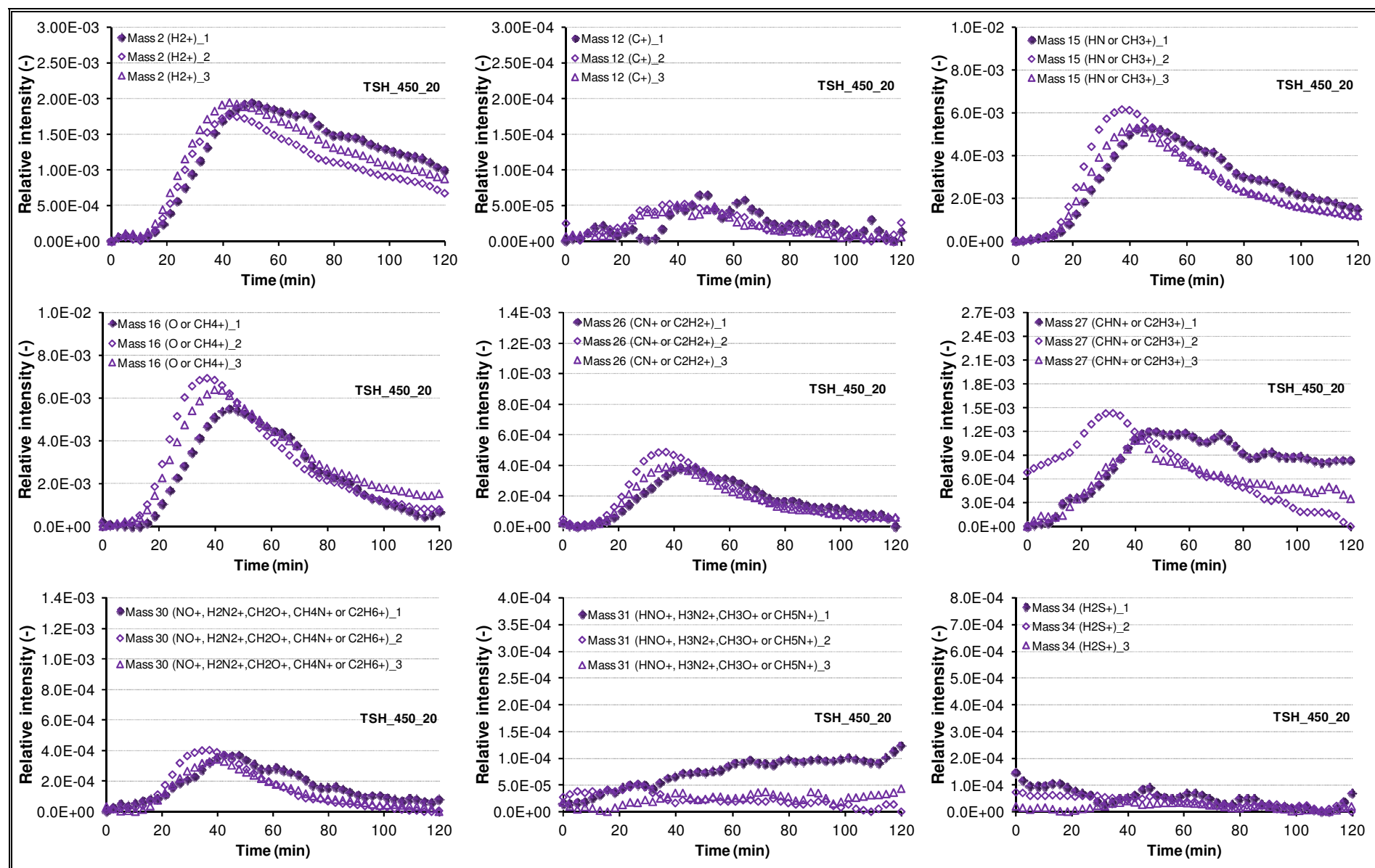


Figure C.6 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm TSH coal at 450°C.

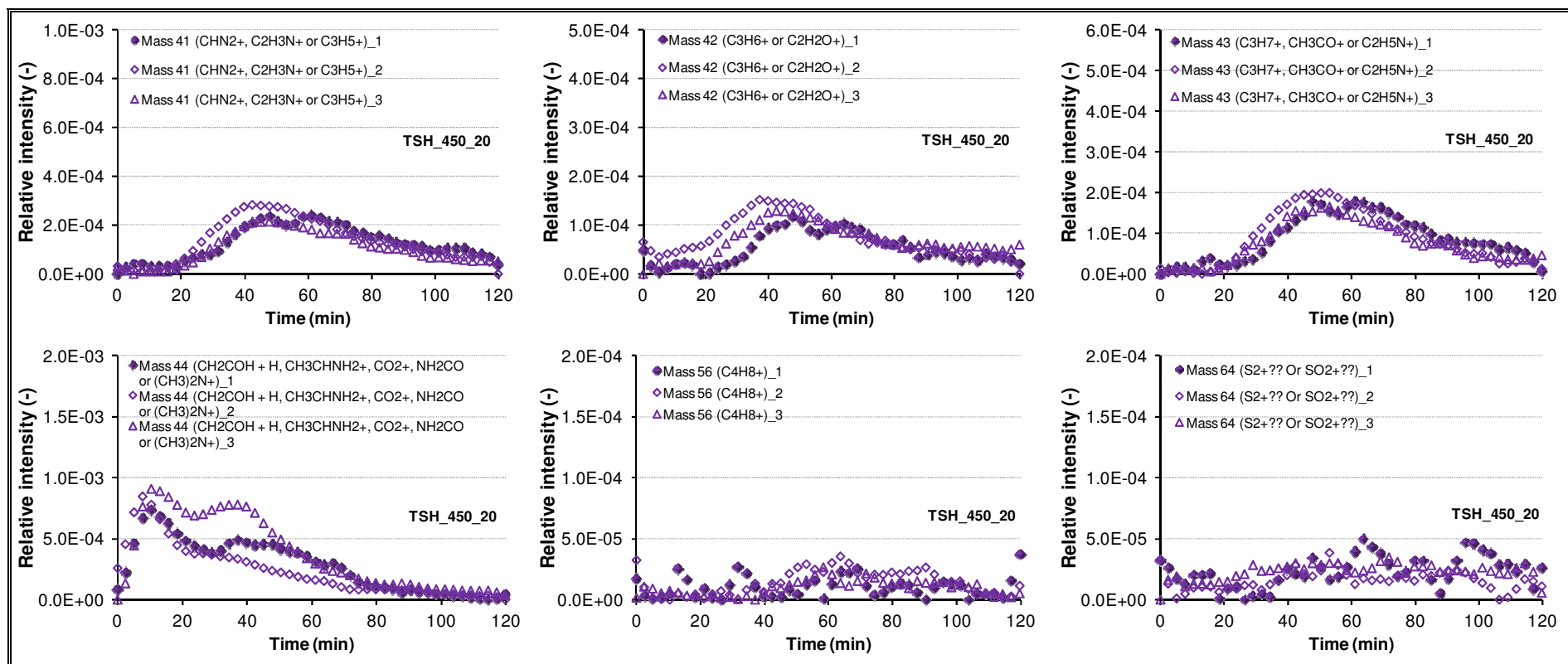


Figure C.6 Reproducibility curves for the different mass ions observed by MS during the devolatilization of 20 mm TSH coal at 450°C (continued).

C.4 Experimental reproducibility of gas evolution profiles determined by GC

Reproducibility measurements were also conducted on all four coals during the quantitative evaluation of gaseous species evolution by gas chromatography (GC). A comparison of the obtained reproducibility curves for the devolatilization of the 20 mm particles at 450°C is provided respectively in Figure C.7 to C.10 for coals UMZ, INY, G#5 and TSH. Gas evolution profiles for the 750°C and 5 mm experiments have not been included but showed similar levels of reproducibility.

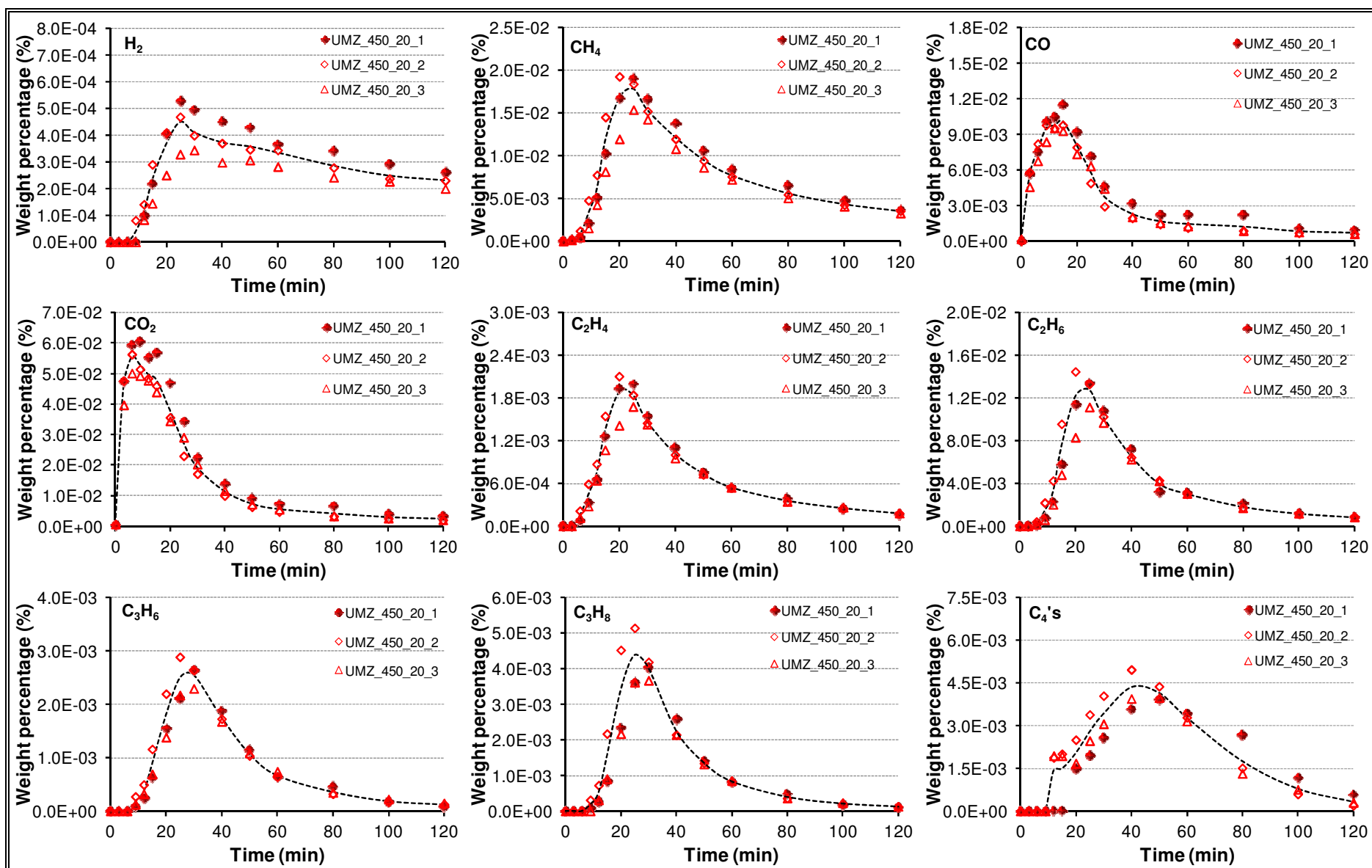


Figure C.7 Reproducibility curves for the different gas species observed by GC during the devolatilization of 20 mm UMZ coal at 450 °C.

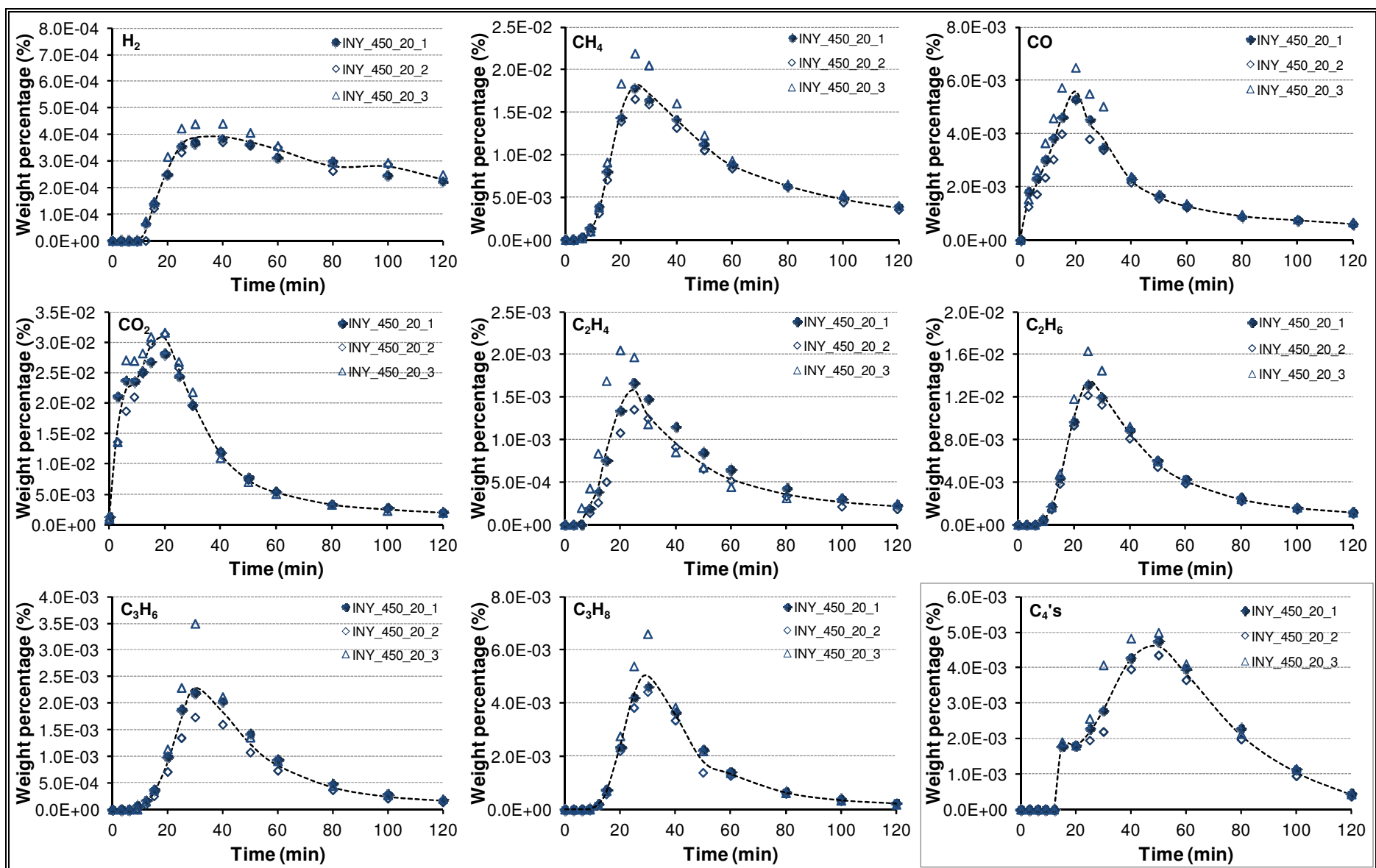


Figure C.8 Reproducibility curves for the different gas species observed by GC during the devolatilization of 20 mm INY coal at 450 °C.

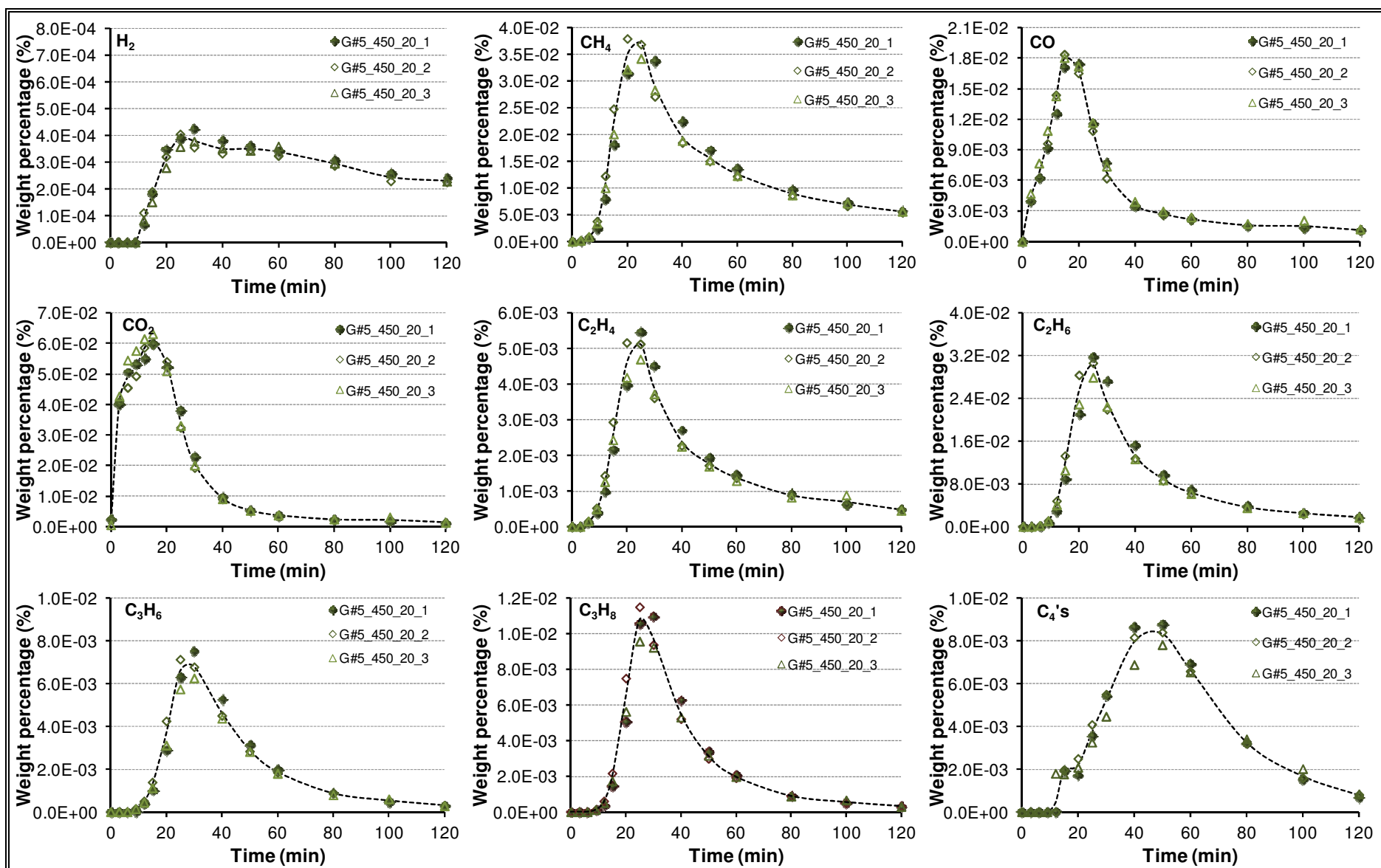


Figure C.9 Reproducibility curves for the different gas species observed by GC during the devolatilization of 20 mm G#5 coal at 450 °C.

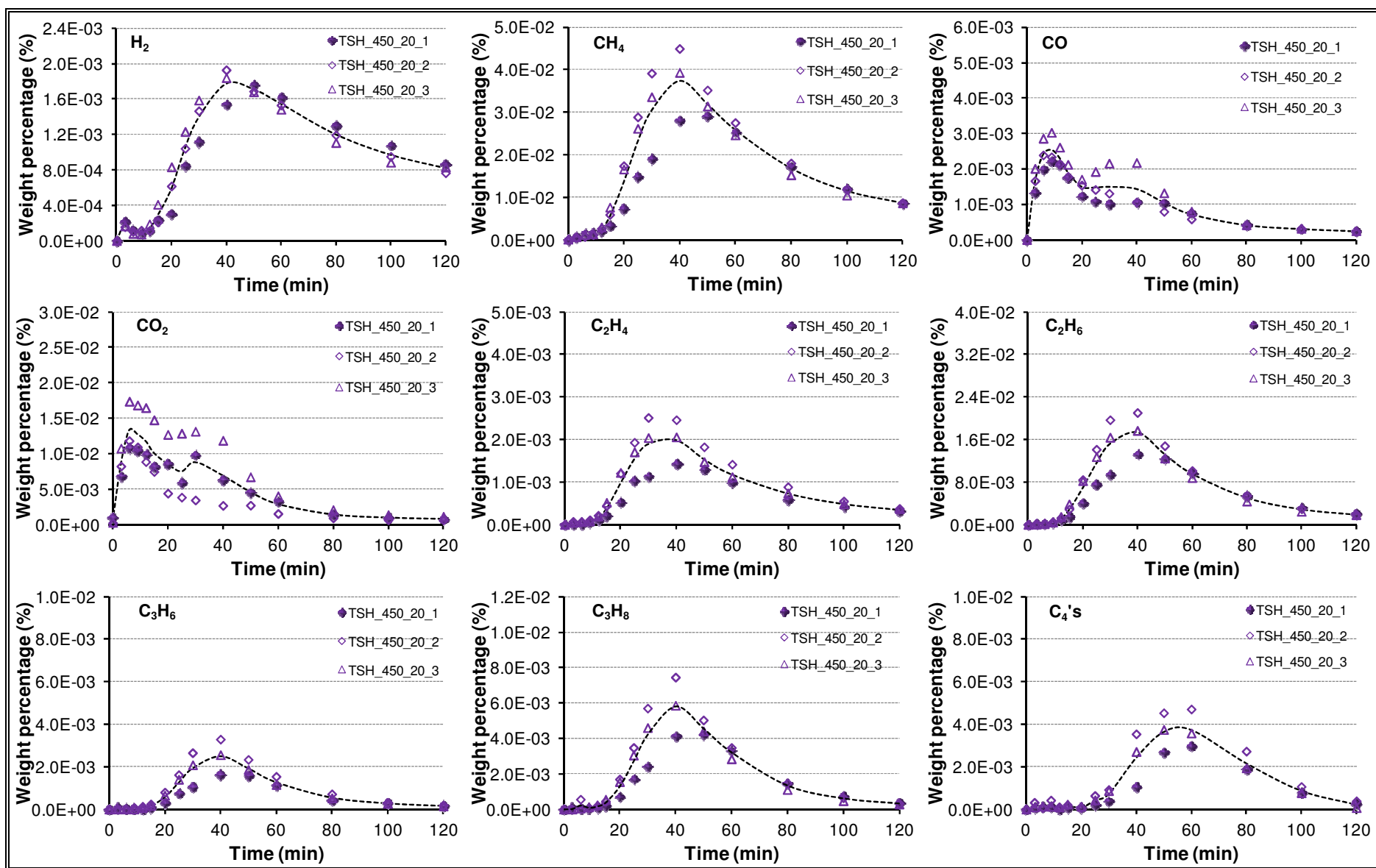


Figure C.10 Reproducibility curves for the different gas species observed by GC during the devolatilization of 20 mm TSH coal at 450 °C.

C.5 Comparison between gas evolution profiles of 5 mm and 20 mm particles

Comparative plots of gas evolution during the devolatilization of the different particle sizes are provided in Figures C.11 to C.13 for the 450°C measurements, while the results obtained from devolatilization at 750°C can be found in Figures C.14-C.16. A detailed discussion of the effect of particle size on gas species evolution has been attended to in Section 6.5.3.1.

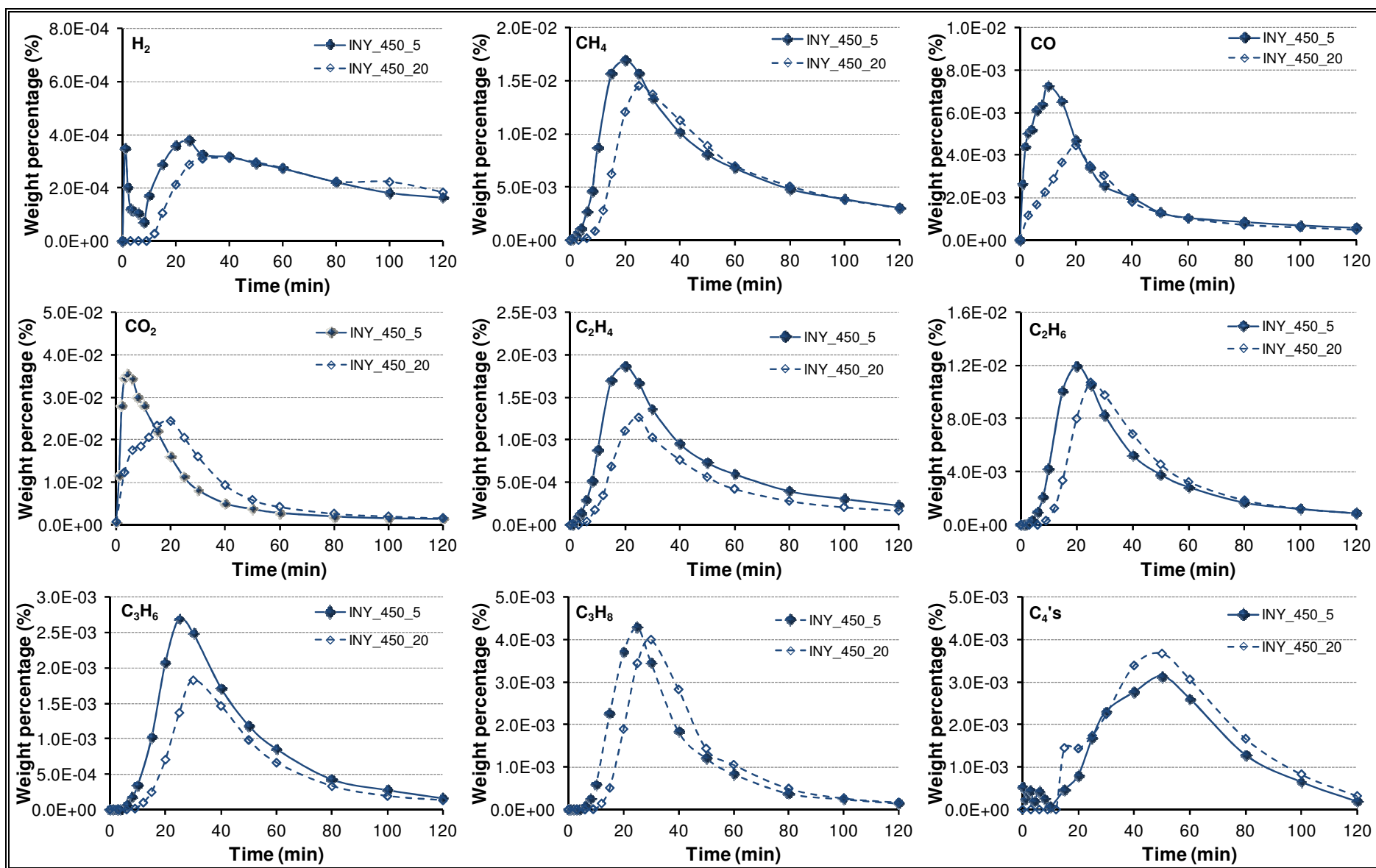


Figure C.11 Gas evolution profiles determined at 450°C for both particle sizes of coal INY.

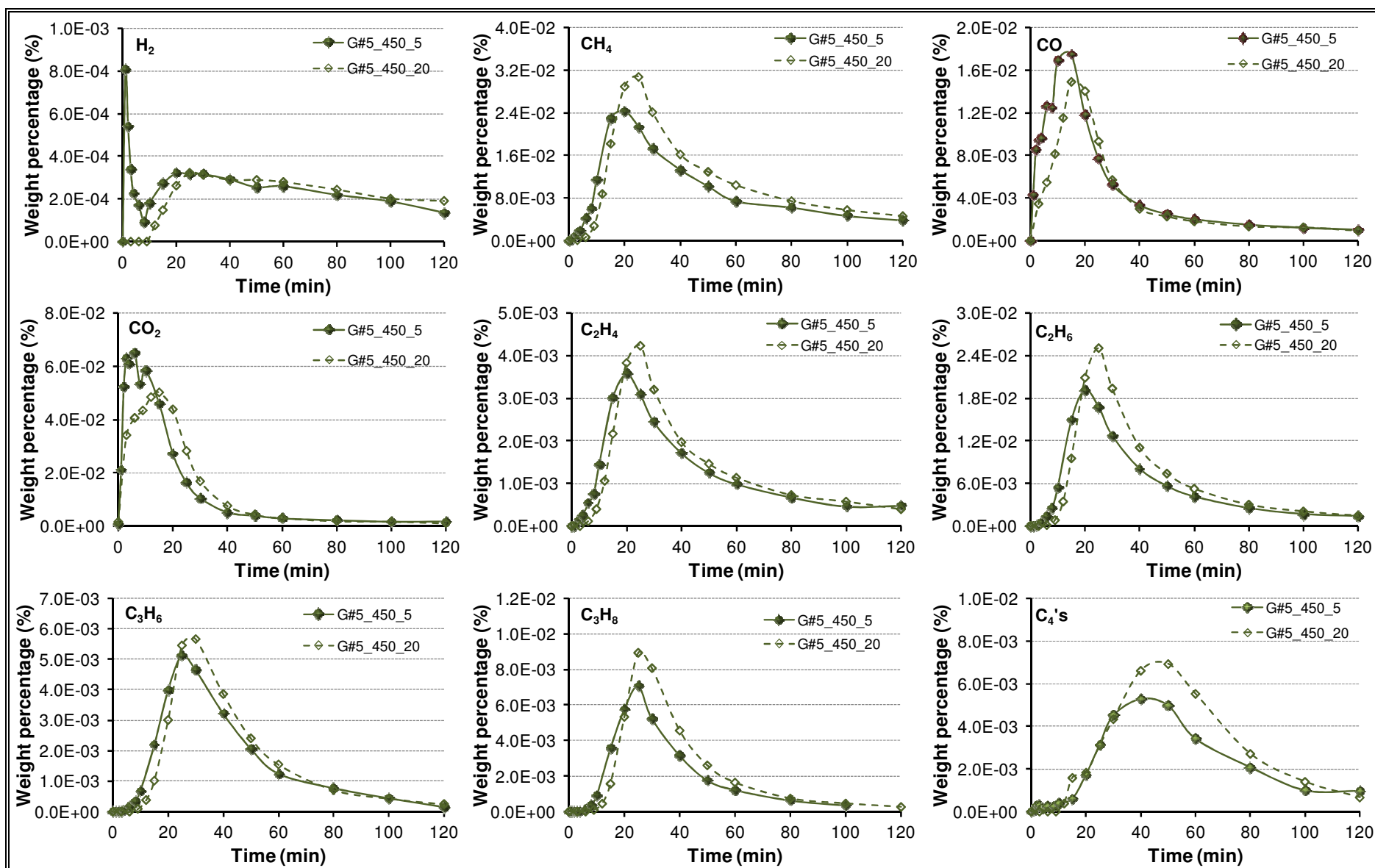


Figure C.12 Gas evolution profiles determined at 450°C for both particle sizes of coal G#5.

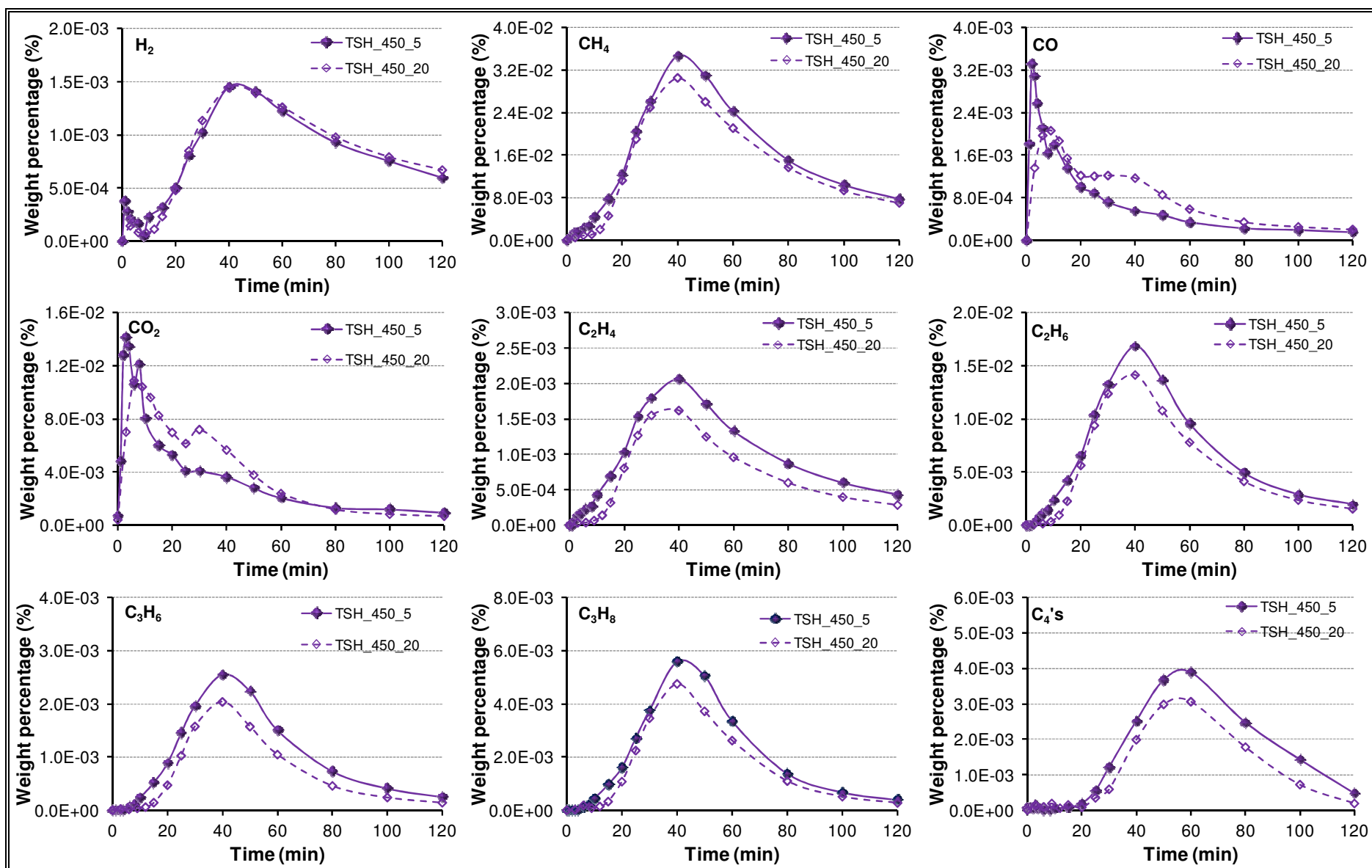


Figure C.13 Gas evolution profiles determined at 450°C for both particle sizes of coal TSH.

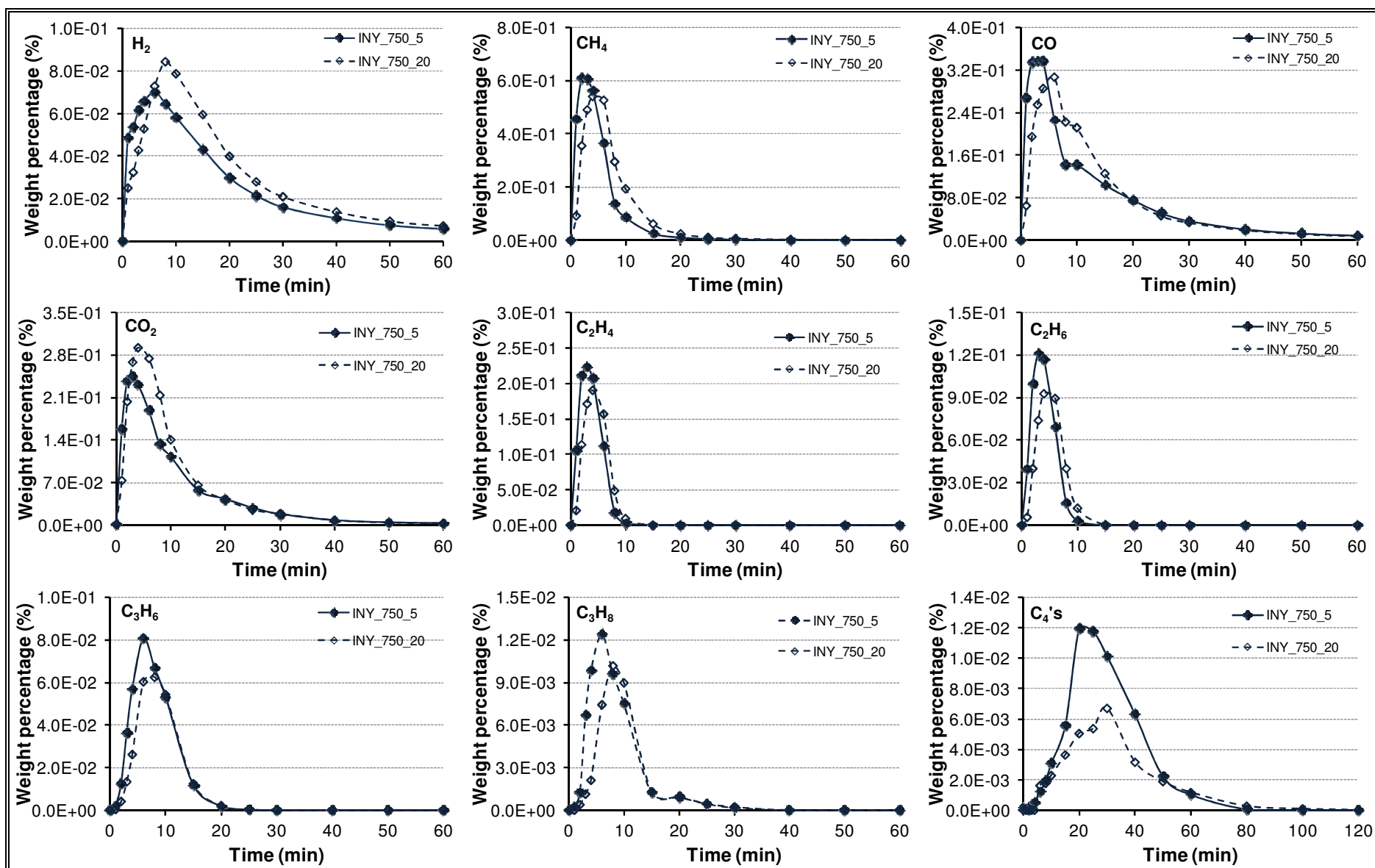


Figure C.14 Gas evolution profiles determined at 750°C for both particle sizes of coal INY.

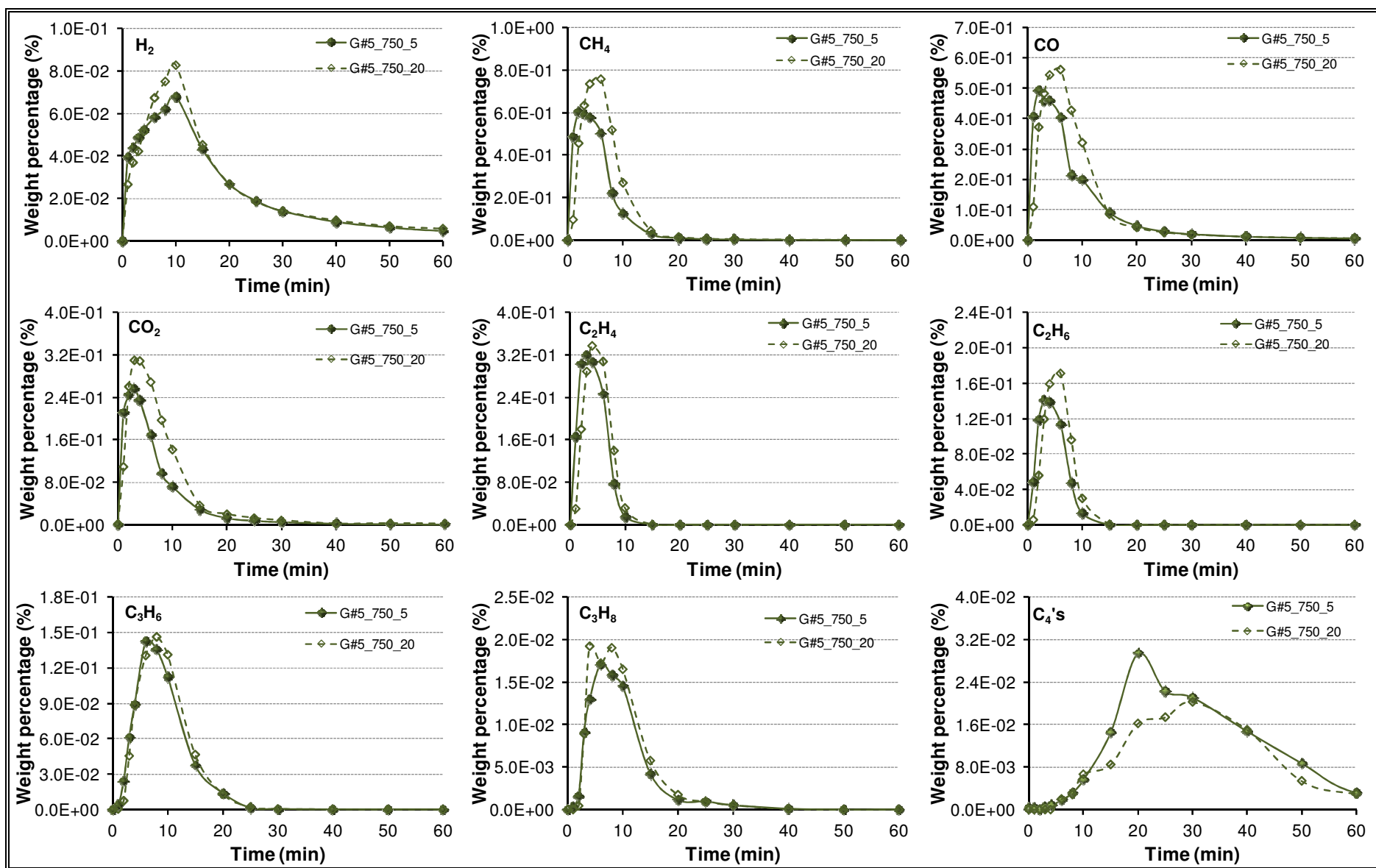


Figure C.15 Gas evolution profiles determined at 750°C for both particle sizes of coal G#5.

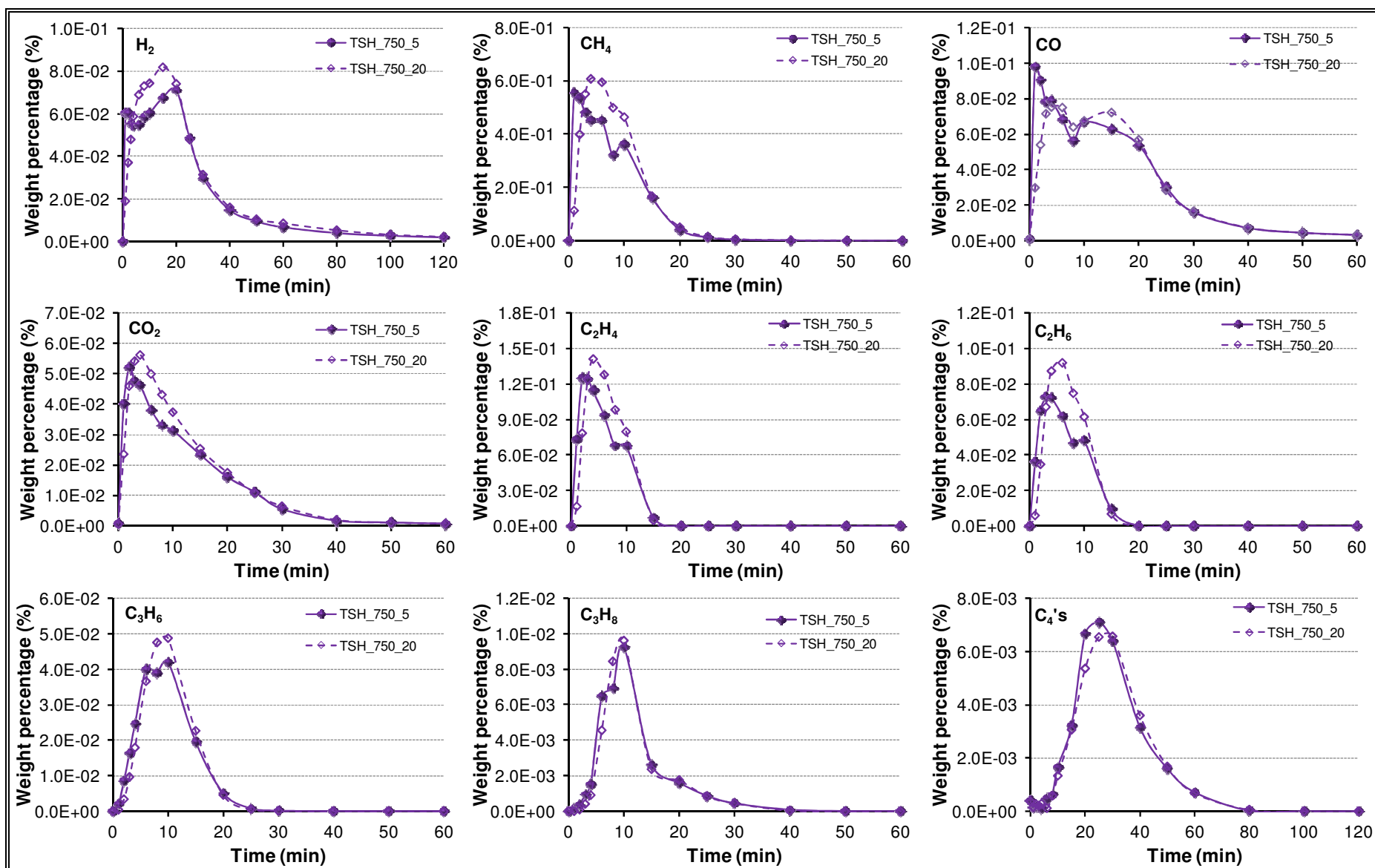


Figure C.16 Gas evolution profiles determined at 750°C for both particle sizes of coal TSH.

C.6 GC/MS and GC/FID results of tars generated from the different coals

This section encloses the results obtained from GC/MS and GC/FID performed on the tar samples generated from the different experimental conditions. Total ion chromatograms (TIC) of the different tar generated from the 5 mm particles can be found in Figures C.17 to C.20 (excluding the TICs of coals UMZ and G#5 which were presented in Section 6.5.3.2.), while the TICs of tars obtained from the 20 mm experiments are presented in Figures C.21 to C.28. Furthermore, a comparison between the relative abundance of detected species (in wt.%) observed in the different tar samples is provided in Tables C.2 and C.3 for the 5 and 20 mm experiments, respectively. A detailed discussion regarding the effect of coal type, temperature and particle size on the product distribution has been provided in Section 6.5.3.2 of Chapter 6.

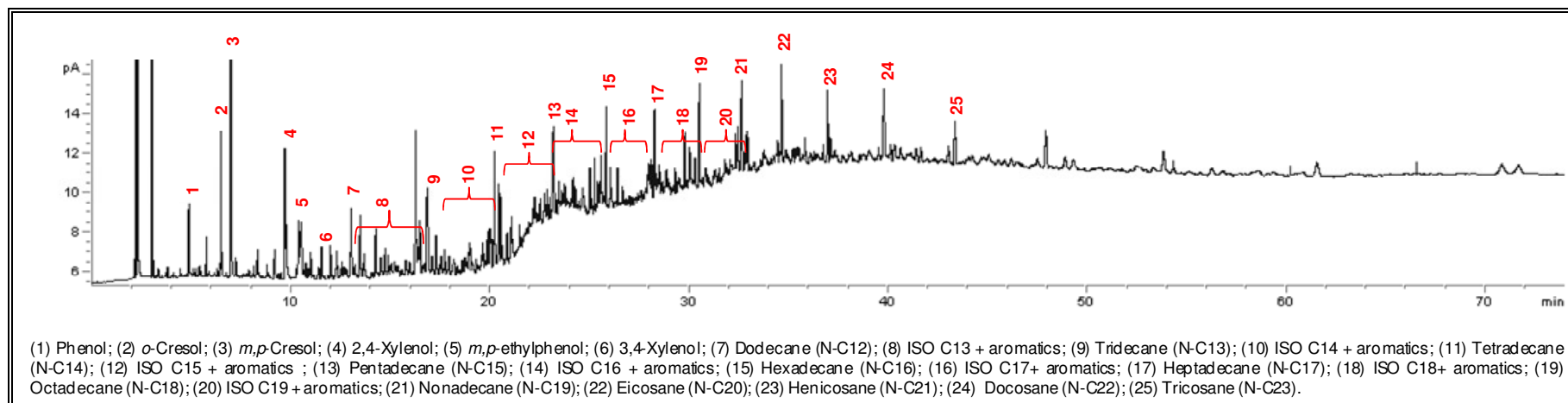


Figure C.17 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal INY at 450°C.

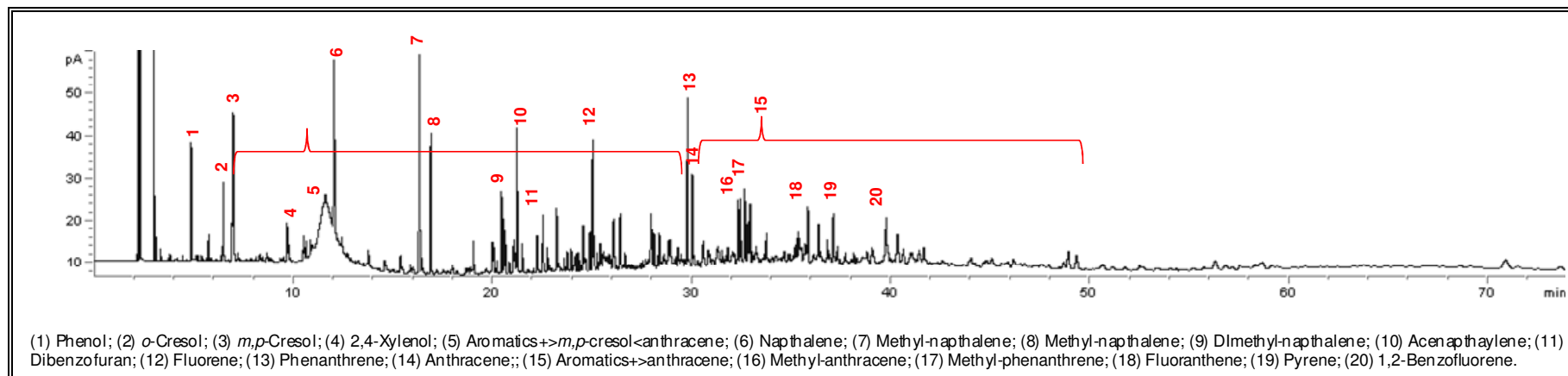


Figure C.18 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal INY at 750°C.

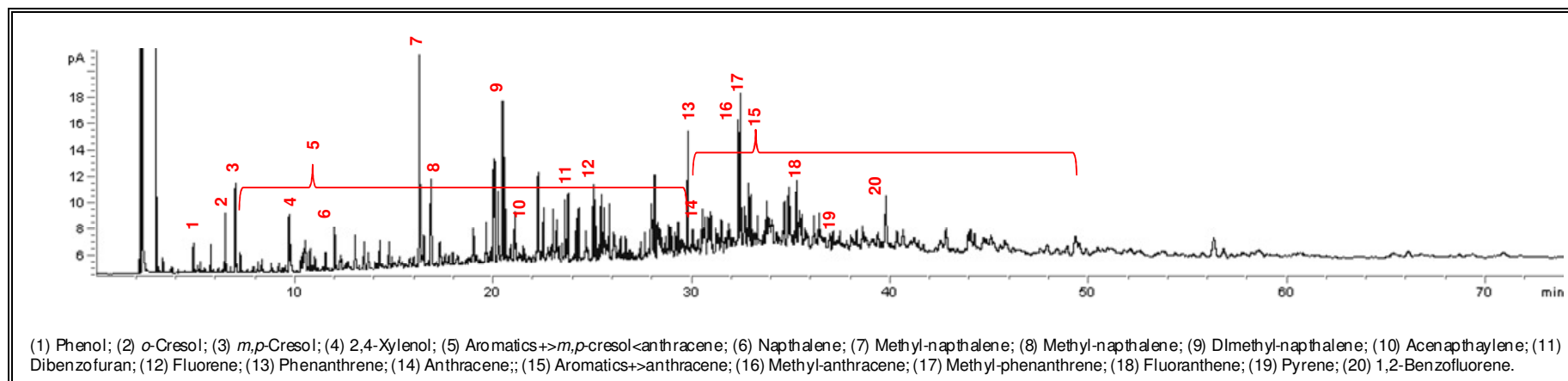


Figure C.19 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal TSH at 450 °C.

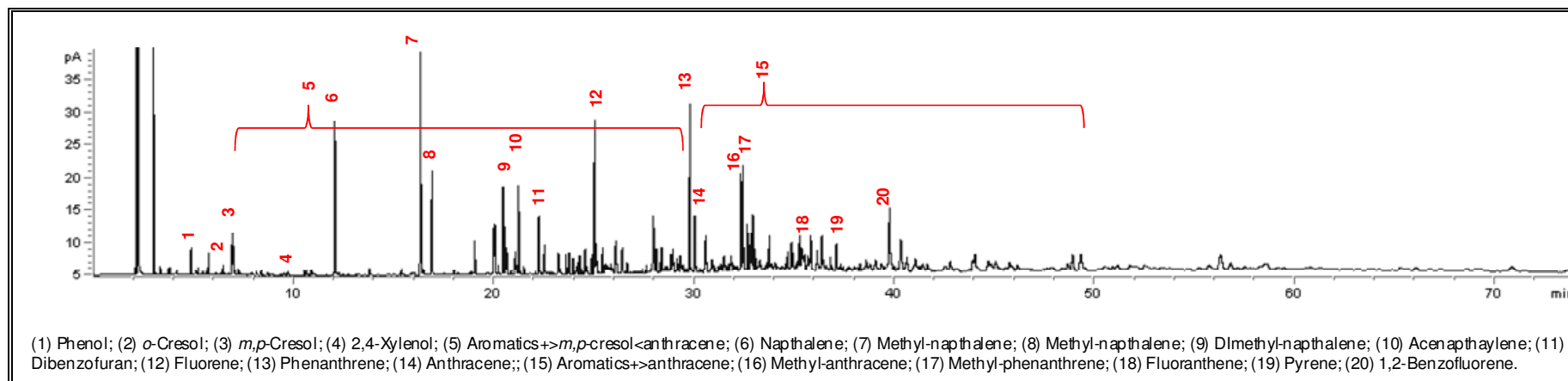


Figure C.20 Total ion chromatogram (TIC) of tar generated from 5 mm particles of coal TSH at 750 °C.

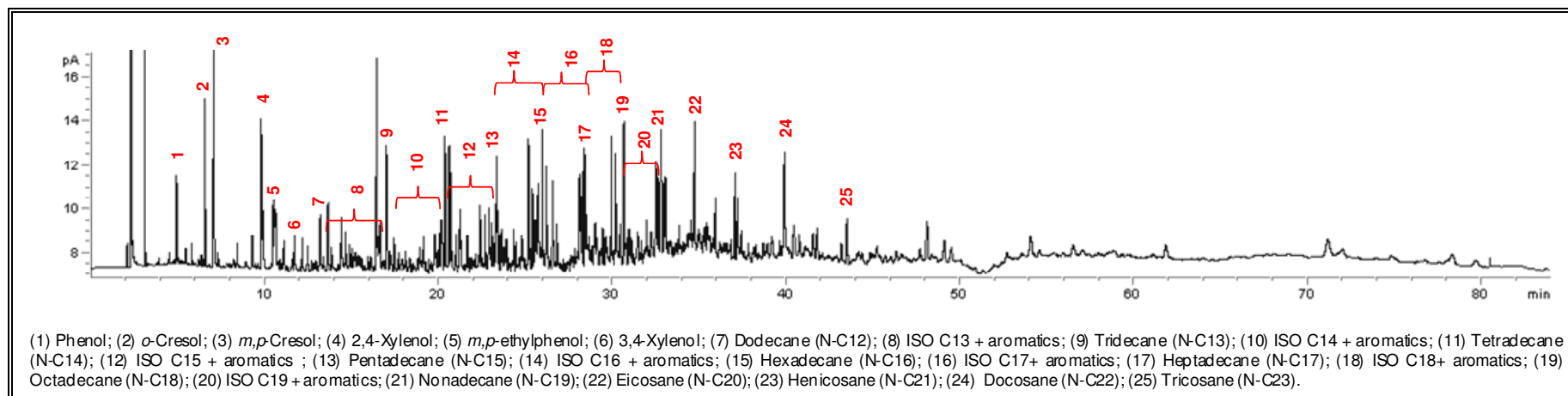


Figure C.21 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal UMZ at 450°C.

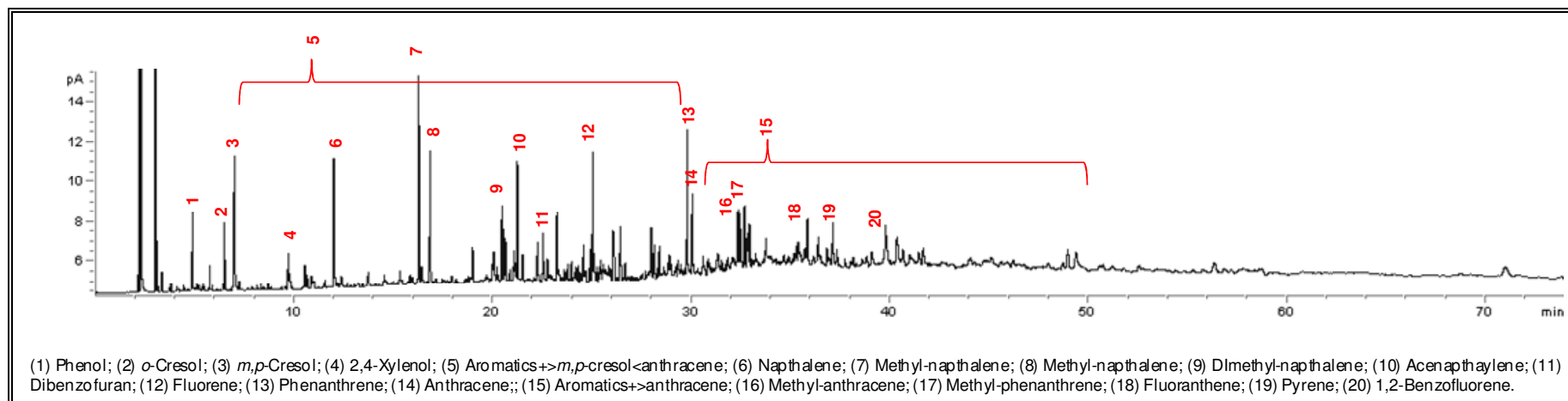


Figure C.22 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal UMZ at 450°C.

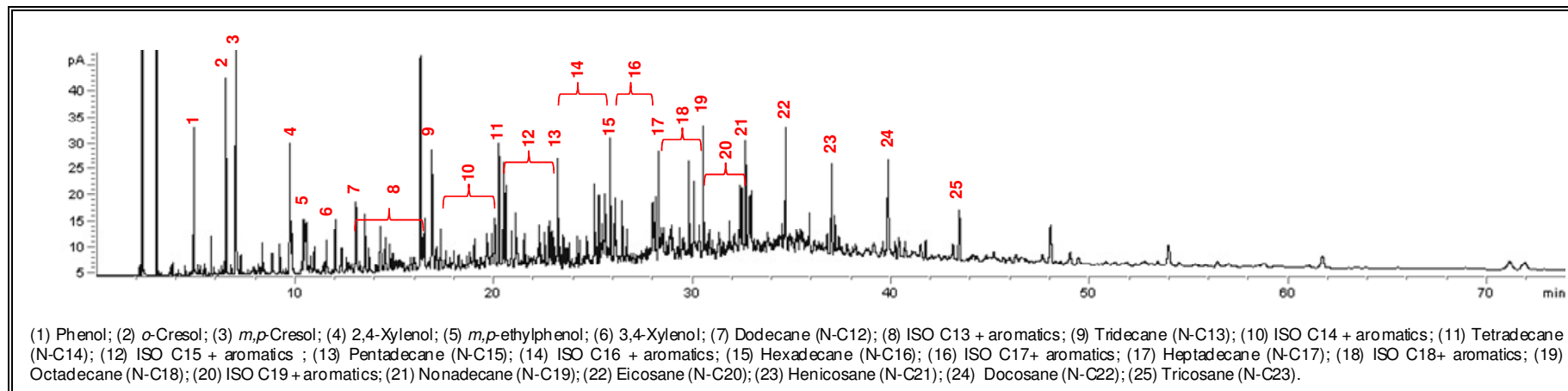


Figure C.23 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal INY at 450 °C.

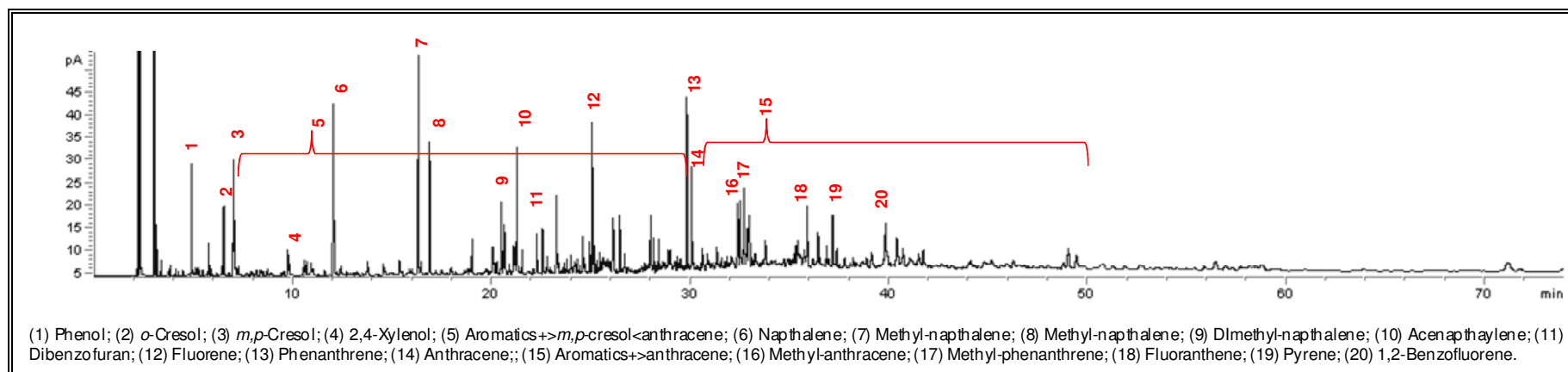


Figure C.24 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal INY at 750 °C.

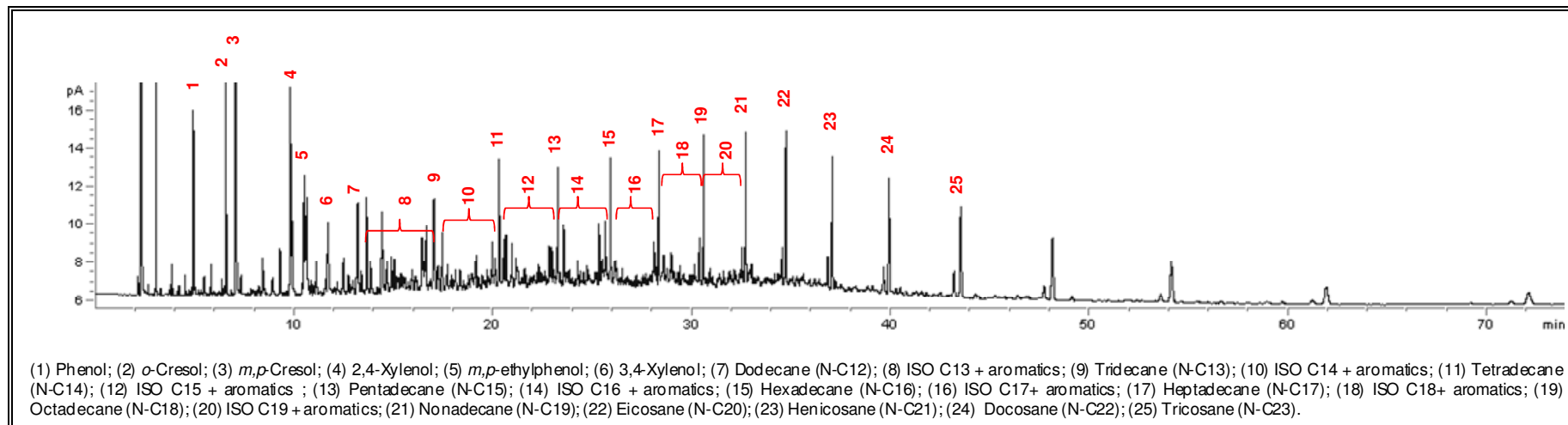


Figure C.25 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal G#5 at 450°C.

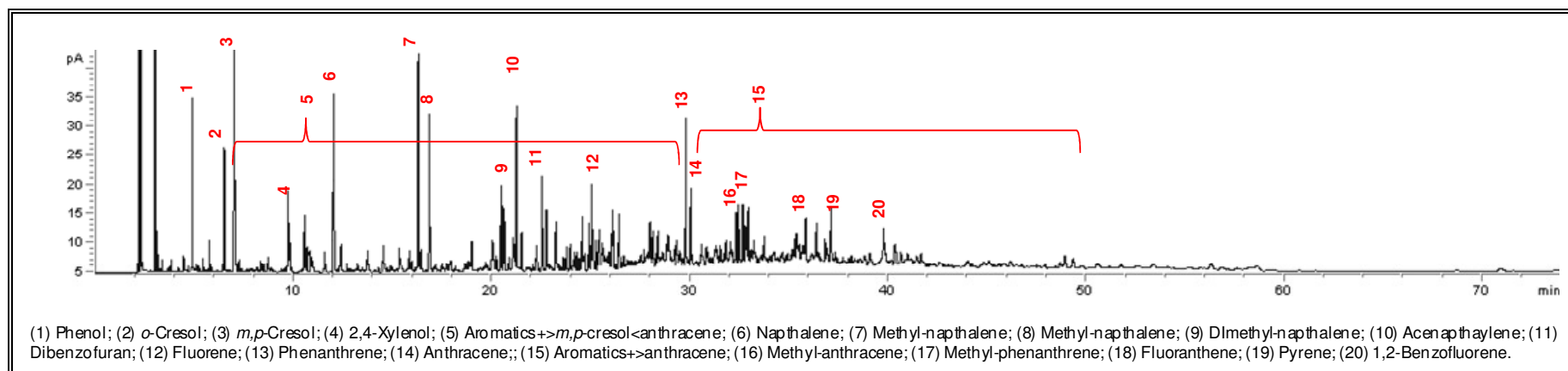


Figure C.26 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal G#5 at 750°C.

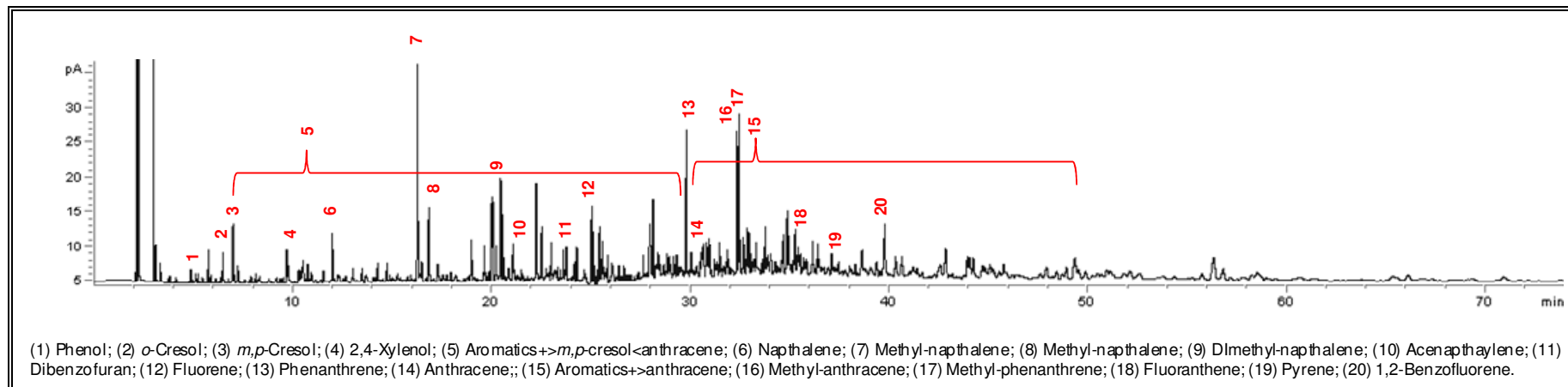


Figure C.27 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal TSH at 450 °C.

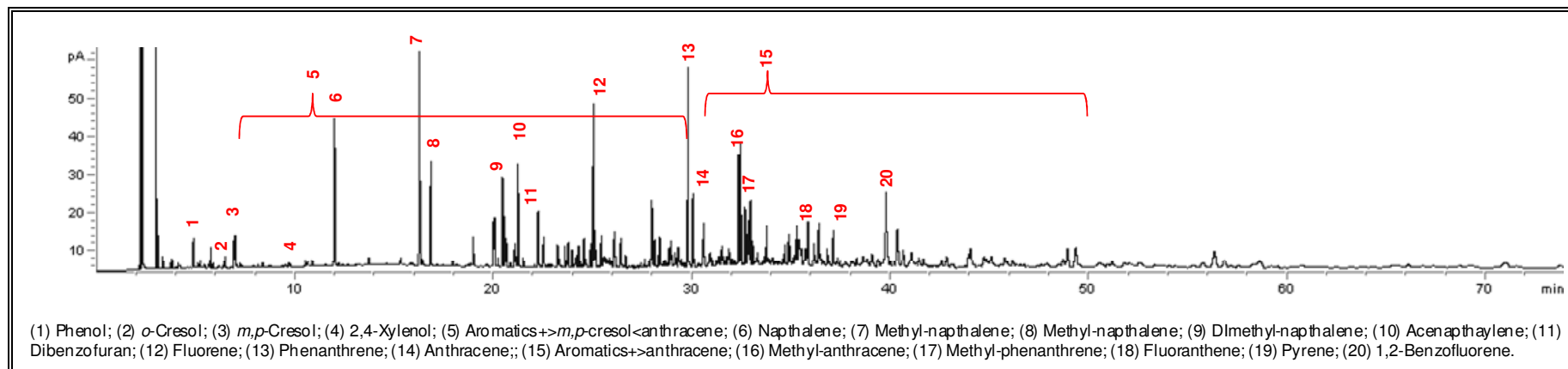


Figure C.28 Total ion chromatogram (TIC) of tar generated from 20 mm particles of coal TSH at 750 °C.

Table C.2 Chemical compound distribution (wt.%) as measured by GC-MS and GC-FID on tars generated from the 5 mm particles.

Chemical compounds (wt.% yields from 5 mm particles)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		G#5		TSH	
	450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Acenaphthylene		1.90		1.58		1.72	0.17	1.61
Analine	0.02							
Anthracene		1.37		1.09		0.86	0.31	1.02
Aromatics < <i>m,p</i> -cresol		0.37		0.61		0.59		0.89
<i>m,p</i> -cresol < Aromatics > anthracene		31.31		26.34	3.63	28.7	32.74	20.43
Aromatics > anthracene		25.29		37.36		36.02	42.46	39.24
Benzene								
Butyl acetate		0.23		0.18		0.16	0.11	
1,2-Benzofluorene		1.54		1.74		0.81	1.25	2.77
Cyclopentene								
DAA		0.15		0.11		0.08		0.13
Dibenzofuran		1.02		0.80		1.01	0.57	0.61
Dimethyl-naphthalene		1.95		1.46		1.44	2.53	2.40
Dimethyl-pyridine		0.09	0.04	0.10	0.29	0.14		0.10
Dodecane	0.59		0.63					
Ethenyl-naphthalene		0.63		0.48		0.56	0.11	0.48
Ethyl-Benzene				0.018		0.02		0.05

Table C.2 Chemical compound distribution (wt.%) as measured by GC-MS and GC-FID on tars generated from the 5 mm particles (cont'd).

Chemical compounds (wt.% yields from 5 mm particles)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		G#5		TSH	
	450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Fluoranthene		1.80		2.58		2.28	1.18	2.65
Fluorene		1.81		1.43		0.96	0.72	2.76
Heptadecane	0.77		0.97		1.59			
Heptane								
1-Heptene								
Hexadecane	0.85				1.63			
Hexane			0.92					
Indene								
ISO aliphatics and/or Aromatics (C ₇ -C ₂₆)	72.34		76.67		46.53			
MEK								
Methyl-anthracene		4.51		4.58		3.70	5.30	6.86
Methyl-benzofuran		0.21		0.15		0.19		0.06
Methyl-cyclopentanone	0.08							
Methyl-cyclopentene								
Methyl-indane	0.03		0.47					
Methyl-indene		0.76		0.49	0.19	0.56	0.13	0.27

Table C.2 Chemical compound distribution (wt.%) as measured by GC-MS and GC-FID on tars generated from the 5 mm particles (cont'd).

Chemical compounds (wt.% yields from 5 mm particles)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		G#5		TSH	
	450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Methyl-naphthalene	0.09	6.07	0.53	4.17		3.96	3.22	6.39
2-Methyl-1-pentene								
Methylene-phenanthrene		0.46		0.53		0.46	0.34	0.47
Methyl-phenanthrene		0.55		0.54		0.45	0.90	0.77
<i>m</i> -Ethylphenol	0.91		0.71	0.09	1.18	0.07	0.34	
Methyl-pyridene								
Methyl-thiophene								
<i>m,p</i> -Cresol	3.48	3.88	2.92	3.32	8.57	4.33	1.57	1.03
Naphthalene	0.34	3.39	0.25	2.45	0.22	2.42	0.47	3.72
Nonadecane	0.90		1.21		1.94			
Nonane	0.02							
Normal aliphatics (n-C ₂₀ - n-C ₂₇)	6.95		4.53		11.74			
<i>o</i> -Cresol	1.60	1.96	1.17	1.13	3.01	1.28	0.64	0.25
Octadecane								
<i>o</i> -Ethylphenol	0.45		0.33					
1-Octene								
Octadecane	1.00		1.03		1.61			

Table C.2 Chemical compound distribution (wt.%) as measured by GC-MS and GC-FID on tars generated from the 5 mm particles (cont'd).

Chemical compounds (wt.% yields from 5 mm particles)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		G#5		TSH	
	450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
<i>p</i> -Ethylphenol	0.17		0.133	0.09	2.41	0.06	0.38	
Pentadecane	0.65		1.35		1.83			
Phenanthrene		1.98		1.89		1.59	1.15	2.97
Phenol	0.92	2.12	0.54	1.40	1.77	1.57	0.26	0.57
Propyl-benzene	0.03		0.02					
Pyrene		0.89		1.04		0.95	0.36	0.77
Pyridine								
Tetradecane	0.90		0.77		1.91			
Tridecane	1.21		0.62		2.00			
Trimethyl-benzene	0.20	0.44	0.23	0.31	0.33	0.29	0.24	0.42
Trimethyl-pyridene	0.04		0.04					
Undecane	0.13		0.07					
2,3-Xylenol	0.48		0.38					
2,4-Xylenol	1.80	1.53	1.58	0.85	4.08	1.23	1.00	0.12
2,5-Xylenol	0.72	0.69	0.76	0.38	1.49	4.49	0.53	
2,6-Xylenol	0.31		0.26					
3,4-Xylenol	0.63	0.29	0.38	0.16	0.40	0.29	0.34	
3,5-Xylenol	0.50	0.76	0.43	0.54	1.65	0.69	0.53	0.17
Not identified	0.03	0.07	0.04	0.02	0.00	0.01	0.00	0.00

Table C.3 Chemical compound distribution (wt.%) as measured by GC-MS and GC-FID on tars generated from the 20 mm particles.

Chemical compounds (wt.% yields from 20 mm particles)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		G#5		TSH	
	450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Acenaphthylene		1.88		1.50		1.58	0.14	1.55
Analine			0.02					
Anthracene	0.92	1.43		1.28		0.63	0.37	1.10
Aromatics < <i>m,p</i> -cresol				0.79	2.03	0.55	0.29	0.76
<i>m,p</i> -cresol < Aromatics > anthracene		25.67		22.80	4.42	30.17	30.09	19.86
Aromatics > anthracene		28.01		40.61		33.87	46.56	42.95
Benzene								
Butyl acetate		0.69		0.47		0.25	0.25	0.33
1,2-Benzofluorene		1.84		0.30		0.79	1.27	2.58
Cyclopentene								
DAA		0.32		0.16		0.09	0.14	0.13
Dibenzofuran	0.47	0.99		0.68		0.98	0.64	0.57
Dimethyl-naphthalene	0.96	2.08		1.47		1.41	1.79	2.10
Dimethyl-pyridine	0.09		0.05	0.17	0.39	0.21	0.05	0.01
Dodecane	0.57		0.66		1.28			
Ethenyl-naphthalene		0.67		0.51		0.47	0.09	0.43
Ethyl-Benzene				0.04		0.02		0.04
Ethyl-methyl-phenol	0.21							

Table C.3 Chemical compound distribution (wt.%) as measured by GC-MS and GC-FID on tars generated from the 20 mm particles (cont'd).

Chemical compounds (wt.% yields from 20 mm particles)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		G#5		TSH	
	450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Fluoranthene		2.39		2.56		2.30	1.30	2.68
Fluorene	0.99	2.07		1.80		0.42	0.76	2.50
Heptadecane	0.71		0.93		1.22			
Heptane								
1-Heptene								
Hexadecane	0.93		0.80		1.16			
Hexane								
5-Indanol	0.35							
Indene								
ISO aliphatics and/or Aromatics (C ₇ -C ₂₆)	64.58		76.15		52.99			
MEK								
Methyl-anthracene		5.81		5.06		3.65	5.34	6.68
Methyl-benzofuran		0.14		0.12		0.08		0.05
Methyl-cyclopentanone								
Methyl-cyclopentene								
Methyl-indane								
Methyl-indene				0.29	1.31	0.55	0.10	0.21

Table C.3 Chemical compound distribution (wt.%) as measured by GC-MS and GC-FID on tars generated from the 20 mm particles (cont'd).

Chemical compounds (wt.% yields from 20 mm particles)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		G#5		TSH	
	450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Methyl-naphthalene	1.76	6.05	0.12	4.67		3.89	3.14	5.10
2-Methyl-1-pentene								
Methylene-phenanthrene		0.52		0.56		0.45	0.21	0.49
Methyl-phenanthrene		0.68		0.56		0.44	0.79	0.77
<i>m</i> -Ethylphenol	0.64		0.67		2.17	0.08	0.26	
Methyl-pyridene			0.01					
Methyl-thiophene								
<i>m,p</i> -Cresol	3.13	5.36	2.93	2.95	8.11	5.69	1.12	0.93
Naphthalene	0.29	2.99	0.41	2.78	0.08	2.38	0.57	2.85
Nonadecane	0.77		0.87		1.47			
Nonane			0.02					
Normal aliphatics (n-C ₂₀ - n-C ₂₇)	6.40		6.18		8.47			
<i>o</i> -Cresol	0.42	1.56	1.44	1.13	0.11		0.37	0.21
Octadecane			0.97		1.27			
<i>o</i> -Ethylphenol	0.41		0.04					
1-Octene			0.01					
Octadecane	0.94							
<i>p</i> -Ethylphenol	0.94		0.19		0.21	0.06	0.25	
Pentadecane	0.74		0.63		1.43			

Table C.3 Chemical compound distribution (wt.%) as measured by GC-MS and GC-FID on tars generated from the 20 mm particles (cont'd).

Chemical compounds (wt.% yields from 20 mm particles)	Inertinite-rich coals				Vitrinite-rich coals			
	UMZ		INY		G#5		TSH	
	450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Phenanthrene	1.08	2.41		2.11		1.47	1.56	2.98
Phenol	0.63	1.63	0.90	1.56	1.89	1.70	0.14	0.49
Propyl-benzene			0.03					
Pyrene		1.17		1.07		1.03	0.51	0.85
Pyridine								
Tetradecane	1.05		0.94		1.55			
Tridecane	1.55		1.33		1.56			
Trimethyl-benzene	0.10	0.31	0.22	0.42	0.35	1.24	0.30	0.30
Trimethyl-phenol	0.37							
Trimethyl-pyridene			0.04					
Undecane	0.05		0.17					
2,3-Xylenol	0.45		0.12					
2,4-Xylenol	1.44	1.22	1.52	0.66	3.75	1.54	0.61	0.12
2,5-Xylenol	0.92	0.48	0.65	0.32	1.46	0.61	0.32	0.06
2,6-Xylenol	0.30		0.28					
3,4-Xylenol	0.45		0.21	0.13	0.30	0.39	0.25	0.04
3,5-Xylenol	0.78	0.79	0.46	0.39	1.02	0.98	0.41	0.18
Not identified	0.50	0.00	0.01	0.03	0.00	0.03	0.03	0.02

C.7 SEC results of tars generated from the different coals

SEC chromatograms expressed as a function of elution time are presented separately for each coal in Figures C.29 and C.30 for tars generated from different coal particle sizes at the two experimental temperatures. A detailed discussion regarding the conversion of time-based SEC results to molecular weight distributions have been attended to in Section 6.5.3.2 of Chapter 6.

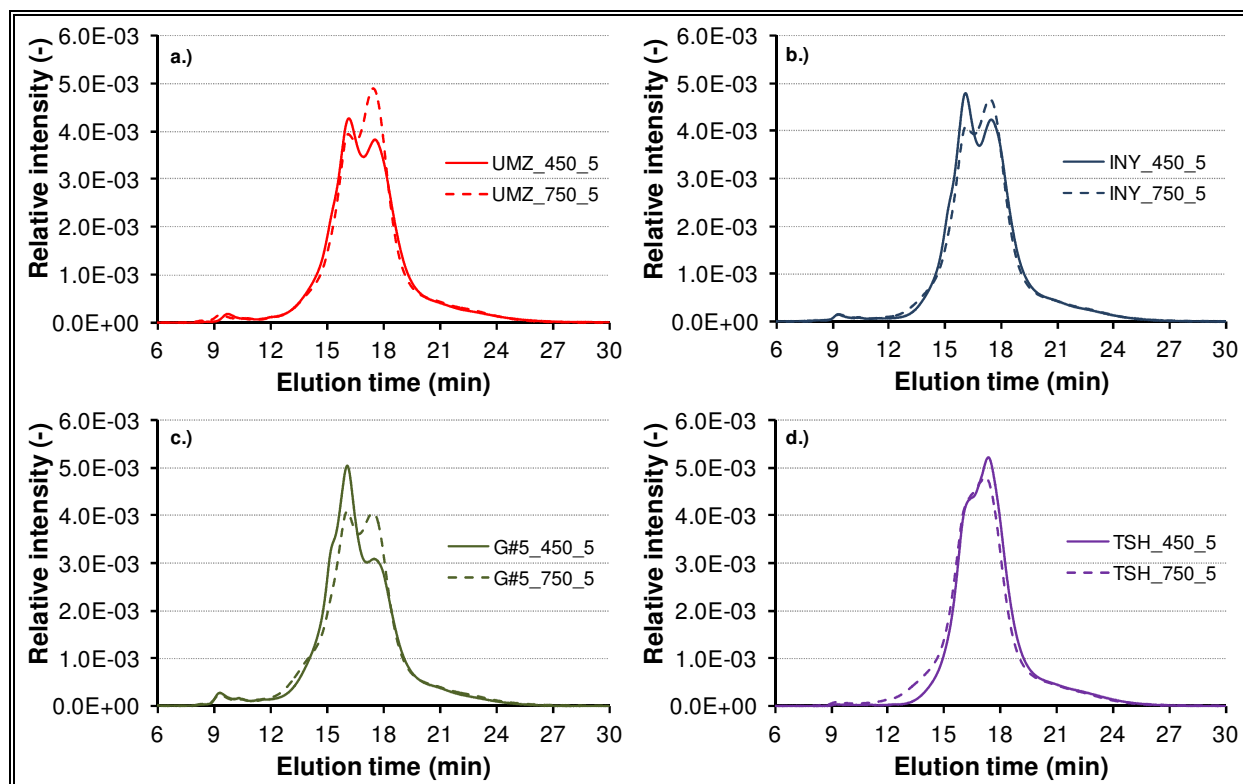


Figure C.29 Raw SEC chromatograms (370 nm) for tar generated from 5 mm particles of coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH at 450°C and 750°C, shown as a function of elution time.

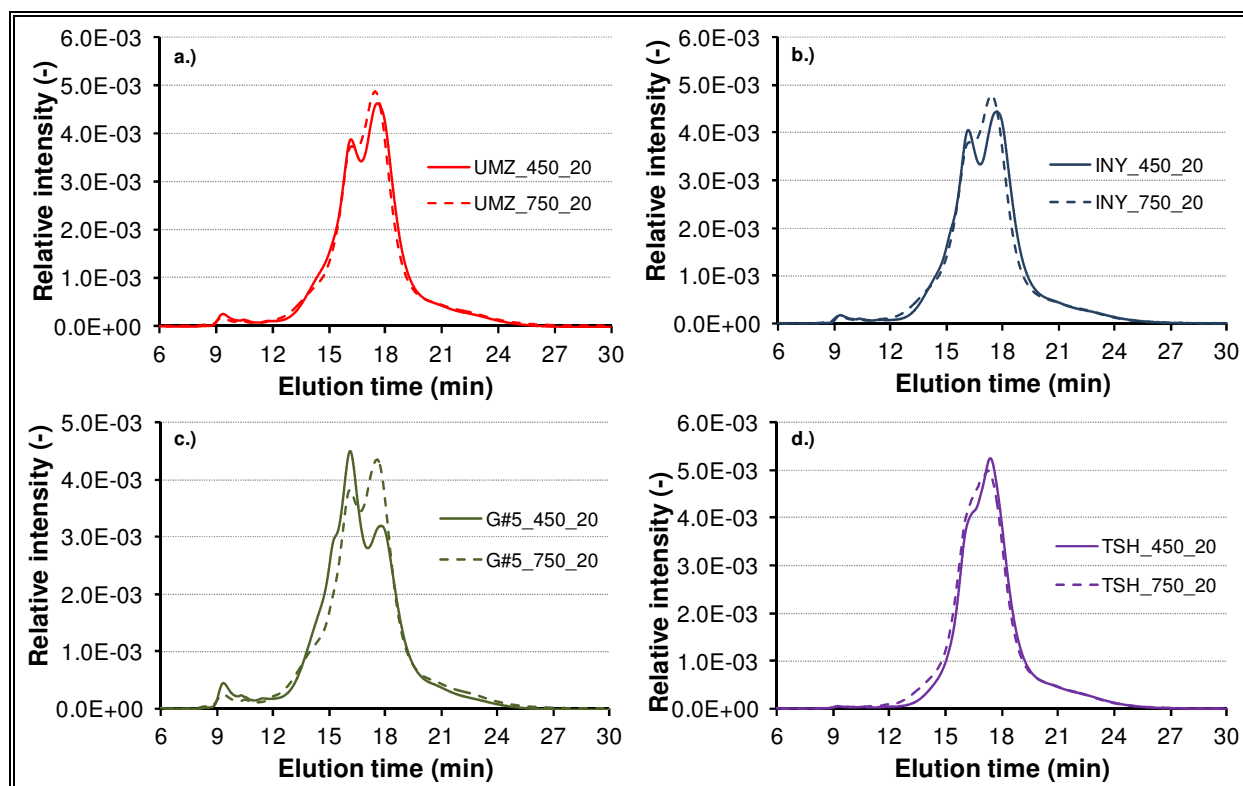


Figure C.30 Raw SEC chromatograms (370 nm) for tar generated from 20 mm particles of coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH at 450 °C and 750 °C, shown as a function of elution time.

C.8 Effect of coal type and temperature on the SEC molecular weight distribution of tars derived from 20 mm coal particles

The effect of coal type and temperature on the molecular weight distribution of tars generated from 20 mm particles is reflected graphically in Figure C.31 for the four different coals, while semi-quantitative comparisons were determined by dividing the molecular mass estimate results according to the amount of peaks detected in the chromatogram. The contribution of each peak to the total molecular mass distribution as well as the regions of interest are summarised in Table C.4 for the 20 mm experiments. Area contributions were estimated with the aid of the Origin 8.0 software. The reader is referred to Section 6.5.3.2 for a detailed discussion regarding the effect of coal type and temperature on the molecular weight distribution of generated tars.

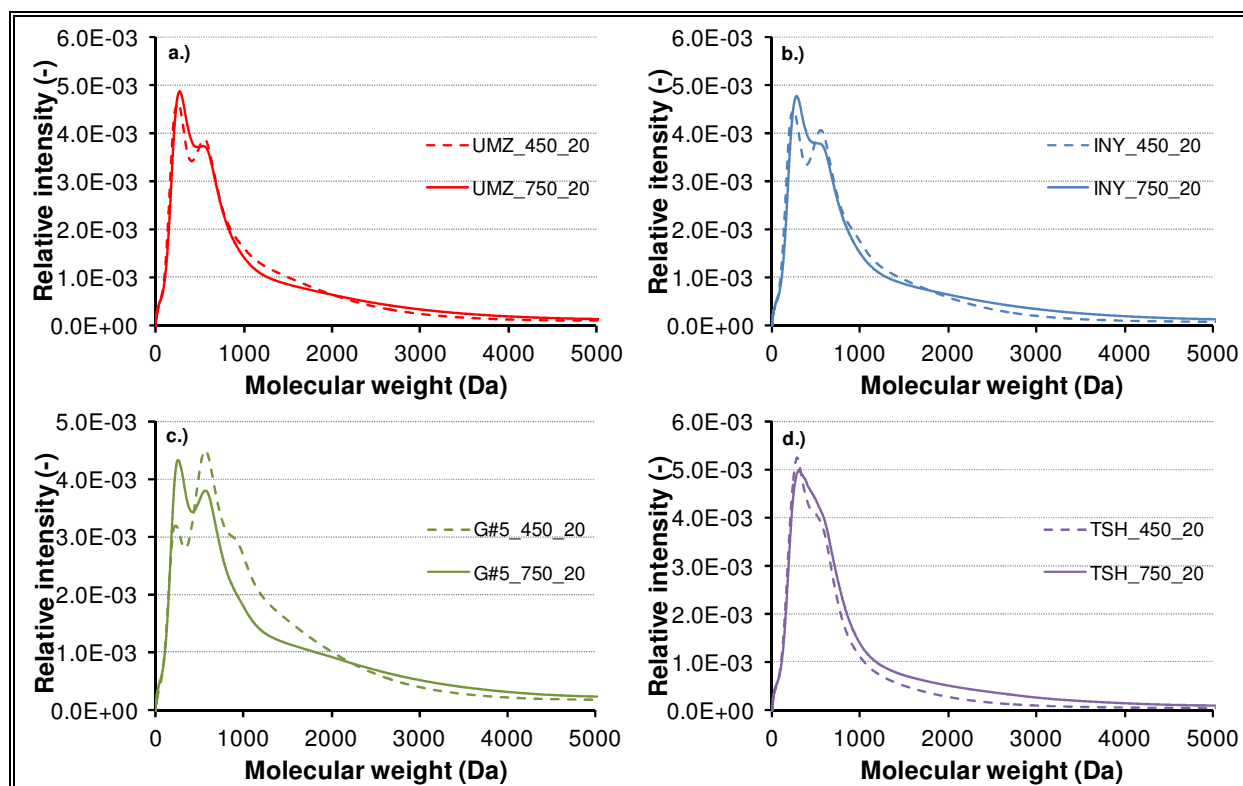


Figure C.31 SEC chromatograms (370 nm) for tars generated at 450°C and 750°C from 20 mm particles of coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH.

Table C.4 Summary of SEC results obtained on different tars generated from 20 mm particles.

Coal tar (20 mm experiments)	Temperature				
	450 °C			750 °C	
	Peak 1	Peak 2	Peak 3	Peak 1	Peak 2
UMZ					
Elution time range (min)	> 16.70	< 16.70	-	> 16.43	< 16.43
Molecular mass range (Da)	< 423	> 423	-	< 476	> 476
Elution time / peak max. (min)	17.56	16.19	-	17.44	16.20
Molecular mass / peak max. (Da)	257	555	-	274	538
Area contribution (%)^a	22.3	77.7	-	28.5	71.5

Table C.4 Summary of SEC results obtained on different tars generated from 20 mm particles (cont'd).

Coal tar (20 mm experiments)	Temperature				
	450 °C			750 °C	
	Peak 1	Peak 2	Peak 3	Peak 1	Peak 2
INY					
Elution time range (min)	> 16.81	< 16.81	-	> 16.43	< 16.43
Molecular mass range (Da)	< 386	> 386	-	< 477	> 477
Elution time / peak max. (min)	17.67	16.16	-	17.41	16.16
Molecular mass / peak max. (Da)	241	553	-	279	554
Area contribution (%)^a	22.2	77.8	-	27.9	72.1
G#5					
Elution time range (min)	> 16.98	16.98 – 17.39	< 15.53	> 16.65	< 16.65
Molecular mass range (Da)	< 352	352 - 780	> 780	< 424	> 424
Elution time / peak max. (min)	17.80	16.11	15.46	17.58	16.13
Molecular mass / peak max. (Da)	225	567	809	254	563
Area contribution (%)^a	10.7	24.6	64.7	18.5	81.5
TSH					
Elution time range (min)	> 16.65	< 16.65		> 16.62	< 16.62
Molecular mass range (Da)	< 421	> 421	-	< 429	> 429
Elution time / peak max. (min)	17.36	16.65	-	17.24	16.62
Molecular mass / peak max. (Da)	286	422	-	306	429
Area contribution (%)^a	34.8	65.2	-	26.6	73.4

C.9 Effect of particle size on the SEC molecular weight distribution of tars derived at the two different temperatures

The effect of particle size on the molecular weight distribution of tars generated from both 5 and 20 mm particles is reflected graphically in Figure C.32 for coals INY and TSH. Similar comparative figures were included in Section 6.5.3.2 for coals UMZ and G#5 (not shown here). A detailed discussion regarding the effect of particle size on the molecular weight distribution of generated tars has been provided in Section 6.5.3.2 of Chapter 6.

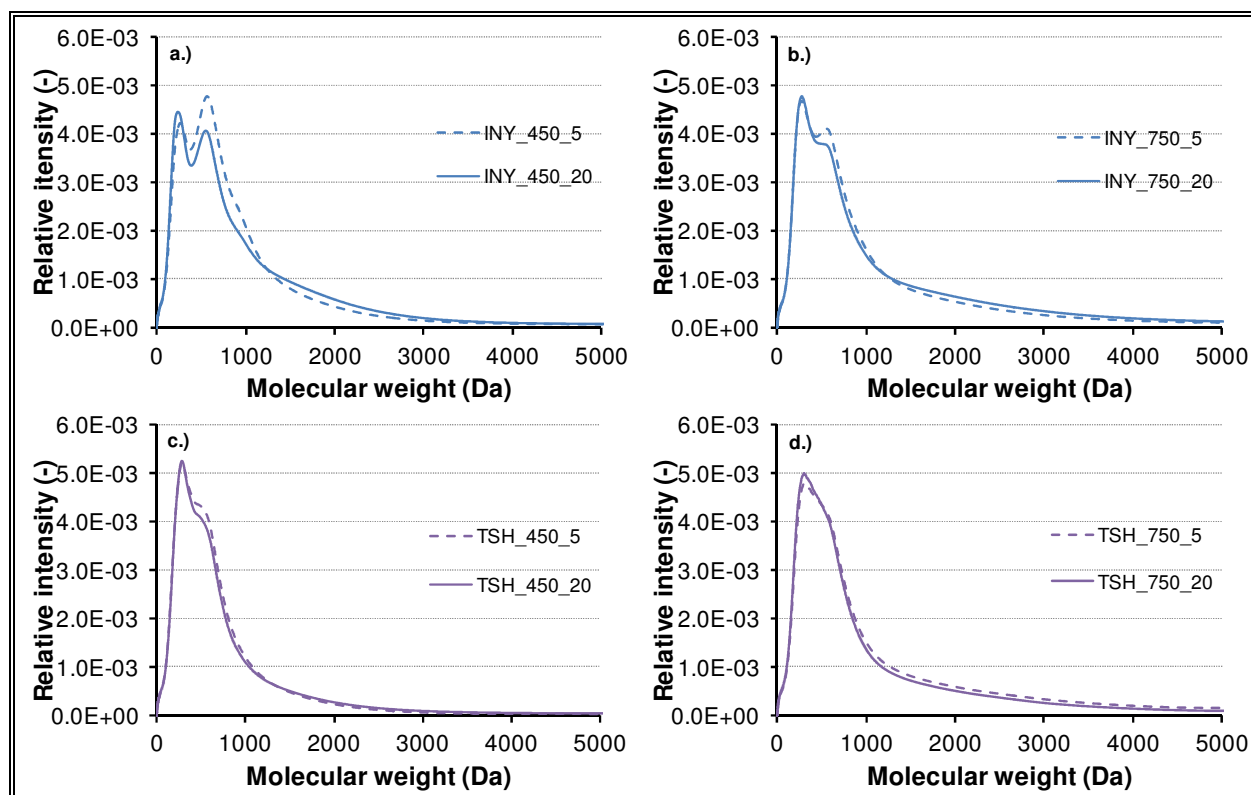


Figure C.32 Comparison between SEC results (370 nm) obtained on tars generated from coals INY (a.) and (b.) and TSH (c.) and (d.) for the different particle sizes.

C.10 Structural features of tars as determined from ^1H - and ^{13}C NMR

Qualitative comparisons of the ^1H and ^{13}C NMR spectra of tars generated at both temperatures from the 20 mm particles of the four coals are given in Figures C.33 and C.34, respectively. Corresponding quantitative results, expressed as a percentage of the total amount of hydrogen/carbon types observed, are provided in Tables C.5 and C.6. Integration limits for ^1H NMR were combined from chemical shift values (δ , ppm) specified in literature (López *et al.*, 2010; Guillén *et al.*, 1998; Morgan *et al.*, 2008a), while the integral reset points for subsets of different types of carbon functionalities were based on chemical shift ranges proposed by Díaz and Blanco (2003), Morgan *et al.* (2008a) and Wang *et al.* (2010). The occurrence of a large triplet peak between 77-80 ppm in the ^{13}C NMR spectra was attributed to the resonance signal of the solvent (CDCl_3) and is in accordance with what was obtained by Fulmer *et al.* (2010), Iglesias *et al.* (2001) and Wang *et al.* (2010). Calculated integrals were area normalised according to the detected TKS signal (~ 0.2338 ppm relative to TMS for ^1H NMR and ~ 2.9519 ppm relative to TMS for ^{13}C NMR) within either the ^1H NMR or ^{13}C NMR spectrum. A detailed discussion of the subsequent solution state NMR results can be found in Section 6.5.3.2 of Chapter 6.

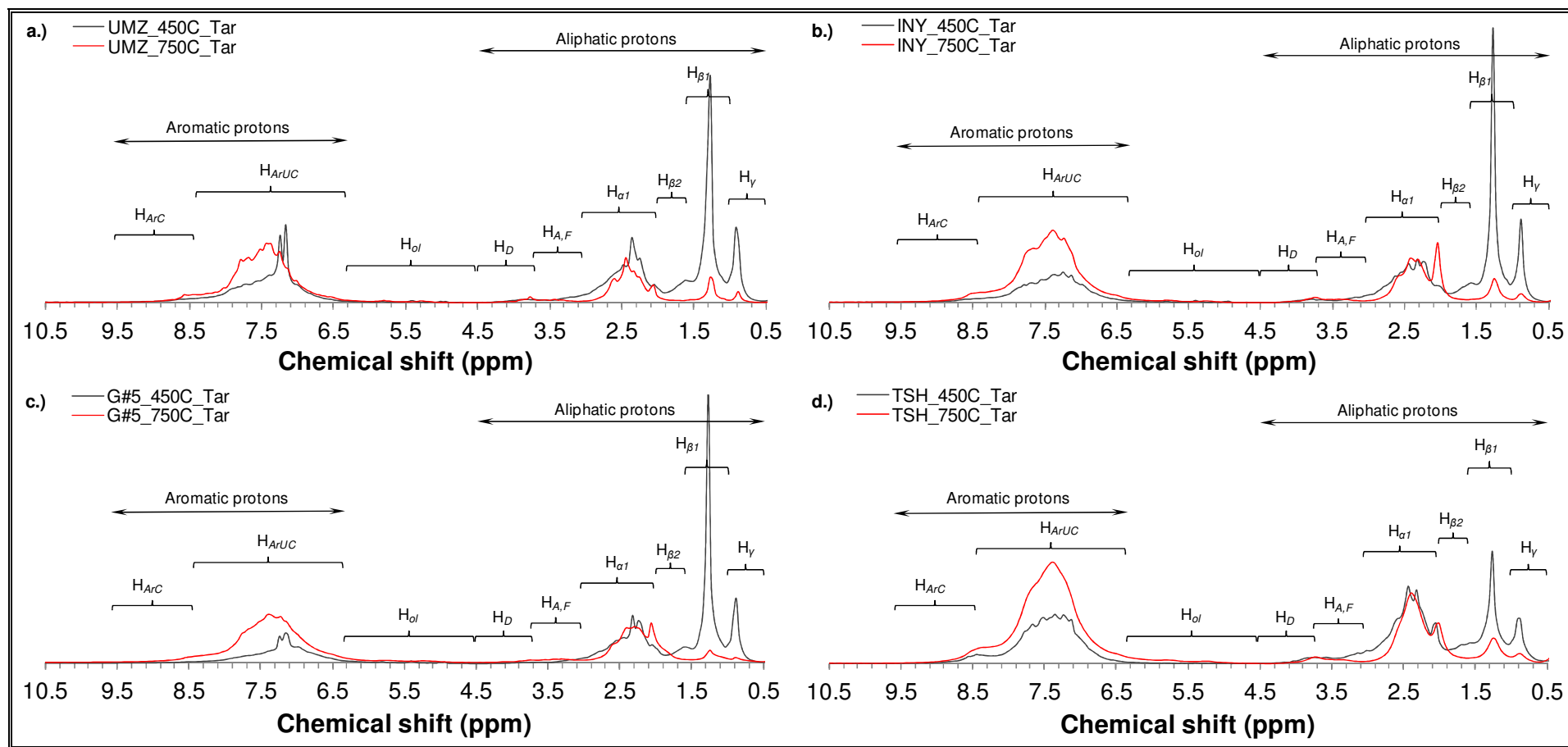


Figure C.33 ^1H NMR spectra of tars generated at the two different temperatures from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH (20 mm particles).

Table C.5 ¹H NMR distribution of tars derived at two different temperatures from 20 mm coal particles.

Proton type (20 mm experiments)	Symbol	Relative abundance expressed in area % of spectra							
		UMZ		INY		TSH		G#5	
		450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Aliphatic protons (0.5-4.5 ppm)	H_{Al}	70.31	33.08	70.90	34.66	63.47	33.75	75.98	37.67
Aliphatic H in methyl or methylene γ to an aromatic ^a	H _γ	8.84	1.47	9.20	1.35	6.33	1.56	9.95	1.38
Aliphatic H in methyl or methylene β to an aromatic ^a	H _{β1}	28.81	5.50	30.19	4.62	16.46	4.85	34.16	3.92
Alicyclic H β to two aromatics (naphthenic, methylenes) ^a	H _{β2}	4.94	1.31	4.83	2.67	4.92	3.40	5.16	4.66
Aliphatic H in methyl or methylene α to an aromatic and possible attachment in γ to another or same ring ^a	H _{α1}	24.58	21.97	23.44	23.47	30.63	21.64	24.78	24.82
Aliphatic H in methylene α to an aromatic ring and β to another or two rings (acenaphthene and fluorene type) ^a	H _{A,F}	2.33	1.64	2.39	1.59	3.78	1.49	1.81	2.20
Aliphatic H in methyl or methylene α to two aromatic rings (diphenylmethane type) ^a	H _D	0.80	1.20	0.86	0.96	1.36	0.83	0.13	0.70
Olefinic protons (4.5-6.3 ppm)	H_O	0.18	1.40	0.71	1.56	0.09	2.41	1.31	2.74
Aromatic protons (6.3-9.5 ppm)	H_{Ar}	29.51	65.51	28.39	63.78	36.44	63.84	22.70	59.59
Aromatic hydrogen ^a	H _{ArUC}	28.03	61.76	26.66	60.29	34.35	60.43	21.84	56.60
Sterically hindered aromatic hydrogen, in angular PAH's, in very peri-condensed PAH's or next to heteroatoms ^a	H _{ArC}	1.49	3.75	1.73	3.49	2.08	3.41	0.86	2.99
TOTAL		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Chemical shift ranges (δ, ppm): Aliphatic protons; H_γ (0.5-1.0), H_{β1} (1.0-1.6), H_{β2} (1.6-2.0), H_{α1} (2.0-3.0), H_{A,F} (3.0-3.69) and H_D (3.69-4.5). Olefinic protons: H_O (4.5-6.3). Aromatic protons; H_{ArUC} (6.3-8.36) and H_{ArC} (8.36-9.5) as adapted from Guillén et al. (1998). ^a Expressed in percentage of total observed protons (area %)

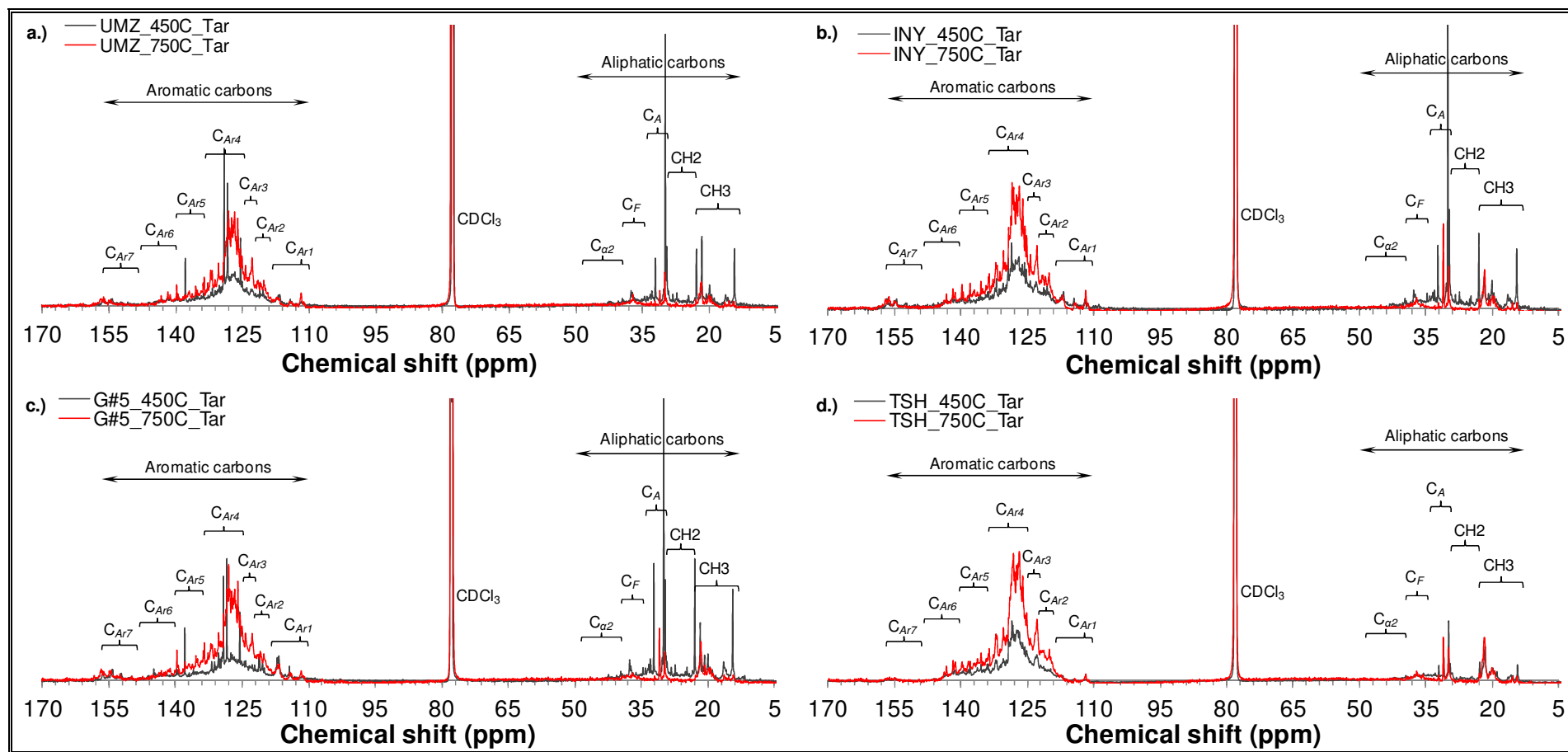


Figure C.34 ^{13}C NMR spectra of tars generated at the two different temperatures from coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH (20 mm particles).

Appendix C: Product yield and quality assessment

Table C.6 ^{13}C NMR distribution of tars derived at two different temperatures from 20 mm coal particles.

Carbon type (20 mm experiments)	Symbol	Relative abundance expressed in area % of spectra							
		UMZ		INY		TSH		G#5	
		450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Aliphatic carbons (13-49.3 ppm)	C_{Al}	39.63	12.78	38.88	10.93	26.80	9.86	46.00	12.27
Methyl carbons ^a	CH_3	11.98	4.60	10.86	3.79	9.28	4.06	13.04	5.41
Methylene (CH_2) and methine (CH) carbons α or further from an aromatic ring (i.e.; ethyl and propyl groups) ^a	CH_2	6.17	0.86	6.19	0.16	3.18	0.17	7.51	0.59
Methylene (CH_2) and methine (CH) carbons α to an aromatic ring and β to another (acenaphthene type) ^a	C_A	13.06	2.62	13.87	3.24	6.24	2.42	17.80	2.63
Methylene (CH_2) and methine (CH) carbons α to two aromatic rings (fluorene type) ^a	C_F	5.21	2.53	5.08	2.09	4.57	1.88	4.90	1.96
Methylene (CH_2) and methine (CH) carbons α to two aromatic rings (diphenylmethane type) ^a	C_{a2}	3.21	2.17	2.88	1.67	3.53	1.32	2.76	1.68
Aromatic carbons (110-160 ppm)	C_{Ar}	60.37	87.22	61.12	89.07	73.20	90.14	54.00	87.73
Pericondensed aromatic- or protonated aromatic carbons ^b	C_{ArP}	43.54	69.47	45.10	71.13	55.43	73.78	38.15	67.37
$C_{ar}\text{-H}$ ortho to $C_{ar}\text{-OH}^a$	C_{Ar1}	3.73	2.87	4.71	2.27	1.56	0.21	6.19	4.04
$C_{ar}\text{-H}$ para to $C_{ar}\text{-OH}$; $C_{ar}\text{-CH}_3$ ortho to $C_{ar}\text{-OH}^a$	C_{Ar2}	4.65	7.89	5.61	7.77	6.18	7.88	5.01	7.54
$C_{ar}\text{-CH}_3$ para to $C_{ar}\text{-OH}^a$	C_{Ar3}	3.75	7.31	4.56	7.38	6.27	8.09	3.23	6.88
Quaternary aromatic carbons; $C_{ar}\text{-H}$ meta to $C_{ar}\text{-OH}^a$	C_{Ar4}	31.41	51.40	30.23	53.71	41.42	57.59	23.73	48.91
Catacondensed aromatic carbons, aromatic carbons both with heteroatomic or aromatic substituents ^b	C_{ArC}	16.83	17.75	16.02	17.94	17.77	16.36	15.84	20.37
$C_{ar}\text{-CH}_3$; CH_2 or CH para to $C_{ar}\text{-OH}^a$	C_{Ar5}	8.16	10.31	7.62	10.58	11.21	11.94	6.90	11.38
CH_2 or CH meta to $C_{ar}\text{-OH}^a$	C_{Ar6}	4.62	4.19	4.53	4.11	5.44	4.08	4.63	4.33
$C_{ar}\text{-OH}^a$	C_{Ar7}	4.05	3.25	3.87	3.24	1.12	0.34	4.31	4.66
TOTAL		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Chemical shift ranges (δ , ppm): Aliphatic carbons; CH_3 (13-23), CH_2 (23-29.5), C_A (29.5-34), C_F (34-39.5), C_{a2} (39.5-49.3) as adapted from Díaz & Blanco (2003) and Morgan et al. (2008a). Aromatic carbons: C_{Ar1} (110-118), C_{Ar2} (118-122), C_{Ar3} (122-124), C_{Ar4} (124-133), C_{Ar5} (133-140), C_{Ar6} (140-147), C_{Ar7} (147-167) as adapted from Wang et al. (2010).

^a Expressed in percentage of total observed carbons (area %). ^b Sum of respective aromatic regions.

C.11 Chemical properties of chars derived from 5 mm coal particles

A comparison of chemical properties, as determined from proximate- and ultimate analyses, of chars derived from 5 mm coal particles at the two different temperatures is provided in Table C.7. Similar results have been obtained for the 20 mm experiments (presented in Chapter 6) and the reader is therefore referred to Section 6.5.3.3 for a detailed discussion regarding the chemical characteristics of the different generated chars.

Table C.7 Chemical properties of chars produced at 450 °C and 750 °C.

Chars derived at 450°C and 750°C for 5 mm coal particles			Inertinite-rich coals				Vitrinite-rich coals			
			INY		UMZ		G#5		TSH	
			450°C	750°C	450°C	750°C	450°C	750°C	450°C	750°C
Proximate analysis (Dry basis)	Unit	Standard								
Ash	wt. %	SABS ISO 1171:1997	21.4	20.4	17.5	21.8	15.3	18.9	22.2	25.8
Volatiles matter (VM)	wt. %	SABS ISO 562:1998	15.3	3.1	15.3	4.0	15.9	3.0	10.0	2.2
Fixed Carbon (FC)	wt. %	By difference	63.3	76.5	67.2	74.2	68.7	78.1	67.8	72.0
TOTAL	wt. %		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Fuel ratio (FC/VM)			4.1	24.5	4.4	18.4	4.3	25.8	6.8	32.7
Proximate analysis (Ash free basis)										
Volatiles matter (VM)	wt. %	SABS ISO 562:1998	19.5	3.9	18.5	5.2	18.8	3.7	12.9	3.0
Fixed Carbon (FC)	wt. %	By difference	80.5	96.1	81.5	94.8	81.2	96.3	87.1	97.0
TOTAL	wt. %		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate analysis (Dry, ash free basis)		ISO 12902								
Carbon	wt. %		84.1	93.4	84.0	91.4	83.6	91.7	88.4	93.2
Hydrogen	wt. %		3.9	1.0	3.7	1.0	4.0	0.9	4.1	0.9
Nitrogen	wt. %		2.3	2.4	2.3	2.3	2.7	2.8	2.2	2.3
Oxygen	wt. %	By difference	7.3	2.1	9.2	3.8	9.3	3.6	4.7	2.9
Total sulphur (IR Spectroscopy)	wt. %	ISO 19759	2.4	1.2	0.8	1.5	0.4	1.0	0.5	0.8
TOTAL	wt. %		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Atomic H/C ratio	-		0.55	0.12	0.53	0.13	0.58	0.11	0.56	0.12
Atomic O/C ratio	-		0.07	0.02	0.08	0.03	0.08	0.03	0.04	0.02

C.12 ^{13}C NMR spectra obtained from CP-MAS DD analyses of all chars

An overview of the results obtained from ^{13}C NMR CP-MAS dipolar dephasing experiments for chars generated at both temperatures from 5 mm coal particles is presented respectively in Figures B.1-B.4. Spectra for chars derived from the inertinite-rich coals (INY and UMZ) are provided in Figures C.35 and C.36 respectively, while the results for the chars derived from the vitrinite-rich coals (G#5 and TSH) are given in Figures C.37 and C.38.

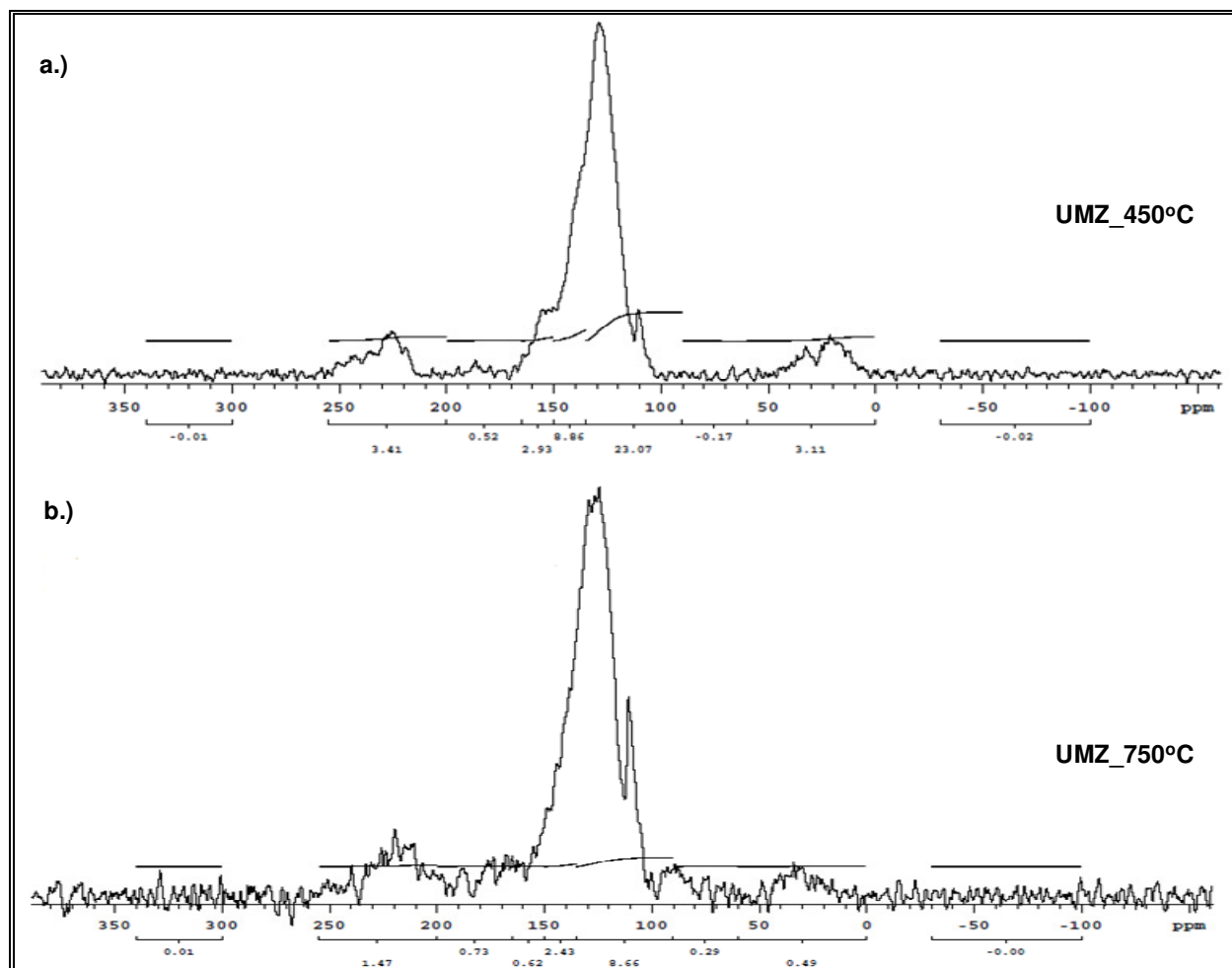


Figure C.35 CP-MAS DD spectra obtained for chars produced from coal UMZ at a.) 450°C and b.) 750°C.

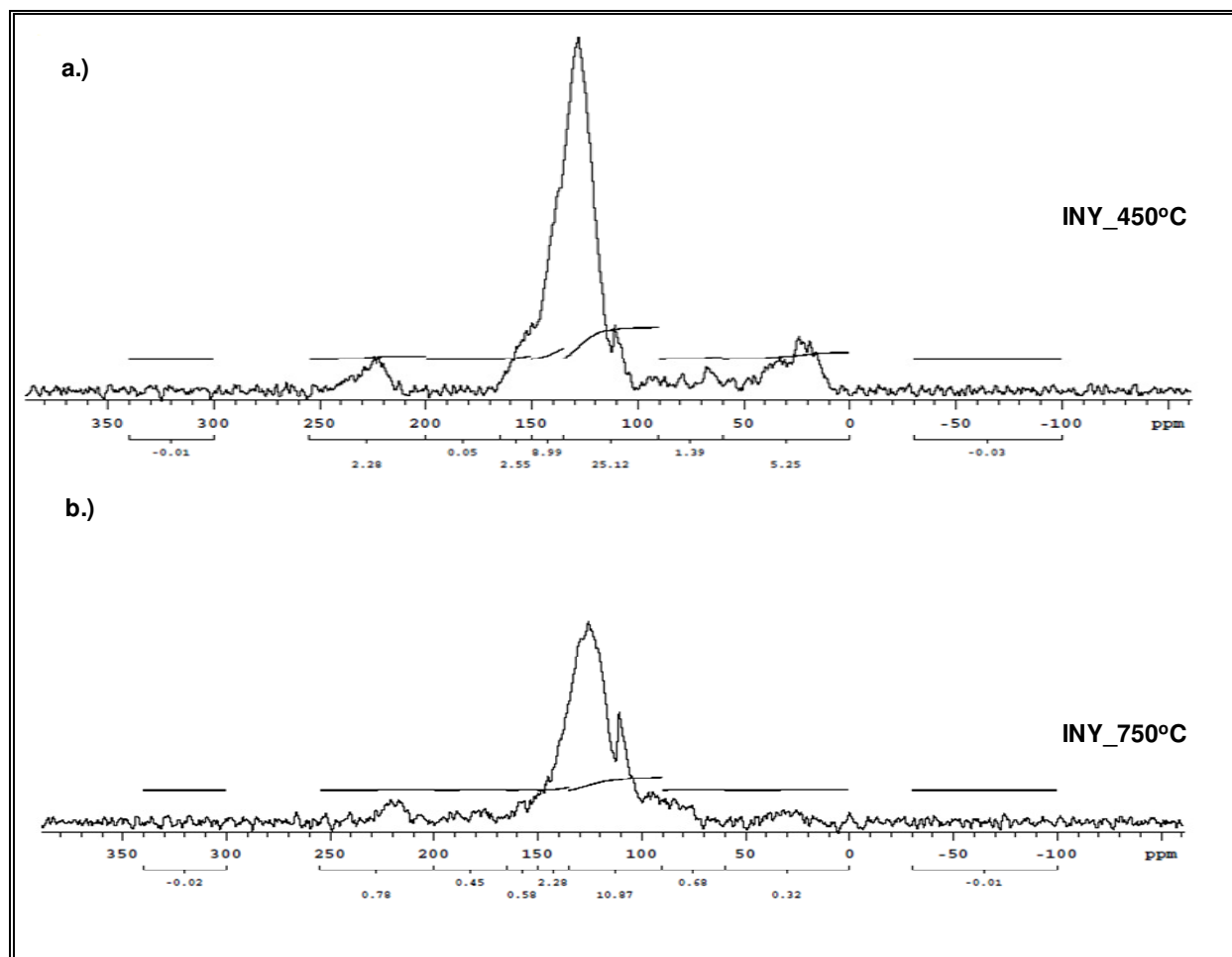


Figure C.36 CP-MAS DD spectra obtained for chars produced from coal INY at a.) 450°C and b.) 750°C.

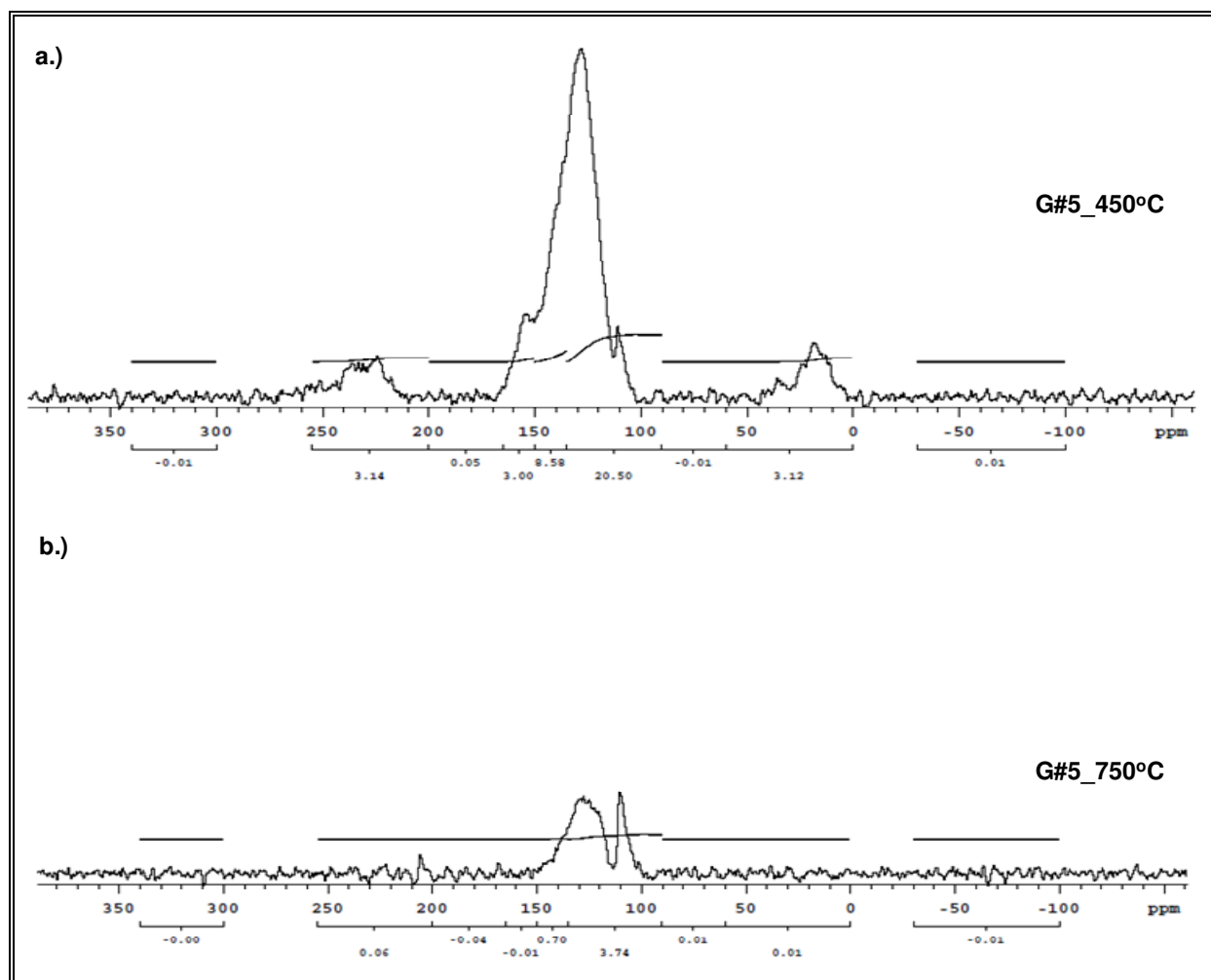


Figure C.37 CP-MAS DD spectra obtained for chars produced from coal G#5 at a.) 450°C and b.) 750°C.

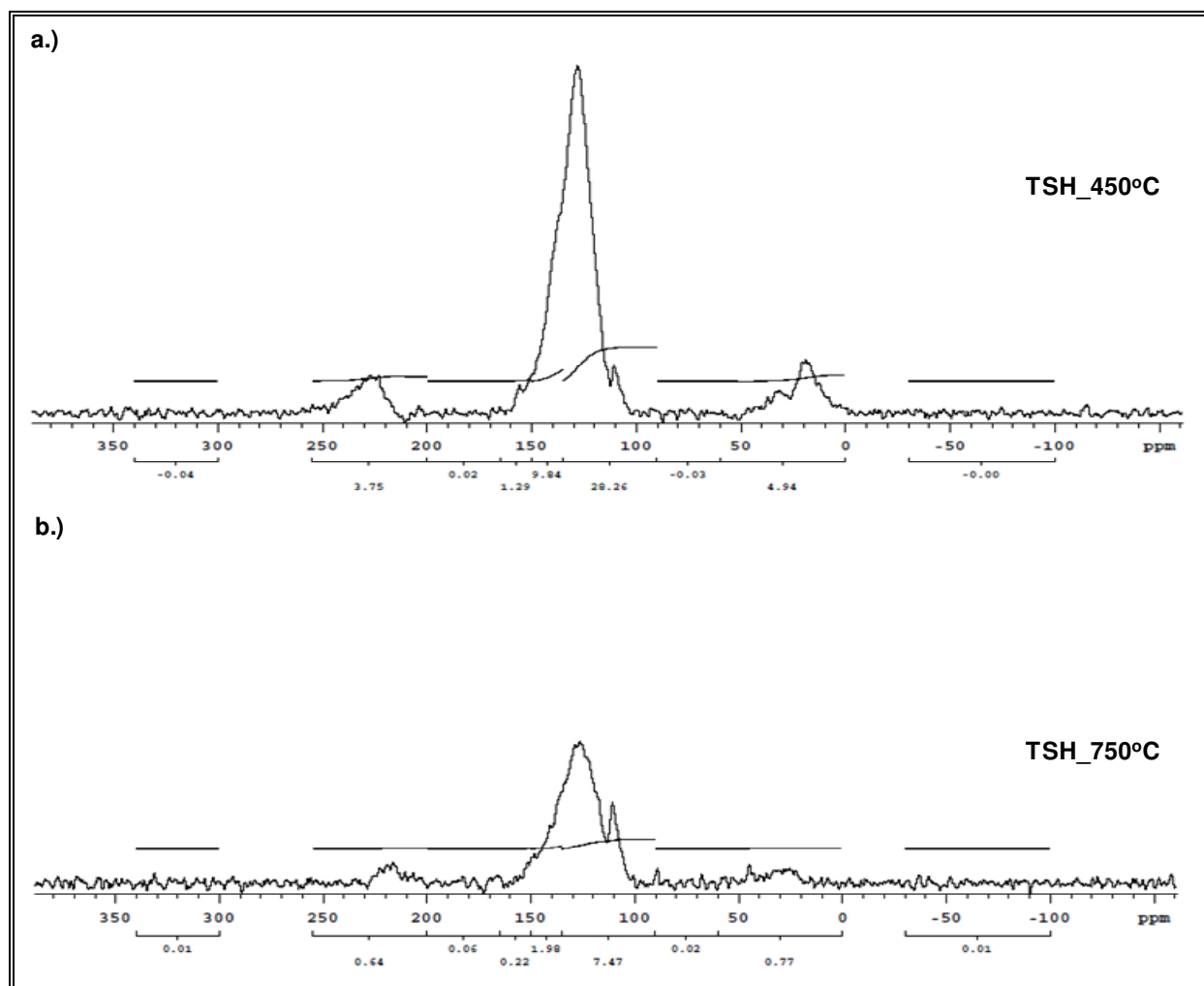


Figure C.38 CP-MAS DD spectra obtained for chars produced from coal TSH at a.) 450°C and b.) 750°C.

C.13 XRD: Deconvolution results for amorphous carbon calculation of chars

The amorphous fraction of carbon was determined according to the method outlined by Wu *et al.* (2008) and Wang *et al.* (2001). A descriptive account of the procedure has been provided in Section 5.4.1.3. An overview of the deconvolution results obtained for chars produced at both temperatures from coals UMZ, INY and TSH is respectively given in Figures C.39 to C.41 (a-b.). The results for chars derived from coal G#5 were provided in Section 6.5.3.3.

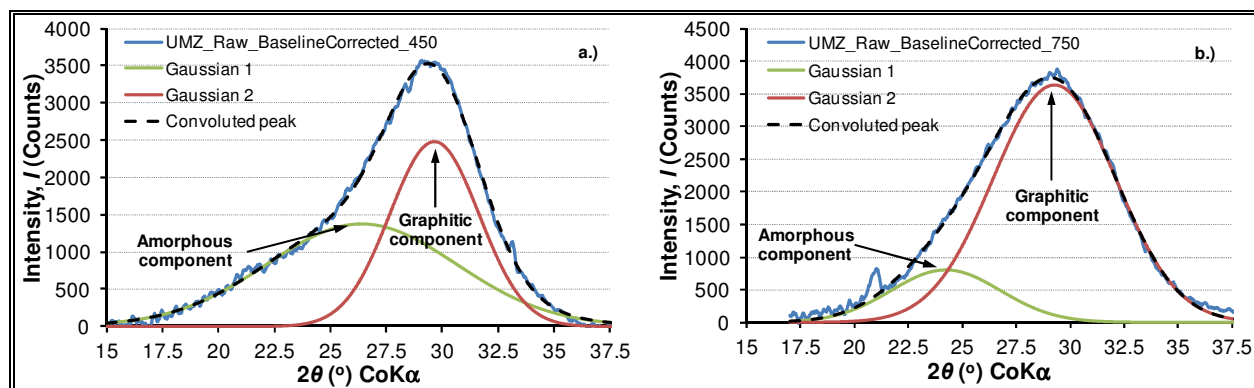


Figure C.39 Estimation of the fraction of amorphous carbon for chars generated at a.) 450°C and b.) 750°C from coal UMZ.

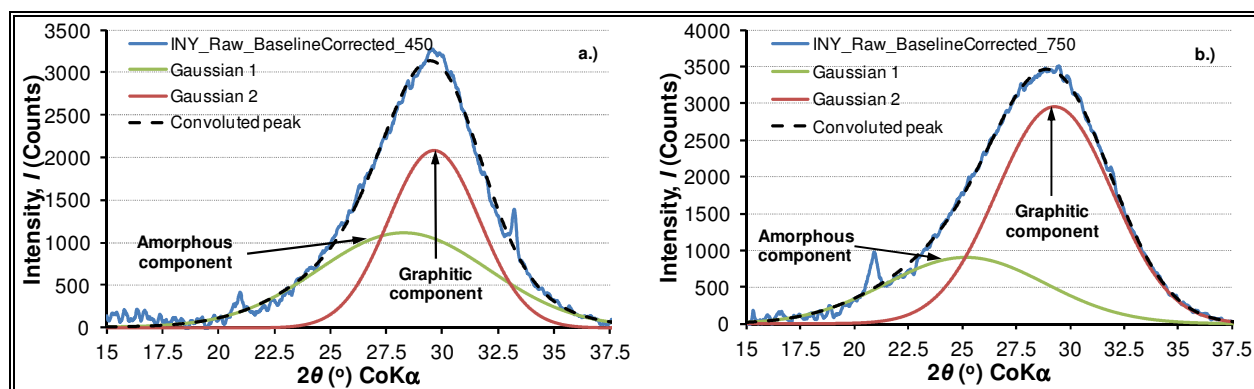


Figure C.40 Estimation of the fraction of amorphous carbon for chars generated at a.) 450°C and b.) 750°C from coal INY.

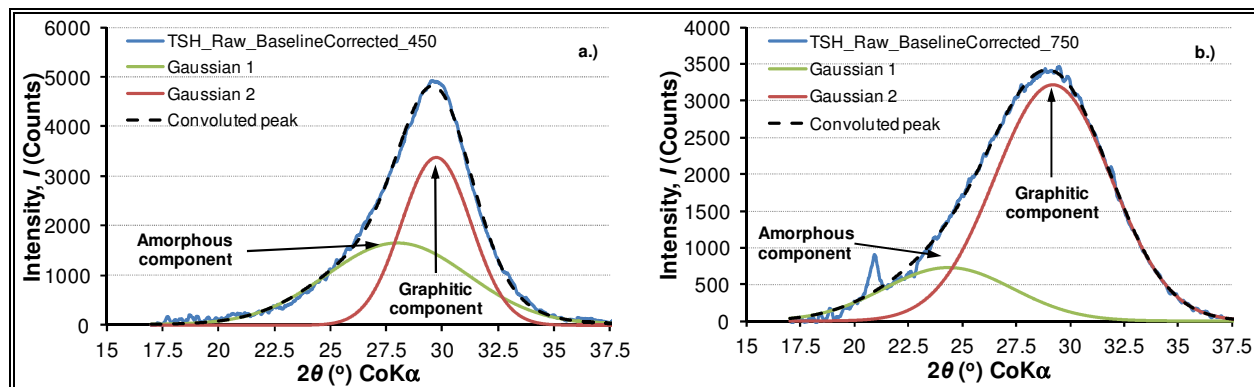


Figure C.41 Estimation of the fraction of amorphous carbon for chars generated at a.) 450°C and b.) 750°C from coal TSH.

C.14 XRD: Deconvolution results for aromaticity calculation of chars

The fraction of aromatic carbon was determined according to the method outlined by Lu *et al.* (2001). A descriptive account of the procedure has been provided in Section 5.4.1.3. An overview of the deconvolution results obtained for chars derived at both temperatures from coals UMZ, INY and TSH is respectively given in Figures C.42 to C.44. The results for chars obtained from coal G#5 were provided in Section 6.5.3.3.

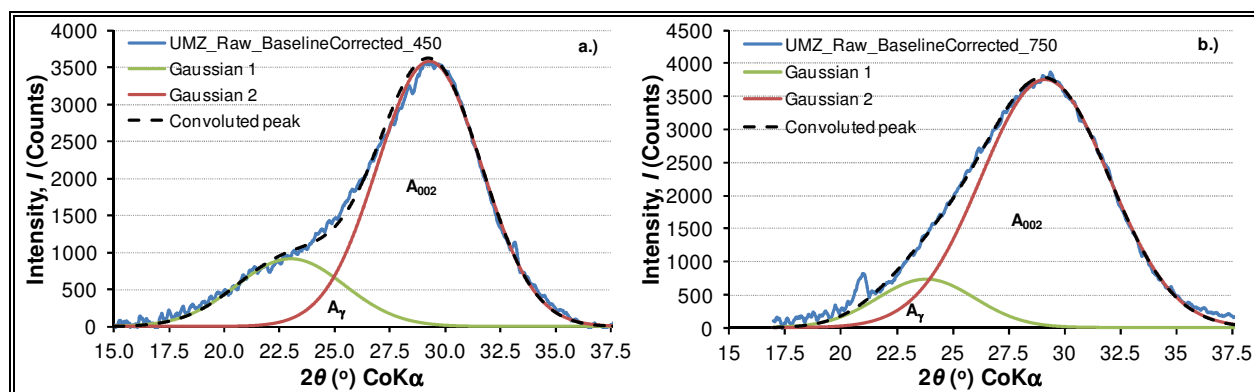


Figure C.42 Estimation of the fraction aromatics for chars generated at a.) 450°C and b.) 750°C from coal UMZ.

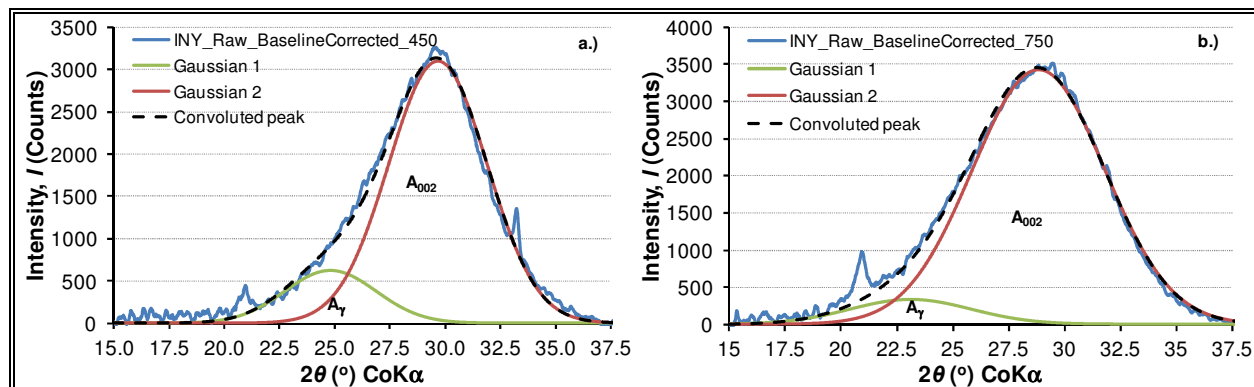


Figure C.43 Estimation of the fraction aromatics for chars generated at a.) 450°C and b.) 750°C from coal INY.

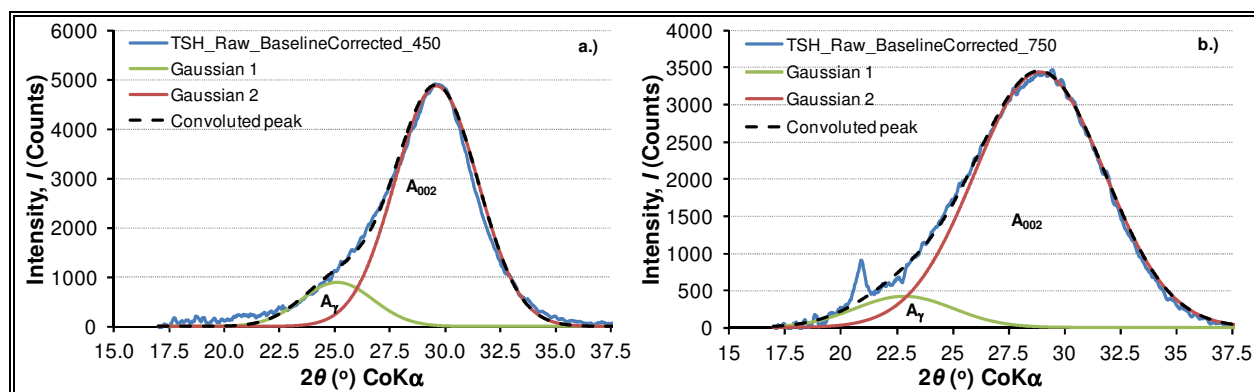


Figure C.44 Estimation of the fraction aromatics for chars generated at a.) 450°C and b.) 750°C from coal TSH.

C.15 HRTEM and image analysis results

Figures C.45 to C.49 provide graphical illustrations of the results obtained during image processing and fringe extraction of HRTEM images taken of the respective chars. A similar lattice fringe extraction and image analysis methodology as proposed by Mathews *et al.* (2010) and Sharma *et al.* (1999) was followed for studying the respective chars of which details can be found elsewhere (Section 5.3.1.5).

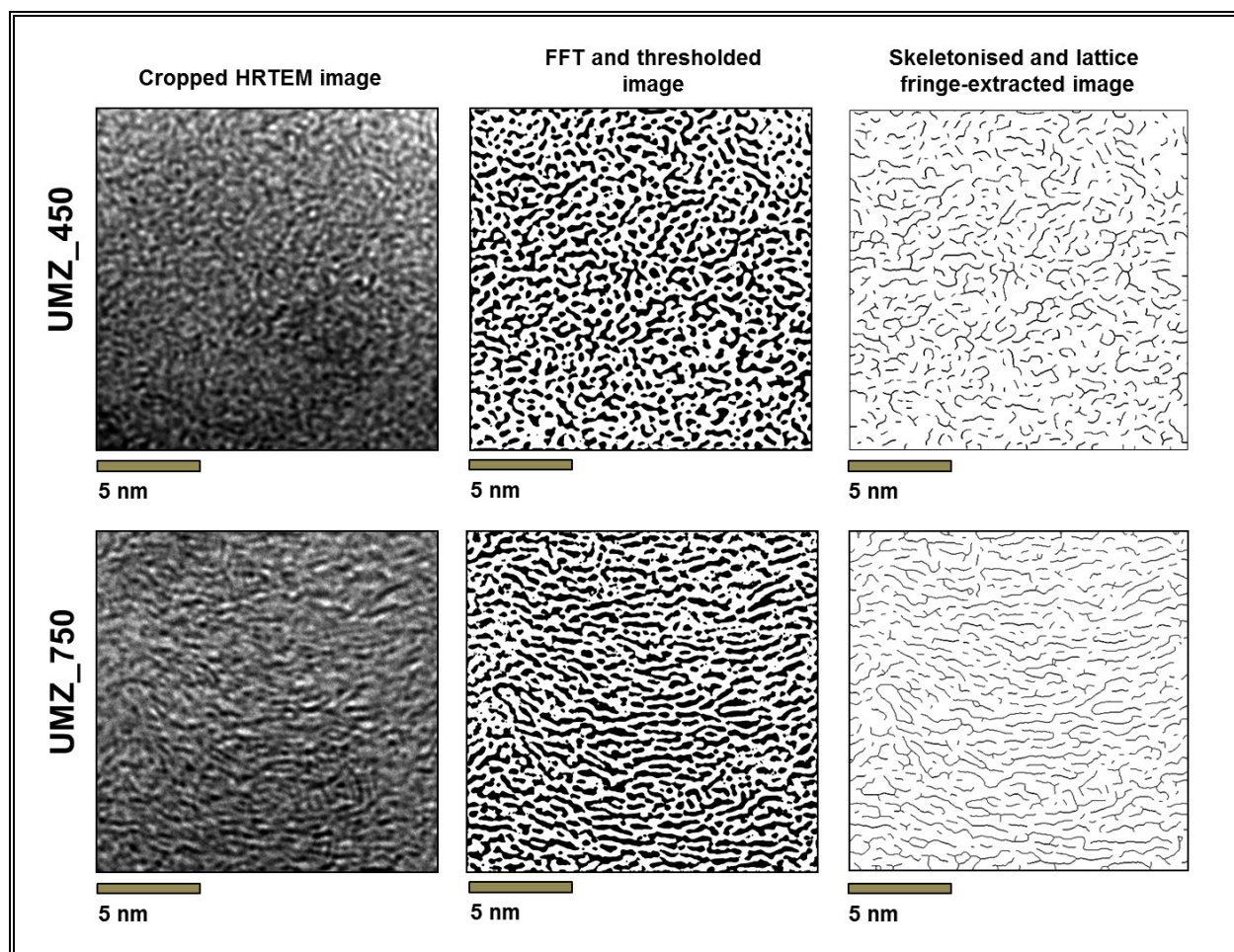


Figure C.45 Overview of some of the processing steps during the lattice fringe-extraction of chars generated from coal UMZ.

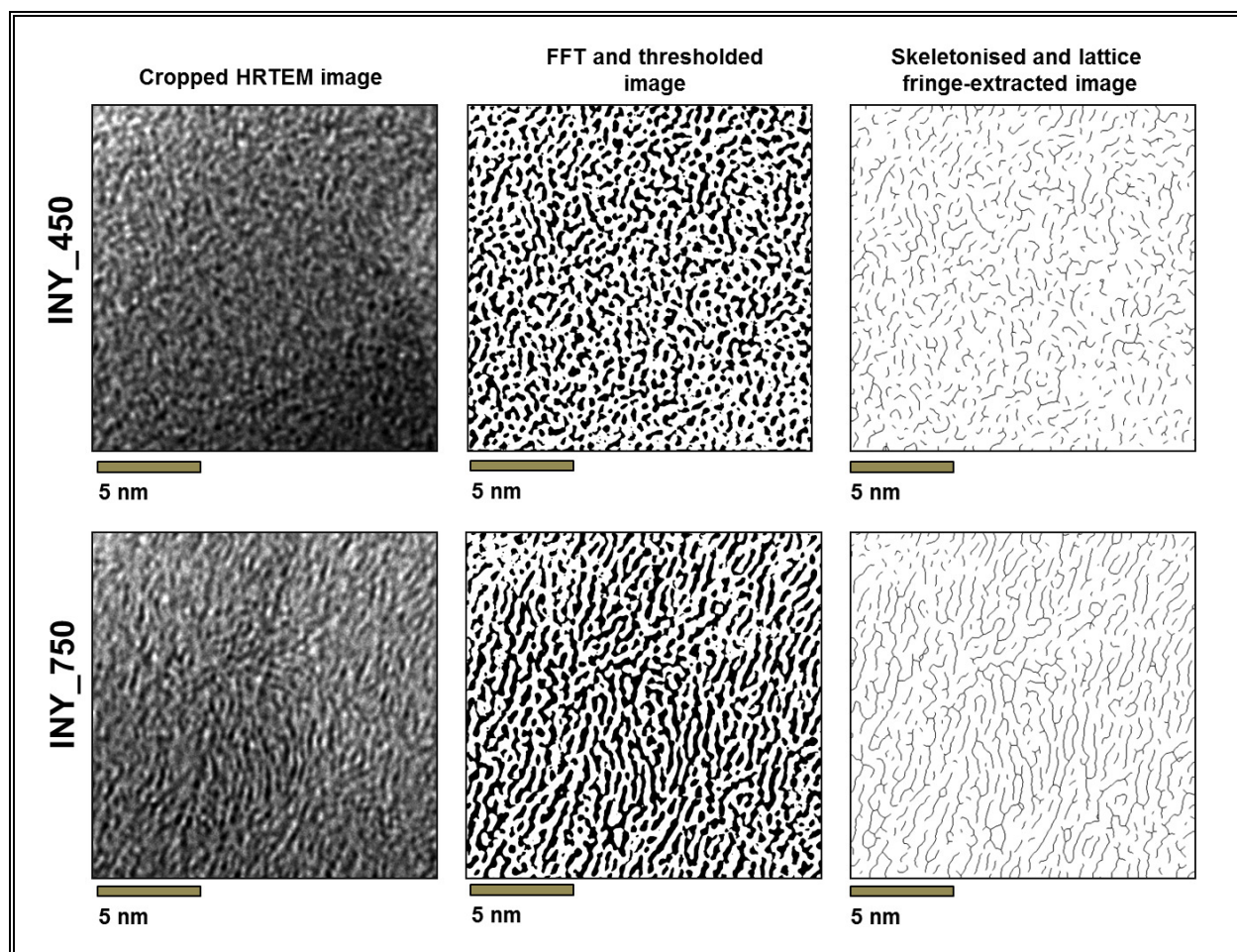


Figure C.46 Overview of some of the processing steps during the lattice fringe-extraction of chars generated from coal INY.

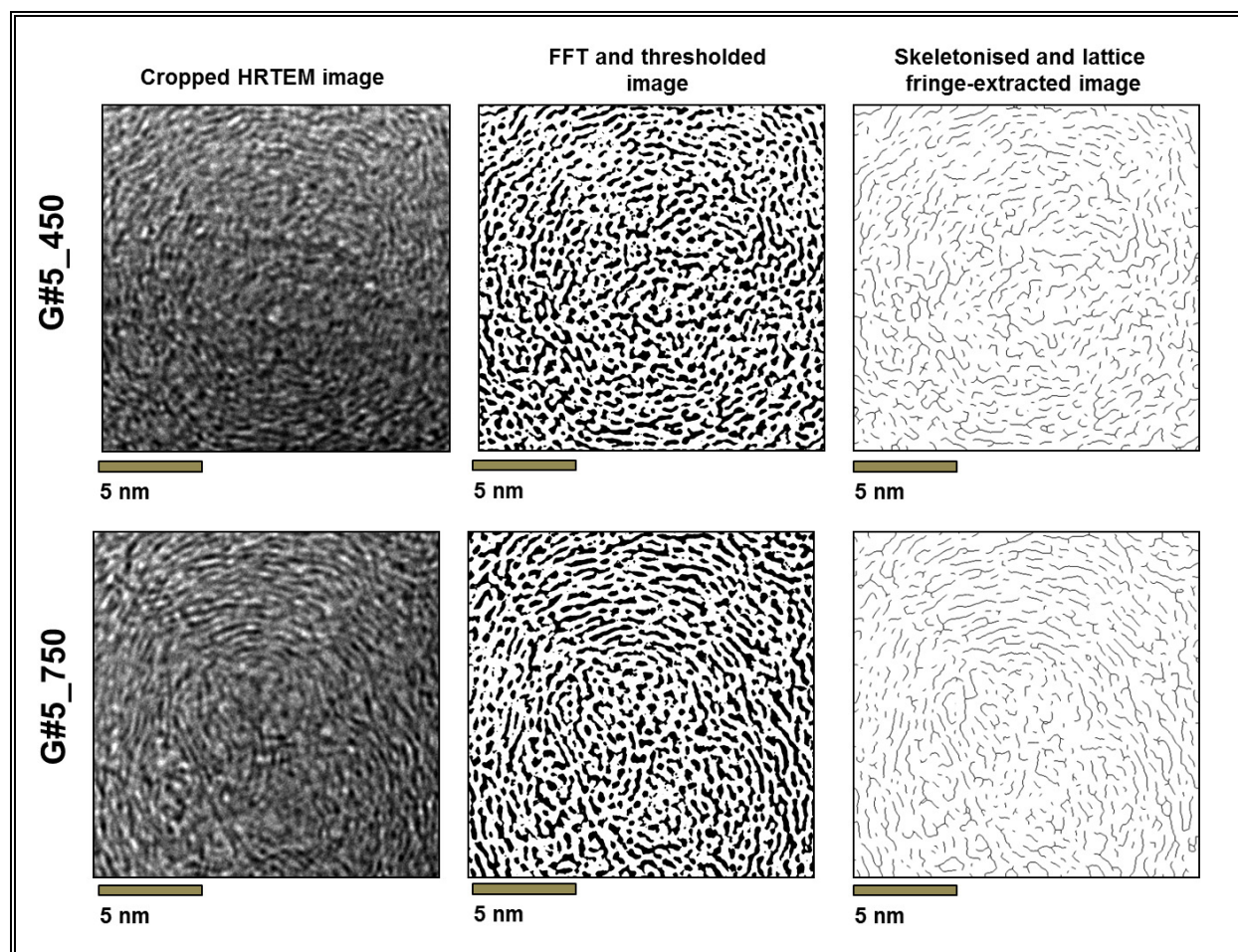


Figure C.47 Overview of some of the processing steps during the lattice fringe-extraction of chars generated from coal G#5.

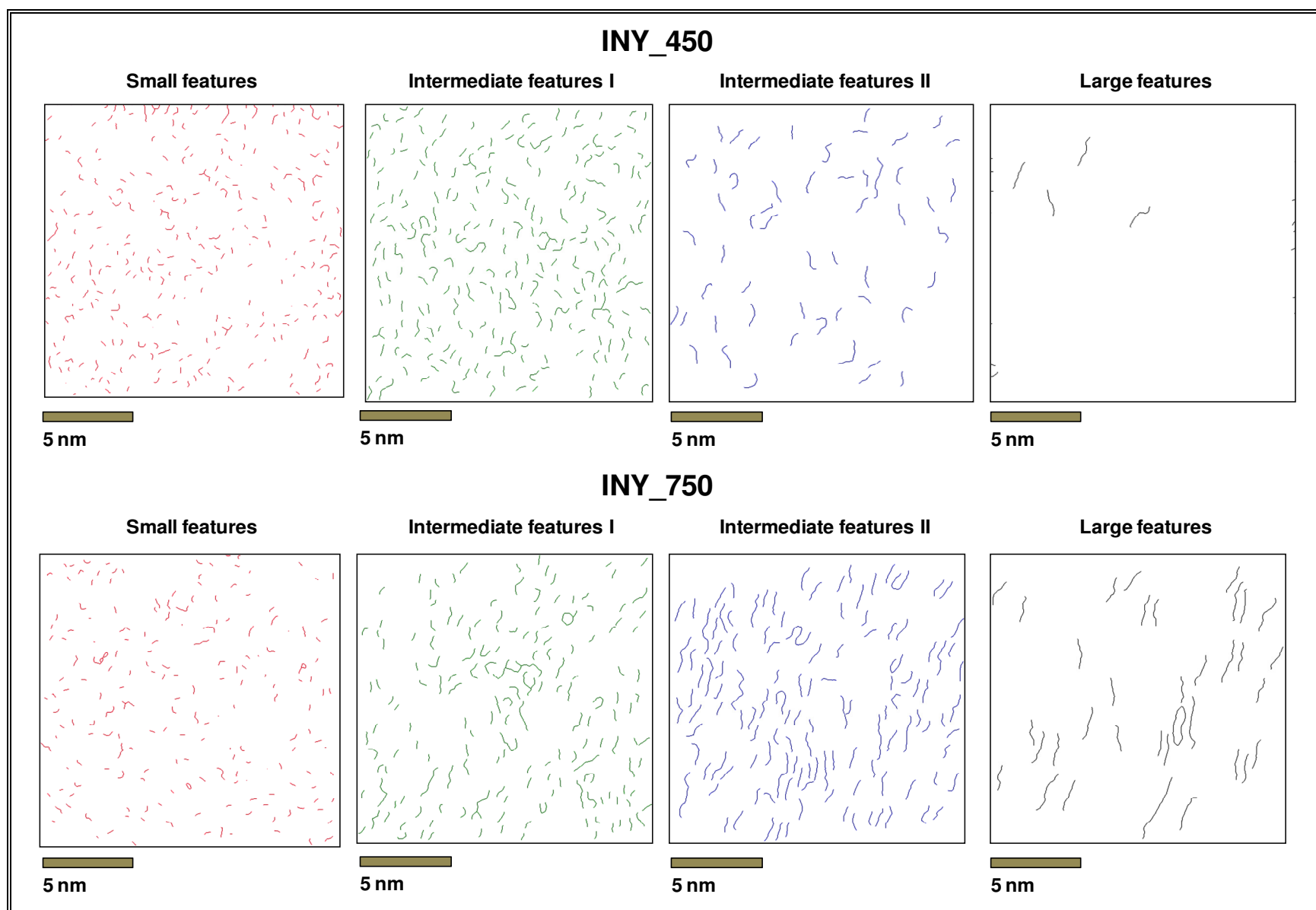


Figure C.48 Selected fringes in different size-ranges for chars derived at 450°C and 750°C from coal INY.

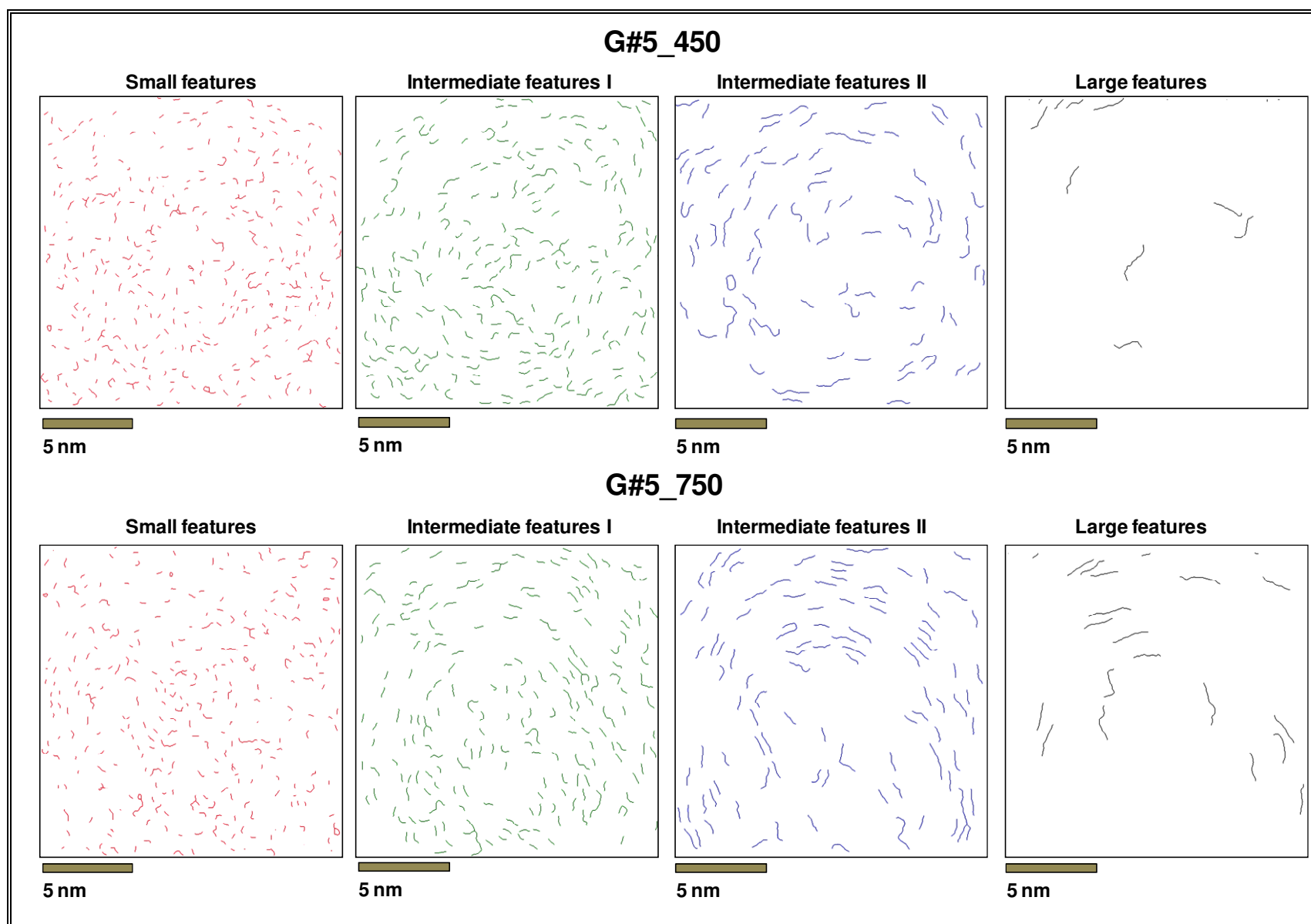


Figure C.49 Selected fringes in different size-ranges for chars derived at 450°C and 750°C from coal G#5.



D

APPENDIX D Reaction modelling

D.1 MATLAB 7.1.1 algorithm for deriving intrinsic kinetic parameters

This appendix provides an overview of the MATLAB algorithm used for evaluating the intrinsic kinetics of devolatilization. Implementation of the Levenberg-Marquardt optimization routine was done in a similar manner as proposed by Belderok (2007). Although only the script for a three pseudo-component approach has been included, modelling of more pseudo-components follows in a similar fashion.

D.1.1 Main script for evaluating reaction kinetics

*% Determination of the kinetic curves for coal devolatilization according
% to the pseudo-component method and on fixed heating rates*

% Definition of variables:

*% T: Temperature raw data, M: Mass fraction raw data, FX: Fractional conversion, Te: Equally
% spaced temperature elements, FXe: Interpolated equally spaced conversion data, dFX: Raw
% derivative-dX/dT, dXFe: Interpolated equally spaced derivative data, EA: Activation energies,
% A0: Pre-exponential constants, f: Fractional contributions of reactions, beta: Heating rate, %
% XFP: Fractional conversion of pseudo-components, dXFP: Derivative-dXp/dT of pseudo-
% components, XFPT: Modelled fractional conversion, dXFPT: Modelled derivative-dXFPT/dT,
% dXet: Derivative with respect to time-dXe/dtime, dXFPT: Derivative with respect to time-
% dXm/dtime, dFXf: Derive data filtered with the aid of Savitzky-Golay FIR filter*

%% Clear command window and close all open m-files

clc; clear all; close all;

Appendix D: Reaction rate modelling

%% Import and separation of data:

results40 = importdata('MyData_40K.txt'); *%Import temperature and mass loss data of 40K/min experiments*

results40.data; *%Retrieve results*

results25 = importdata('MyData_25K.txt'); *%Import temperature and mass loss data of 25K/min experiments*

results25.data; *%Retrieve results*

results10 = importdata('MyData_10K.txt'); *%Import temperature and mass loss data of 10K/min experiments*

results10.data; *%Retrieve results*

results5 = importdata('MyData_5K.txt'); *%Import temperature and mass loss data of 5K/min experiments*

results5.data; *%Retrieve results*

nHR = 4; *% Number of heating rate experiments used*

T40 = results40.data(:,1); *% Retrieve temperature data in Kelvin for the 40K/min experiment*

M40 = results40.data(:,2); *% Retrieve non-normalised mass data (dimensionless) for the 40K/min experiment*

T25 = results25.data(:,1); *% Retrieve temperature data in Kelvin for the 25K/min experiment*

M25 = results25.data(:,2); *% Retrieve non-normalised mass data (dimensionless) for the 25K/min experiment*

T10 = results10.data(:,1); *% Retrieve temperature data in Kelvin for the 10K/min experiment*

M10 = results10.data(:,2); *% Retrieve non-normalised mass data (dimensionless) for the 10K/min experiment*

T5 = results5.data(:,1); *% Retrieve temperature data in Kelvin for the 5K/min experiment*

M5 = results5.data(:,2); *% Retrieve non-normalised mass data (dimensionless) for the 5K/min experiment*

Tr5 = T5'; *% Transpose temperature vector for the 5K/min experiment*

Mr5 = M5'; *% Transpose mass loss vector for the 5K/min experiment*

Tr10 = T10'; *% Transpose temperature vector for the 10K/min experiment*

Mr10 = M10'; *% Transpose mass loss vector for the 10K/min experiment*

```

Tr25 = T25'; % Transpose temperature vector for the 25K/min experiment
Mr25 = M25'; % Transpose mass loss vector for the 25K/min experiment
Tr40 = T40'; % Transpose temperature vector for the 40K/min experiment
Mr40 = M40'; % Transpose mass loss vector for the 40K/min experiment
%% Conversion of mass loss data to fractional conversion and derivative dX/dT for the 5K/min
%% experiment

FX5(1,:) = Mr5(1,:)./Mr5(1,length(Mr5)); % Experimental fractional conversion FX = M/M0

dFX5(1,1)=(FX5(1,2)-FX5(1,1))/(Tr5(1,2)-Tr5(1,1));
for i=2:length(Tr5)-1
    dFX5(1,i)=(FX5(1,i+1)-FX5(1,i-1))/(Tr5(1,i+1)-Tr5(1,i-1));
end
dFX5(1,length(Tr5))=(FX5(1,length(Tr5))-FX5(1,length(Tr5)-1))/(Tr5(1,length(Tr5))-
Tr5(1,length(Tr5)-1));

dFX5f = sgolayfilt(dFX5,4,9); % Use of the Savitzky-Golay filter to smooth the derivative curve:
polynomial order of 4 and frame size of 9

%% Conversion of mass loss data to fractional conversion and derivative dX/dT for the 10K/min
%% experiment

FX10(1,:) = Mr10(1,:)./Mr10(1,length(Mr10)); % Experimental fractional conversion FX = M/M0

dFX10(1,1)=(FX10(1,2)-FX10(1,1))/(Tr10(1,2)-Tr10(1,1));
for i=2:length(Tr10)-1
    dFX10(1,i)=(FX10(1,i+1)-FX10(1,i-1))/(Tr10(1,i+1)-Tr10(1,i-1));
end
dFX10(1,length(Tr10))=(FX10(1,length(Tr10))-FX10(1,length(Tr10)-1))/(Tr10(1,length(Tr10))-
Tr10(1,length(Tr10)-1));

dFX10f = sgolayfilt(dFX10,4,9); % Use of the Savitzky-Golay filter to smooth the derivative
curve: polynomial order of 4 and frame size of 9

```

Appendix D: Reaction rate modelling

*%% Conversion of mass loss data to fractional conversion and derivative dX/dT for the 25K/min
%% experiment*

```
FX25(1,:) = Mr25(1,:)./Mr25(1,length(Mr25)); % Experimental fractional conversion FX = M/M0  
dFX25(1,1)=(FX25(1,2)-FX25(1,1))/(Tr25(1,2)-Tr25(1,1));  
for i=2:length(Tr25)-1  
    dFX25(1,i)=(FX25(1,i+1)-FX25(1,i-1))/(Tr25(1,i+1)-Tr25(1,i-1));  
end  
dFX25(1,length(Tr25))=(FX25(1,length(Tr25))-FX25(1,length(Tr25)-1))/(Tr25(1,length(Tr25))-  
    Tr25(1,length(Tr25)-1));  
  
dFX25f = sgolayfilt(dFX25,4,9); % Use of the Savitzky-Golay filter to smooth the derivative  
curve: polynomial order of 4 and frame size of 9
```

*%% Conversion of mass loss data to fractional conversion and derivative dX/dT for the 40K/min
%% experiment*

```
FX40(1,:) = Mr40(1,:)./Mr40(1,length(Mr40)); % Experimental fractional conversion FX = M/M0  
  
dFX40(1,1)=(FX40(1,2)-FX40(1,1))/(Tr40(1,2)-Tr40(1,1));  
for i=2:length(Tr40)-1  
    dFX40(1,i)=(FX40(1,i+1)-FX40(1,i-1))/(Tr40(1,i+1)-Tr40(1,i-1));  
end  
dFX40(1,length(Tr40))=(FX40(1,length(Tr40))-FX40(1,length(Tr40)-1))/(Tr40(1,length(Tr40))-  
    Tr40(1,length(Tr40)-1));  
  
dFX40f = sgolayfilt(dFX40,4,9); % Use of the Savitzky-Golay filter to smooth the derivative  
curve: polynomial order of 4 and frame size of 9
```

%% Equal spacing of temperature elements to ensure consistency for all three heating rates

```
n5 = length(Tr5);  
n10 = length(Tr10);  
n25 = length(Tr25);
```

```

n40 = length(Tr40);
Te = [linspace(Tr5(1,1),Tr5(1,n5),200);linspace(Tr5(1,1),Tr5(1,n5),200);
linspace(Tr5(1,1),Tr5(1,n5),200);linspace(Tr5(1,1),Tr5(1,n5),200)]; % Choosing equally spaced
elements of temperature
FXe = [interp1(Tr5,FX5,Te(1,:)); interp1(Tr10,FX10,Te(2,:));
interp1(Tr25,FX25,Te(3,:));interp1(Tr40,FX40,Te(4,:))]; % Interpolation of selected points on the
FX-curve
dFXe = [interp1(Tr5,dFX5f,Te(1,:)); interp1(Tr10,dFX10f,Te(2,:)); interp1(Tr25,dFX25f,Te(3,:));
interp1(Tr40,dFX40f,Te(4,:))]; % Interpolation of selected points on the dX-curve

%% Constants and initial values

nR = 3; % Number of reactions
R = 8.314; % Universal gas constant
beta = [5/60 10/60 25/60 40/60]; % Heating rate in K/s
A0 = [1e2 1e2 1e2]; % Initial values for the pre-exponential constant
EA0 = [1e1 1e1 1e1]; % Initial values for the activation energy
f0 = [0.2 0.2]; % Initial values for the fractional contributions

C_low = [0 0 0 0 0 0 0 0]; % Lower boundary conditions for constants
C_high = [inf inf 1 inf inf 1 inf inf]; % Higher boundary conditions for constants

dFXet = [beta(1,1)*dFXe(1,:); beta(1,2)*dFXe(2,:); beta(1,3)*dFXe(3,:); beta(1,4)*dFXe(4,:)]; %
Matrix containing dX/dtime experimental values

%% Loop for providing different initial values to the lsqcurvefit solver

RegressedConstants=[]; % Saves all the regressed constants in matrix form

for a = 1:1:150 %This for loop determines random new initial values for use in the lsqcurvefit
algorithm
    C0 = [A0(1)*(a)/10 EA0(1)*(a)/10 f0(1) A0(2)*(a)/10 EA0(2)*(a)/10 f0(2) A0(3)*(a)/10
EA0(3)*(a)/10];

```

Appendix D: Reaction rate modelling

% Lsqcurvefit is done in two sequences where the error is gradually lowered to a lower value

```
options = optimset('Algorithm','levenberg-marquardt','Display','iter','TolFun', 1e-10,'TolX',  
1e-08,'MaxFunEvals',500000,'MaxIter', 50000);
```

```
[Ci,resnorm,residual,exitflag,output,lambda,jacobian]=lsqcurvefit('Pseudo_3M3HR',C0,Te,  
dFXet,C_low,C_high,options);
```

C0 = Ci; % Replace values in Ci into C0

```
options = optimset('Algorithm','levenberg-marquardt','Display','iter','TolFun', 1e-10,'TolX',  
1e-10,'MaxFunEvals',500000,'MaxIter', 50000);
```

```
[Ci,resnorm,residual,exitflag,output,lambda,jacobian]=lsqcurvefit('Pseudo_3M3HR',C0,Te,  
dFXet,C_low,C_high,options);
```

*A0_end = [C0(1)*1e8 C0(4)*1e8 C0(7)*1e8]; % Vector of regressed pre-exponential constants*

*EA0_end = [C0(2)*1e4 C0(5)*1e4 C0(8)*1e4]; % Vector of regressed activation energies*

f0_end = [C0(3) C0(6) 1-C0(3)-C0(6)]; % Vector of regressed fractional contributions

resnorm; % Returns the value for the residual sum of squares

```
RegressedValues = [A0_end(1) EA0_end(1) f0_end(1) A0_end(2) EA0_end(2) f0_end(2)  
A0_end(3) EA0_end(3) f0_end(3) resnorm];
```

```
RegressedConstants = [RegressedConstants; RegressedValues];
```

end

```
[r,s] = size(RegressedConstants); % Calculates the size of the regressed matrix
```

```
k = 1;
```

% This loop searches the regressed matrix for a solution where f0_end(3) is not smaller than 0

```

for j = 1:1:r
    if (RegressedConstants(j,9)<0)
    else
        Constants_New(k,:) = RegressedConstants(j,:);
        k = k+1;
    end
end

[r1,s1] = size(Constants_New); % Calculates the size of filtered regressed matrix

minimum = min(Constants_New(:,10)); % Searches for the minimum residual sum of squares in the filtered regressed matrix

%% This loop searches for the smallest residual sum of squares and returns the respective kinetic parameters sought after

for i = 1:1:r1
    if (Constants_New(i,10) == minimum)
        KParam(1,:) = Constants_New(i,:);
    end
end

%% Solved kinetic parameters for the different reactions

KParam_R1 = [KParam(1,1) KParam(1,2) KParam(1,3)]; % Reaction 1
KParam_R2 = [KParam(1,4) KParam(1,5) KParam(1,6)]; % Reaction 2
KParam_R3 = [KParam(1,7) KParam(1,8) KParam(1,9)]; % Reaction 3

%% Calculating the model curves from the obtained parameters

for s = 1:nHR
    K1_1_end(1,s) = KParam_R1(1)/beta(1,s); % Reaction 1
    K1_2_end = KParam_R1(2)./(R); % Reaction 1
    K2_1_end(1,s) = KParam_R2(1)/beta(1,s); % Reaction 2

```

Appendix D: Reaction rate modelling

```
K2_2_end = KParam_R2(2)./(R); % Reaction 2
```

```
K3_1_end(1,s) = KParam_R3(1)/beta(1,s); % Reaction 3
```

```
K3_2_end = KParam_R3(2)./(R); % Reaction 3
```

```
end
```

```
Predict5 = [K1_1_end(1,1) K1_2_end KParam_R1(3); K2_1_end(1,1)  
K2_2_end KParam_R2(3); K3_1_end(1,1) K3_2_end KParam_R3(3)];  
Predict10 = [K1_1_end(1,2) K1_2_end KParam_R1(3); K2_1_end(1,2)  
K2_2_end KParam_R2(3); K3_1_end(1,2) K3_2_end KParam_R3(3)];  
Predict25 = [K1_1_end(1,3) K1_2_end KParam_R1(3); K2_1_end(1,3)  
K2_2_end KParam_R2(3); K3_1_end(1,3) K3_2_end KParam_R3(3)];  
Predict40 = [K1_1_end(1,4) K1_2_end KParam_R1(3); K2_1_end(1,4)  
K2_2_end KParam_R2(3); K3_1_end(1,4) K3_2_end KParam_R3(3)];
```

```
%% For loop for initializing model curves for 5K/min
```

```
for m = 1:nR
```

```
    for t = 1:length(Te(1,:))
```

```
        XFP5(m,t) = Predict5(m,3).*(1-exp(-Predict5(m,1).*(Predict5(m,2)).*  
        ((exp(-Predict5(m,2)./Te(1,t))./(Predict5(m,2)./Te(1,t)))-expint(Predict5(m,2)./Te(1,t)))));
```

```
    end
```

```
    dXFP5(m,1)=(XFP5(m,2)-XFP5(m,1))/(Te(1,2)-Te(1,1));
```

```
    for j=2:length(Te(2,:))-1
```

```
        dXFP5(m,j)=(XFP5(m,j+1)-XFP5(m,j-1))/(Te(1,j+1)-Te(1,j-1));
```

```
    end
```

```
    dXFP5(m,length(Te(1,:)))=(XFP5(m,length(Te(1,:)))-XFP5(m,length(Te(2,:))-  
    1))/(Te(1,length(Te(1,:)))-Te(1,length(Te(1,:))-1));
```

```
    XFPT5=sum(XFP5); % Initialize conversion matrix of model
```

```
    dXFPT5=sum(dXFP5);
```

```
end
```

```
dXFPT5C= beta(1,1).*dXFP5;
```

```
dXFPT5= beta(1,1).*dXFPT5;
```

%% For loop for initializing model curves for 10K/min

```

for m = 1:nR
    for t = 1:length(Te(2,:))
        XFP10(m,t) = Predict10(m,3).*(1-exp(-Predict10(m,1).*(Predict10(m,2)).*
        ((exp(-Predict10(m,2)./Te(2,t))./(Predict10(m,2)./Te(2,t)))-expint(Predict10(m,2)./Te(2,t)))));
    end
    dXFP10(m,1)=(XFP10(m,2)-XFP10(m,1))/(Te(2,2)-Te(2,1));
    for j=2:length(Te(2,:))-1
        dXFP10(m,j)=(XFP10(m,j+1)-XFP10(m,j-1))/(Te(2,j+1)-Te(2,j-1));
    end
    dXFP10(m,length(Te(2,:)))=(XFP10(m,length(Te(2,:)))-XFP10(m,length(Te(2,:))-
    1))/(Te(2,length(Te(2,:)))-Te(2,length(Te(2,:))-1));

    XFPT10=sum(XFP10); % Initialize conversion matrix of model
    dXFPT10=sum(dXFP10);
end

dXFPT10C= beta(1,2).*dXFP10;
dXFPT10 = beta(1,2).*dXFPT10;

```

%% For loop for initializing model curves for 25K/min

```

for m = 1:nR
    for t = 1:length(Te(3,:))
        XFP25(m,t) = Predict25(m,3).*(1-exp(-Predict25(m,1).*(Predict25(m,2)).*
        ((exp(-Predict25(m,2)./Te(3,t))./(Predict25(m,2)./Te(3,t)))-expint(Predict25(m,2)./Te(3,t)))));
    end
    dXFP25(m,1)=(XFP25(m,2)-XFP25(m,1))/(Te(3,2)-Te(3,1));
    for j=2:length(Te(3,:))-1
        dXFP25(m,j)=(XFP25(m,j+1)-XFP25(m,j-1))/(Te(3,j+1)-Te(3,j-1));
    end
    dXFP25(m,length(Te(3,:)))=(XFP25(m,length(Te(3,:)))-XFP25(m,length(Te(3,:))-

```

```
1))/(Te(3,length(Te(3,:))-Te(3,length(Te(3,:))-1));

XFPT25=sum(XFP25); % Initialize conversion matrix of model
dXFPT25=sum(dXFP25);
end

dXFPT25C= beta(1,3).*dXFP25;
dXFPT25 = beta(1,3).*dXFPT25;

dXFPHR = [dXFPT5; dXFPT10; dXFPT25];

%% For loop for initializing model curves for 40K/min

for m = 1:nR
    for t = 1:length(Te(4,:))
        XFP40(m,t) = Predict40(m,3).*(1-exp(-Predict40(m,1).*(Predict40(m,2)).*
        ((exp(-Predict40(m,2)./Te(4,t))./(Predict40(m,2)./Te(4,t)))-expint(Predict40(m,2)./Te(4,t)))));
    end
    dXFP40(m,1)=(XFP40(m,2)-XFP40(m,1))/(Te(4,2)-Te(4,1));
    for j=2:length(Te(4,:))-1
        dXFP40(m,j)=(XFP40(m,j+1)-XFP40(m,j-1))/(Te(4,j+1)-Te(4,j-1));
    end
    dXFP40(m,length(Te(4,:)))=(XFP40(m,length(Te(4,:)))-XFP40(m,length(Te(4,:))-
    1))/(Te(4,length(Te(4,:))-Te(4,length(Te(4,:))-1));

    XFPT40=sum(XFP40); % Initialize conversion matrix of model
    dXFPT40=sum(dXFP40);
end

dXFPT40C= beta(1,4).*dXFP40;
dXFPT40 = beta(1,4).*dXFPT40;

dXFPHR = [dXFPT5; dXFPT10; dXFPT25; dXFPT40];
```

%% Calculating the objective function and quality of fit

```
for l = 1:nHR
    Err(l,:) = (dFXet(l,:)-dXFPHR(l,:)).^2;
    ESS = sum(Err);
    Term(l,:) = (sqrt(Err(l,:))./length(Te(1,:))./max(dFXet(l,:)));
    TermT(l,:) = (sqrt(Err(l,:))./(nHR.*length(Te(1,:))./max(dFXet(l,:)));
end
```

```
TermTsum = sum(TermT);
OBF = sum(ESS);
QOF5 = 100*sum(Term(1,:)); % Estimate quality of fit
QOF10 = 100*sum(Term(2,:)); % Estimate quality of fit
QOF25 = 100*sum(Term(3,:)); % Estimate quality of fit
QOF40 = 100*sum(Term(4,:)); % Estimate quality of fit
QOF = 100*sum(TermTsum); % Estimate quality of fit
```

%% Plots of experimental data against model data

```
subplot(2,4,1)
plot(Te(1,:),FXe(1,:),'--rs',Te(1,:),XFPT5,'-', 'Color','k','LineWidth',2, 'MarkerEdgeColor',
'r','MarkerSize',4);
xlabel('Temperature [K]');
ylabel('Fractional Conversion [-]');
subplot(2,4,2)
plot(Te(1,:),dFXe(1,:),'--rs',Te(1,:),dXFP5(1,:),'-',Te(1,:),dXFP5(2,:),'-',Te(1,:),dXFP5(3,:),'-',
Te(1,:),dXFPT5,'-');
xlabel('Temperature [K]');
ylabel('Rate dX/dt [min^-1]');
hold on
hold off
```

%% Plots of experimental data against model data

```
subplot(2,4,3)
plot(Te(2,:),FXe(2,:), '--rs', Te(2,:),XFPT10, '-', 'Color','k','LineWidth',2, 'MarkerEdgeColor','r',
'MarkerSize',4);
xlabel('Temperature [K]');
ylabel('Fractional Conversion [-]');
subplot(2,4,4)
plot(Te(2,:),dFXe(2,:), '--rs', Te(2,:),dXFP10(1,:), '-', Te(2,:),dXFP10(2,:), '-', Te(2,:),dXFP10(3,:), '-',
Te(2,:),dXFPT10, '-');
xlabel('Temperature [K]');
ylabel('Rate dX/dt [min^-1]');
hold on
hold off
```

%% Plots of experimental data against model data

```
subplot(2,4,5)
plot(Te(3,:),FXe(3,:), '--rs', Te(3,:),XFPT25, '-', 'Color','k','LineWidth',2, 'MarkerEdgeColor','r',
'MarkerSize',4);
xlabel('Temperature [K]');
ylabel('Fractional Conversion [-]');
subplot(2,4,6)
plot(Te(3,:),dFXe(3,:), '--rs', Te(3,:),dXFP25(1,:), '-', Te(3,:),dXFP25(2,:), '-', Te(3,:),dXFP25(3,:), '-',
Te(3,:),dXFPT25, '-');
xlabel('Temperature [K]');
ylabel('Rate dX/dt [min^-1]');
hold on
hold off
```

%% Plots of experimental data against model data

```
subplot(2,4,7)
plot(Te(4,:),FXe(4,:), '--rs', Te(4,:),XFPT40, '-', 'Color','k','LineWidth',2, 'MarkerEdgeColor','r',
```

```
'MarkerSize',4);
xlabel('Temperature [K]');
ylabel('Fractional Conversion [-]');
subplot(2,4,8)
plot(Te(4,:),dFXe(4,:), '--rs', Te(4,:),dXFP40(1,:), '- ', Te(4,:),dXFP40(2,:), '- ', Te(4,:),dXFP40(3,:), '- '
, Te(4,:),dXFPT40, '- ');
xlabel('Temperature [K]');
ylabel('Rate dX/dt [min^-1]');
hold on
hold off
```

%% Writing the modelling results for 5K/min to a txt file

```
y1 = [Te(1,:);dFXe(1,:);XFP5(1,:);dXFP5(1,:);XFP5(2,:);dXFP5(2,:);XFP5(3,:);dXFP5(3,:);
XFPT5(1,:);dXFPT5(1,:)];
fid = fopen('Modelling_Results_5K.txt', 'w');
fprintf(fid, 'Modelling results for the 5K/min experiment\n');
fprintf(fid, '%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s', 'Temperature(K)', 'dX/dT(exp)',
'XFP1_5', 'dXFP1_5', 'XFP2_5', 'dXFP2_5', 'XFP3_5', 'dXFP3_5', 'XFPT_5', 'dXFPT_5');
fprintf(fid, '\n');
fprintf(fid, '%f %f %f %f %f %f %f %f %f %f %f\n', y1);
fclose(fid);
```

%% Writing the modelling results for 10K/min to a txt file

```
y2 = [Te(2,:);dFXe(2,:);XFP10(1,:);dXFP10(1,:);XFP10(2,:);dXFP10(2,:);XFP10(3,:);dXFP10(3,:);
XFPT10(1,:);dXFPT10(1,:)];
fid = fopen('Modelling_Results_10K.txt', 'w');
fprintf(fid, 'Modelling results for the 5K/min experiment\n');
fprintf(fid, '%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s', 'Temperature(K)', 'dX/dT(exp)',
'XFP1_10', 'dXFP1_10', 'XFP2_10', 'dXFP2_10', 'XFP3_10', 'dXFP3_10', 'XFPT_10', 'dXFPT_10');
fprintf(fid, '\n');
fprintf(fid, '%f %f %f %f %f %f %f %f %f %f %f\n', y2);
fclose(fid);
```

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%% Writing the modelling results for 25K/min to a txt file

```
y3 = [Te(3,:);dFXe(3,:);XFP25(1,:);dXFP25(1,:);XFP25(2,:);dXFP25(2,:);XFP25(3,:);dXFP25(3,:);
XFPT25(1,:);dXFPT25(1,:)];
fid = fopen('Modelling_Results_25K.txt', 'w');
fprintf(fid, 'Modelling results for the 5K/min experiment\n');
fprintf(fid, '%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s', 'Temperature(K)', 'dX/dT(exp)',
'XFP1_25', 'dXFP1_25', 'XFP2_25', 'dXFP2_25', 'XFP3_25', 'dXFP3_25', 'XFPT_25', 'dXFPT_25');
fprintf(fid, '\n');
fprintf(fid, '%f %f %f %f %f %f %f %f %f %f %f %f', y3);
fclose(fid);
```

%% Writing the modelling results for 40K/min to a txt file

```
y4 = [Te(4,:);dFXe(4,:);XFP40(1,:);dXFP40(1,:);XFP40(2,:);dXFP40(2,:);XFP40(3,:);dXFP40(3,:);
XFPT40(1,:);dXFPT40(1,:)];
fid = fopen('Modelling_Results_40K.txt', 'w');
fprintf(fid, 'Modelling results for the 5K/min experiment\n');
fprintf(fid, '%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s', 'Temperature(K)', 'dX/dT(exp)',
'XFP1_40', 'dXFP1_40', 'XFP2_40', 'dXFP2_40', 'XFP3_40', 'dXFP3_40', 'XFPT_40', 'dXFPT_40');
fprintf(fid, '\n');
fprintf(fid, '%f %f %f %f %f %f %f %f %f %f %f %f', y4);
fclose(fid);
```

% Writing the solved kinetic parameters to a txt file

```
y5 = [KParam_R1 KParam_R2 KParam_R3 OBF QOF5 QOF10 QOF25 QOF40 QOF];
fid = fopen('Derived_Kinetic_Param.txt', 'w');
fprintf(fid, 'Kinetic parameters\n');
fprintf(fid, '%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s',
'A1', 'EA1', 'f1', 'A2', 'EA2', 'f2', 'A3', 'EA3', 'f3', 'OBF', 'QOF5', 'QOF10', 'QOF25', 'QOF40', 'QOF');
fprintf(fid, '\n');
fprintf(fid, '%f \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s \t%s', y5);
fclose(fid);
```

D.1.2 MATLAB 7.1.1 script for Pseudo 3M3HR function file

%% MATLAB script for Pseduo_3M3HR Function file

function dFXF = Pseudo_3M3HR(Ci,Te)

R = 8.314; *% Universal gas constant*

Beta = [5/60 10/60 25/60 40/60]; *% Matrix of heating rates in K/s*

nHR = 4; *% Number of heating rates*

%% Scaling of kinetic rate constants

A1 = Ci(1)*1e8;

E1 = Ci(2)*1e4;

f1 = Ci(3);

A2 = Ci(4)*1e8;

E2 = Ci(5)*1e4;

f2 = Ci(6);

A3 = Ci(7)*1e8;

E3 = Ci(8)*1e4;

% t_variables used in the integral approximation algorithm

t1_5(1,:)=E1./(R.*Te(1,:)); *% t_values for 5 K/min*

t2_5(1,:)=E2./(R.*Te(1,:)); *% t_values for 5 K/min*

t3_5(1,:)=E3./(R.*Te(1,:)); *% t_values for 5 K/min*

t1_10(1,:)=E1./(R.*Te(2,:)); *% t_values for 10 K/min*

t2_10(1,:)=E2./(R.*Te(2,:)); *% t_values for 10 K/min*

t3_10(1,:)=E3./(R.*Te(2,:)); *% t_values for 10 K/min*

t1_25(1,:)=E1./(R.*Te(3,:)); *% t_values for 25 K/min*

t2_25(1,:)=E2./(R.*Te(3,:)); *% t_values for 25 K/min*

t3_25(1,:)=E3./(R.*Te(3,:)); *% t_values for 25 K/min*

t1_40(1,:)=E1./(R.*Te(4,:)); *% t_values for 40 K/min*

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```
t2_40(1,:)=E2./(R.*Te(4,:)); % t_values for 40 K/min
```

```
t3_40(1,:)=E3./(R.*Te(4,:)); % t_values for 40 K/min
```

```
%% Pseudo-component model for 5 K/min:
```

```
FXF5(1,:) = ((f1.*(1-exp(-A1./Beta(1,1).*(E1/R).*((exp(-t1_5)./t1_5)-expint(t1_5)))))+  
(f2.*(1-exp(-A2./Beta(1,1).*(E2/R).*((exp(-t2_5)./t2_5)-expint(t2_5)))))+  
((1-f1-f2).*(1-exp(-A3./Beta(1,1).*(E3/R).*((exp(-t3_5)./t3_5)-expint(t3_5))))));
```

```
%% Pseudo-component model for 10 K/min:
```

```
FXF10(1,:) = ((f1.*(1-exp(-A1./Beta(1,2).*(E1/R).*((exp(-t1_10)./t1_10)-expint(t1_10)))))+  
(f2.*(1-exp(-A2./Beta(1,2).*(E2/R).*((exp(-t2_10)./t2_10)-expint(t2_10)))))+  
((1-f1-f2).*(1-exp(-A3./Beta(1,2).*(E3/R).*((exp(-t3_10)./t3_10)-expint(t3_10))))));
```

```
%% Pseudo-component model for 25 K/min:
```

```
FXF25(1,:) = ((f1.*(1-exp(-A1./Beta(1,3).*(E1/R).*((exp(-t1_25)./t1_25)-expint(t1_25)))))+  
(f2.*(1-exp(-A2./Beta(1,3).*(E2/R).*((exp(-t2_25)./t2_25)-expint(t2_25)))))+  
((1-f1-f2).*(1-exp(-A3./Beta(1,3).*(E3/R).*((exp(-t3_25)./t3_25)-expint(t3_25))))));
```

```
%% Pseudo-component model for 40 K/min:
```

```
FXF40(1,:) = ((f1.*(1-exp(-A1./Beta(1,4).*(E1/R).*((exp(-t1_40)./t1_40)-expint(t1_40)))))+  
(f2.*(1-exp(-A2./Beta(1,4).*(E2/R).*((exp(-t2_40)./t2_40)-expint(t2_40)))))+  
((1-f1-f2).*(1-exp(-A3./Beta(1,4).*(E3/R).*((exp(-t3_40)./t3_40)-expint(t3_40))))));
```

```
%% Generate derivative model curve for 5 K/min:
```

```
dFXF5(1,1)=(FXF5(1,2)-FXF5(1,1))/(Te(1,2)-Te(1,1));
```

```
for i=2:length(Te(1,:))-1
```

```
dFXF5(1,i)=(FXF5(1,i+1)-FXF5(1,i-1))/(Te(1,i+1)-Te(1,i-1));
```

```
end
```

```
dFXF5(1,length(Te(1,:)))=(FXF5(1,length(Te(1,:)))-FXF5(1,length(Te(1,:))-1))/  
(Te(1,length(Te(1,:)))-Te(1,length(Te(1,:))-1));
```

```
%% Generate derivative model curve for 10 K/min:
```

```
dFXF10(1,1)=(FXF10(1,2)-FXF10(1,1))/(Te(2,2)-Te(2,1));
```

```
for i=2:length(Te(2,:))-1
```

```
dFXF10(1,i)=(FXF10(1,i+1)-FXF10(1,i-1))/(Te(2,i+1)-Te(2,i-1));
```

end

```
dFXF10(1,length(Te(2,:)))=(FXF10(1,length(Te(2,:)))-FXF10(1,length(Te(2,:))-1))/
(Te(2,length(Te(2,:)))-Te(2,length(Te(2,:))-1));
```

%% Generate derivative model curve for 25 K/min:

```
dFXF25(1,1)=(FXF25(1,2)-FXF25(1,1))/(Te(3,2)-Te(3,1));
```

for i=2:length(Te(3,:))-1

```
dFXF25(1,i)=(FXF25(1,i+1)-FXF25(1,i-1))/(Te(3,i+1)-Te(3,i-1));
```

end

```
dFXF25(1,length(Te(3,:)))=(FXF25(1,length(Te(3,:)))-FXF25(1,length(Te(3,:))-1))/
(Te(3,length(Te(3,:)))-Te(3,length(Te(3,:))-1));
```

%% Generate derivative model curve for 40 K/min:

```
dFXF40(1,1)=(FXF40(1,2)-FXF40(1,1))/(Te(4,2)-Te(4,1));
```

for i=2:length(Te(4,:))-1

```
dFXF40(1,i)=(FXF40(1,i+1)-FXF40(1,i-1))/(Te(4,i+1)-Te(4,i-1));
```

end

```
dFXF40(1,length(Te(4,:)))=(FXF40(1,length(Te(4,:)))-FXF40(1,length(Te(4,:))-1))/
(Te(4,length(Te(4,:)))-Te(4,length(Te(4,:))-1));
```

%% Generate derivative matrix for all four heating rates:

```
dFXF = [Beta(1,1).*dFXF5; Beta(1,2).*dFXF10; Beta(1,3).*dFXF25; Beta(1,4).*dFXF40];
```

D.2 Scaling of the intrinsic rate equation for volatile release

According to the pseudo-component modelling approach, the total rate of volatile evolution can be described by the following equation:

$$\frac{dV_t}{dt} = \sum_i^n \frac{dV_i}{dt} \quad \text{Equation (D.1)}$$

Volatile matter yields of each pseudo-component as well as the overall process can also be expressed in terms of fractional conversion with the aid of the following two equations:

$$X_i = \frac{V_i}{V_i^*} \quad \text{Equation (D.2a)}$$

and

$$X_{v,t} = \frac{V_t}{V_t^*} \quad \text{Equation (D.2b)}$$

With the inclusion of first order kinetic expressions for each pseudo-component, Equation (D.1) subsequently translates to the following mathematical expression describing the release of total volatiles:

$$V_t^* \cdot \frac{dX_{v,t}}{dt} = \sum_i^n V_i^* k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i) \quad \text{Equation (D.3)}$$

Rearranging to account for the fractional contribution of each pseudo-component provides the following:

$$\frac{dX_{v,t}}{dt} = \sum_i^n \frac{V_i^*}{V_t^*} k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i) = \sum_i^n \xi_i k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i) \quad \text{Equation (D.4)}$$

Solution of the above equation requires the normalisation of the overall mass loss curve in order to derive the respective fractional contribution and kinetic parameters of each pseudo-component. For this investigation intrinsic kinetic parameters and fractional contributions were

derived from normalised, non-isothermal TG results obtained at four different heating rates and a final isothermal temperature of 950°C. The use of a different final isothermal temperature would therefore require the re-normalisation of experimental data according to the final mass loss value obtained at the new isothermal temperature. As an illustration, Figure D.1 provides typical isothermal simulations of the devolatilization rate of coal UMZ using the derived kinetic parameters and two different isothermal temperatures.

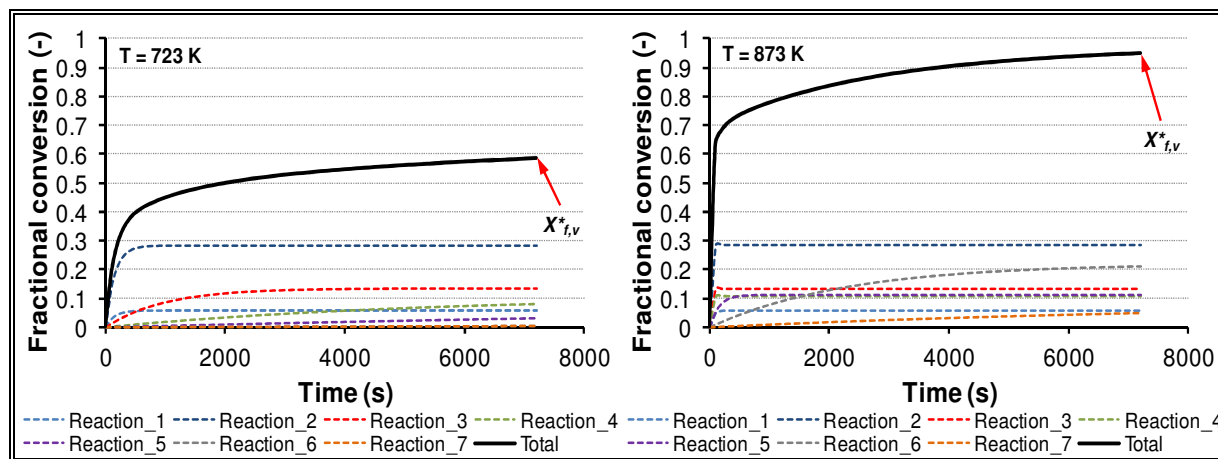


Figure D.1 Isothermal small particle simulation studies using derived kinetic parameters.

From the Figure it is evident that the use of the derived intrinsic, kinetic parameters yields final conversion values of below 1 for some temperatures lower in value than those used during non-isothermal analysis. This is overcome by re-scaling/re-normalisation of the conversion values according to the final constant conversion value ($X_{f,v}^*$), determined through the simulation of isothermal small particle devolatilization, in order to enable direct multiplication with the final ultimate volatile yield at fixed operating conditions (in theory X_i should approach 1 in the limit as t approaches ∞). In mathematical terms this can be expressed as:

$$X_{f,v}^* \frac{dX'_{v,t}}{dt} = \sum_i^n \xi_i k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i) \text{ where } X'_{v,t} = \frac{X_{v,t}}{X_{f,v}^*} \quad \text{Equation (D.5a)}$$

Or more generally as:

$$\frac{dX'_{v,t}}{dt} = \frac{1}{X_{f,v}^*} \sum_i^n \xi_i k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i) \quad \text{Equation (D.5b)}$$

Appendix D: Reaction rate modelling

The above equation can then be included with the term accounting for moisture evolution into an overall rate equation describing the release of total volatile matter (moisture and volatiles) as shown in Equation (7.10a):

$$\frac{dV_{t,T}}{dt} = V_a^* \cdot k_{0,a} \cdot \exp\left(\frac{-E_{a,a}}{RT}\right) \cdot (1 - X_a) + \frac{(V_{t,T}^* - V_a^*)}{X_{f,v}^*} \cdot \sum_{i=j}^7 \xi_i^* k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \cdot (1 - X_i)$$

Equation (7.10a)

Time- and temperature dependent values of the total ultimate volatile matter yield (moisture and volatiles) ($V_{t,T}^*$) and the ultimate amount of moisture released (V_a^*) can be directly derived from thermogravimetric results obtained during large particle devolatilization.

D.3 Repeatability curves obtained from small particle TGA

A summary of the results obtained from repeatability measurements during the non-isothermal TG analysis of the four different coals at 5K/min is provided in Figure D.2.

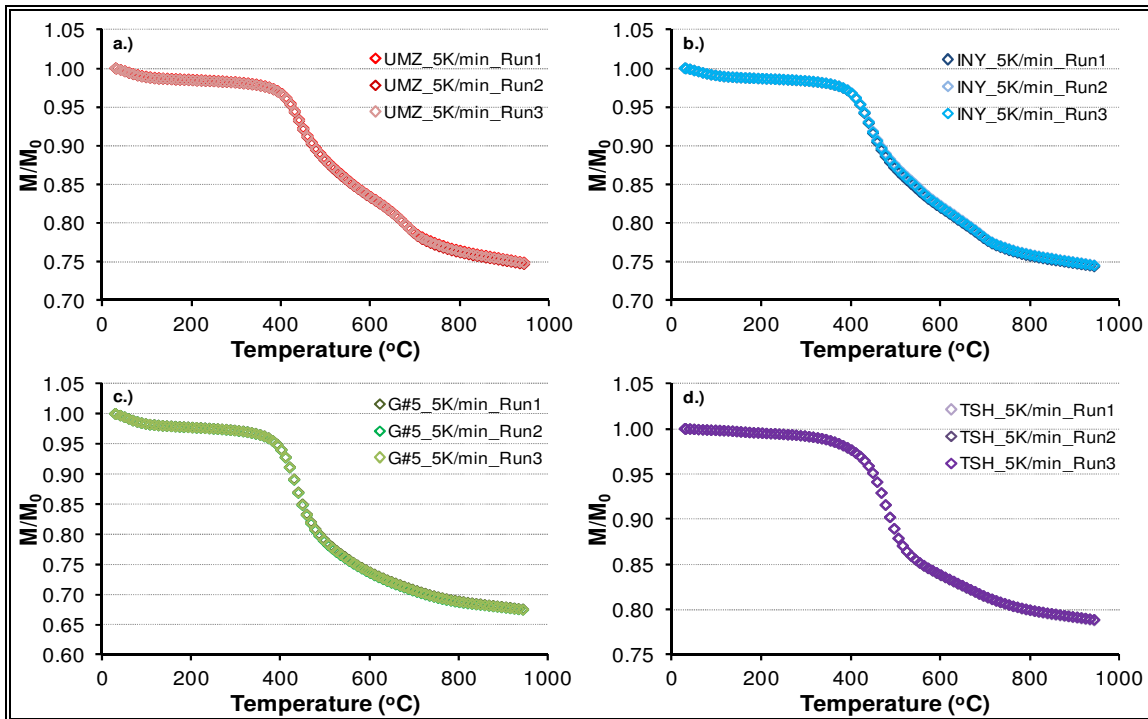


Figure D.2 Repeatability curves obtained for coals a.) UMZ, b.) INY, c.) G#5 and d.) TSH at 5 K/min.

D.4 Qualitative physical changes during large particle devolatilization

Figures D.3 and D.4 provide an overview of qualitative changes occurring in the physical structure of large coal particles derived from inertinite-rich and vitrinite-rich coals, respectively.

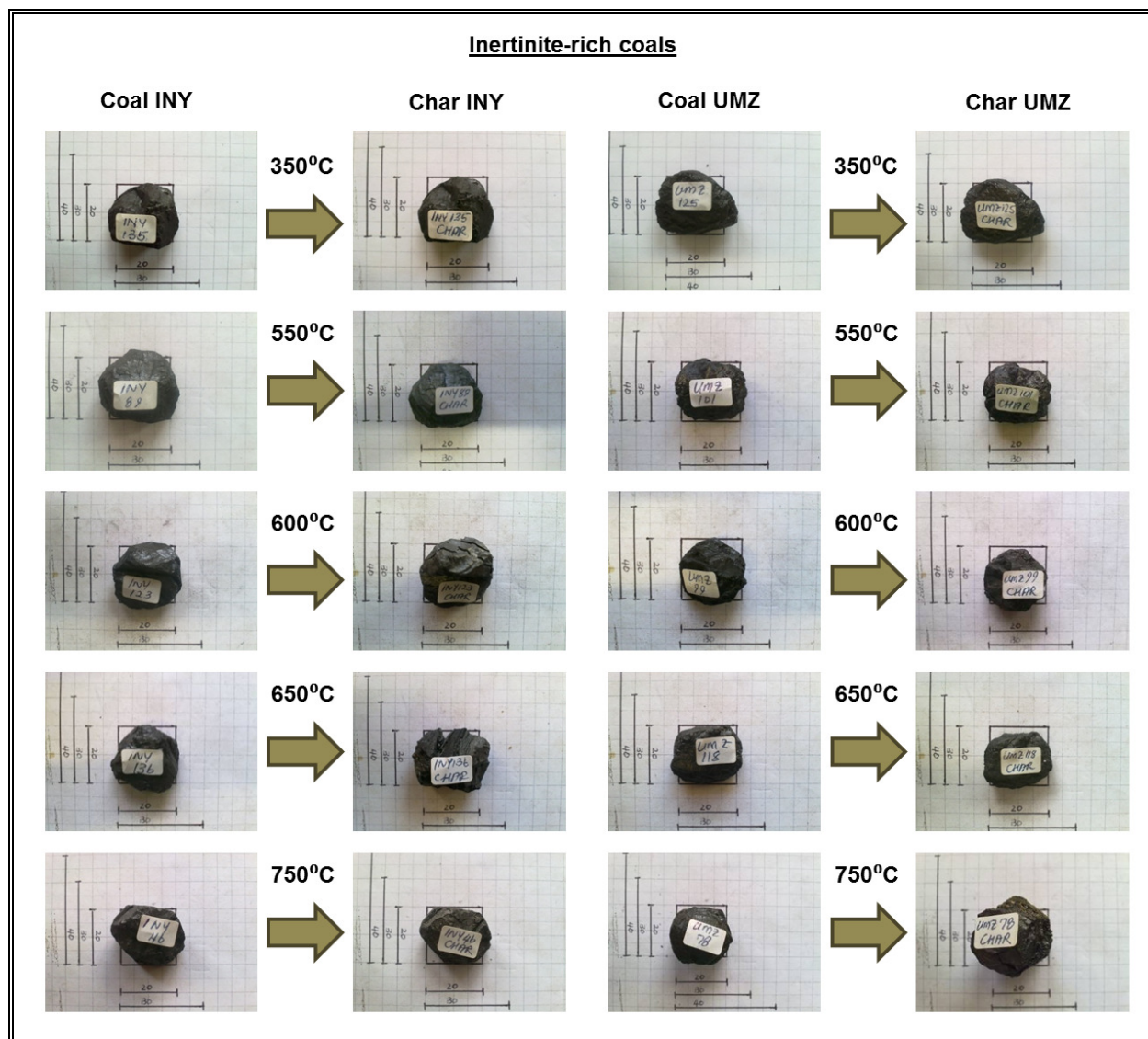


Figure D.3 Particles from inertinite-rich coal before and after devolatilization at 350, 550, 600, 650 and 750 °C.

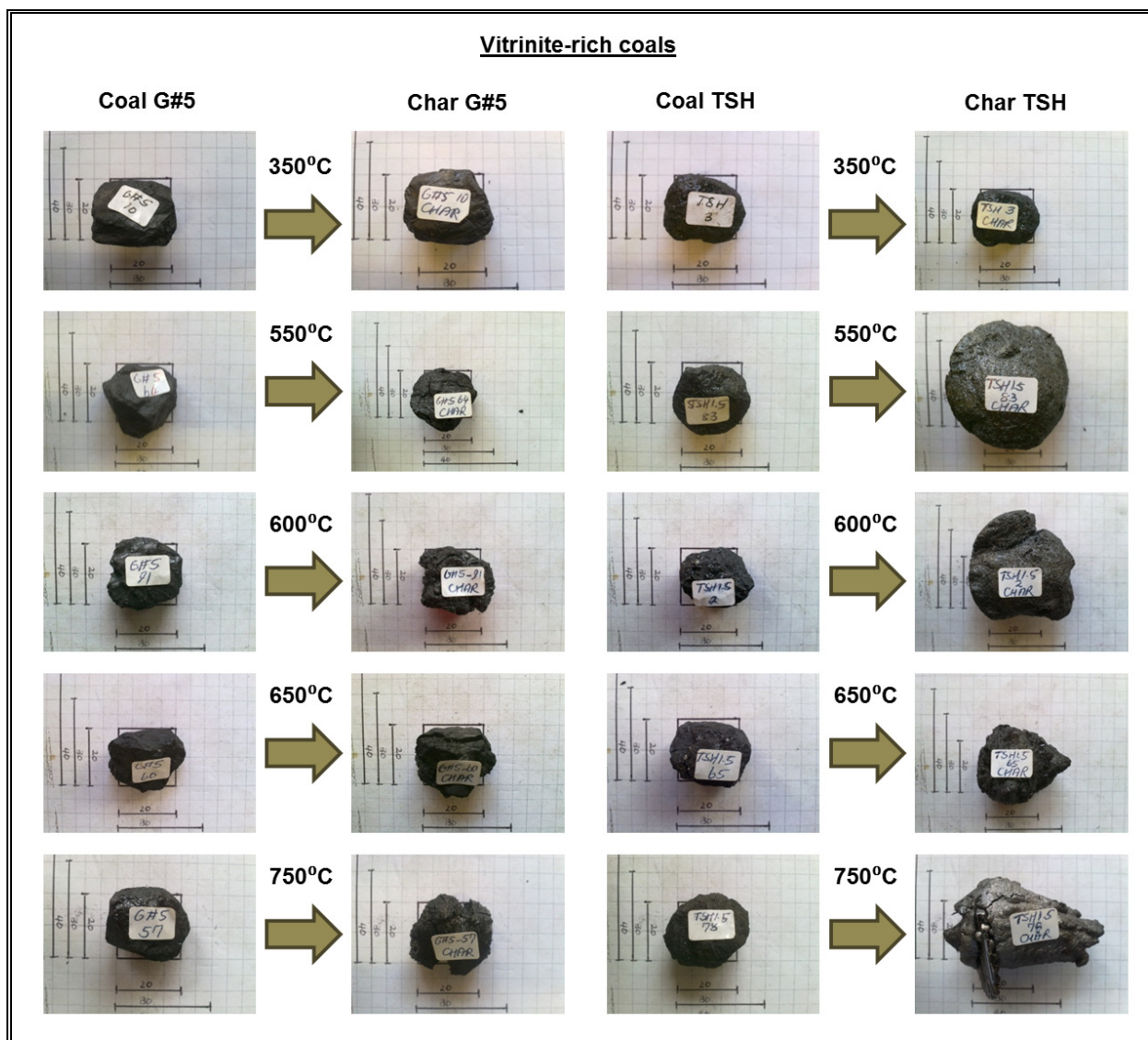


Figure D.4 Particles from vitrinite-rich coal before and after devolatilization at 350, 550, 600, 650 and 750 °C.

D.5 Repeatability curves obtained from large particle TGA

This appendix provides a summary of the results obtained from isothermal TG analysis of the 20 mm coal particles at the seven different temperatures (350°C to 900°C). Results for each temperature are provided respectively in Figures D.5 to D.11.

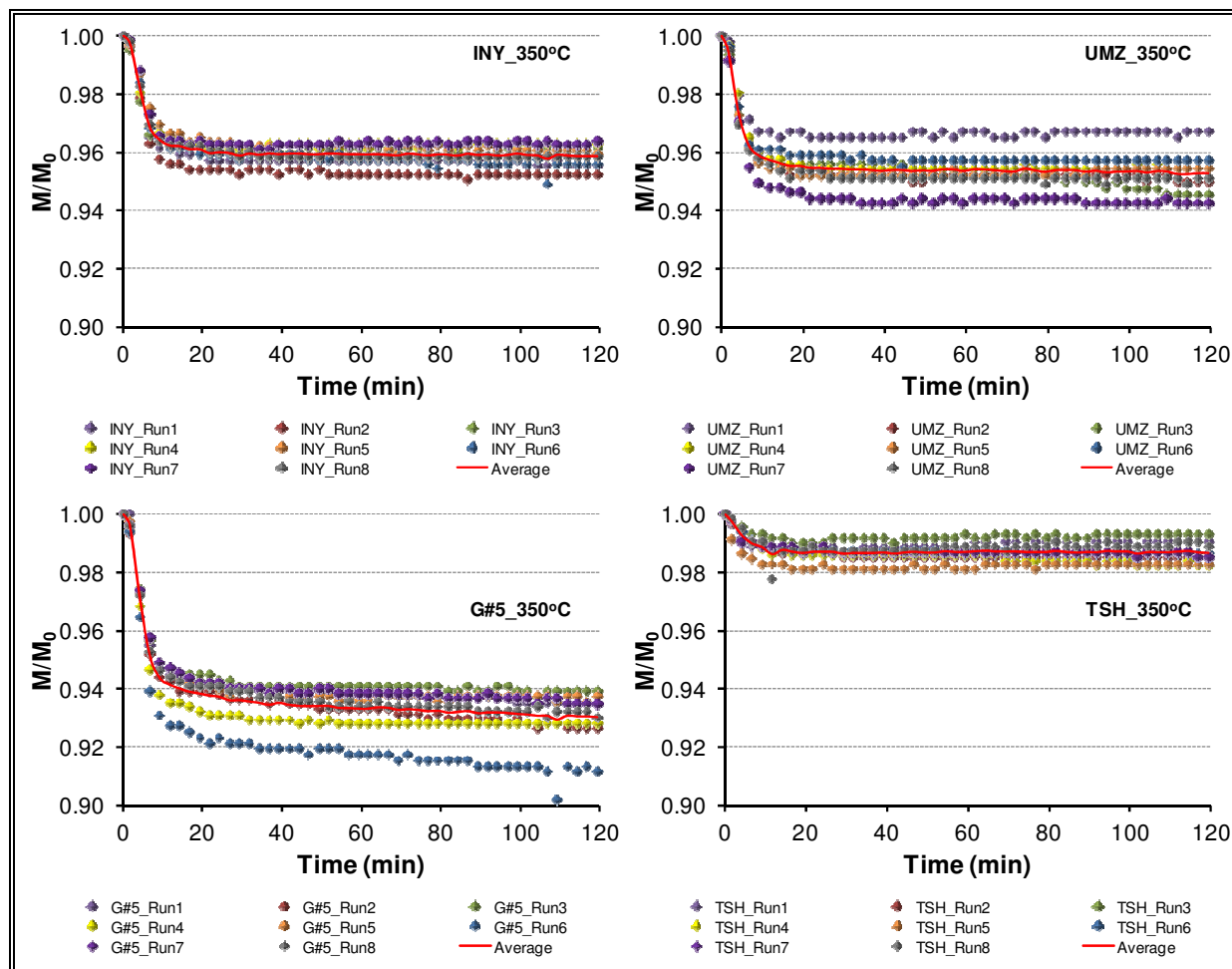


Figure D.5 Normalised devolatilization results for all four coals at 350°C.

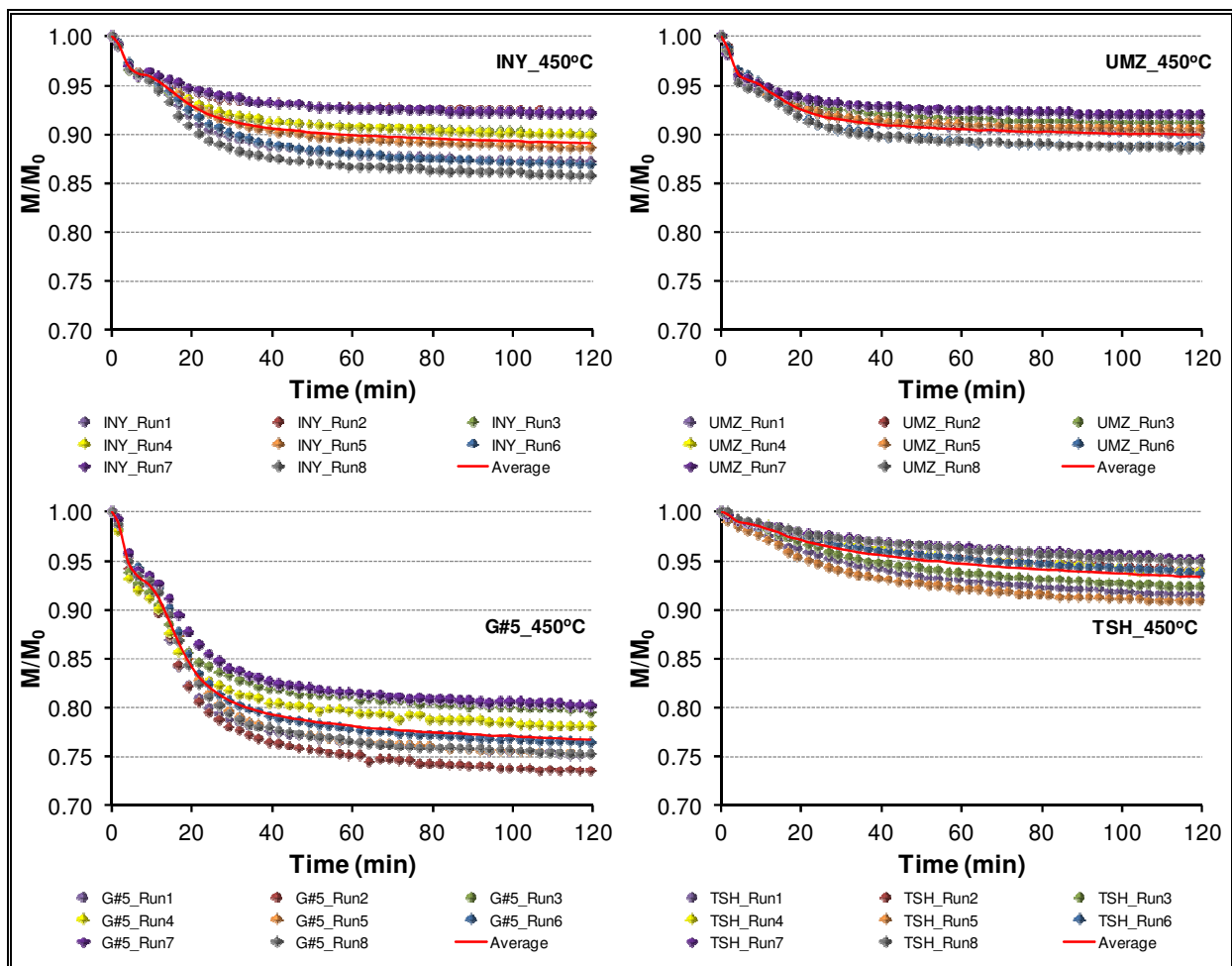


Figure D.6 Normalised devolatilization results for all four coals at 450°C.

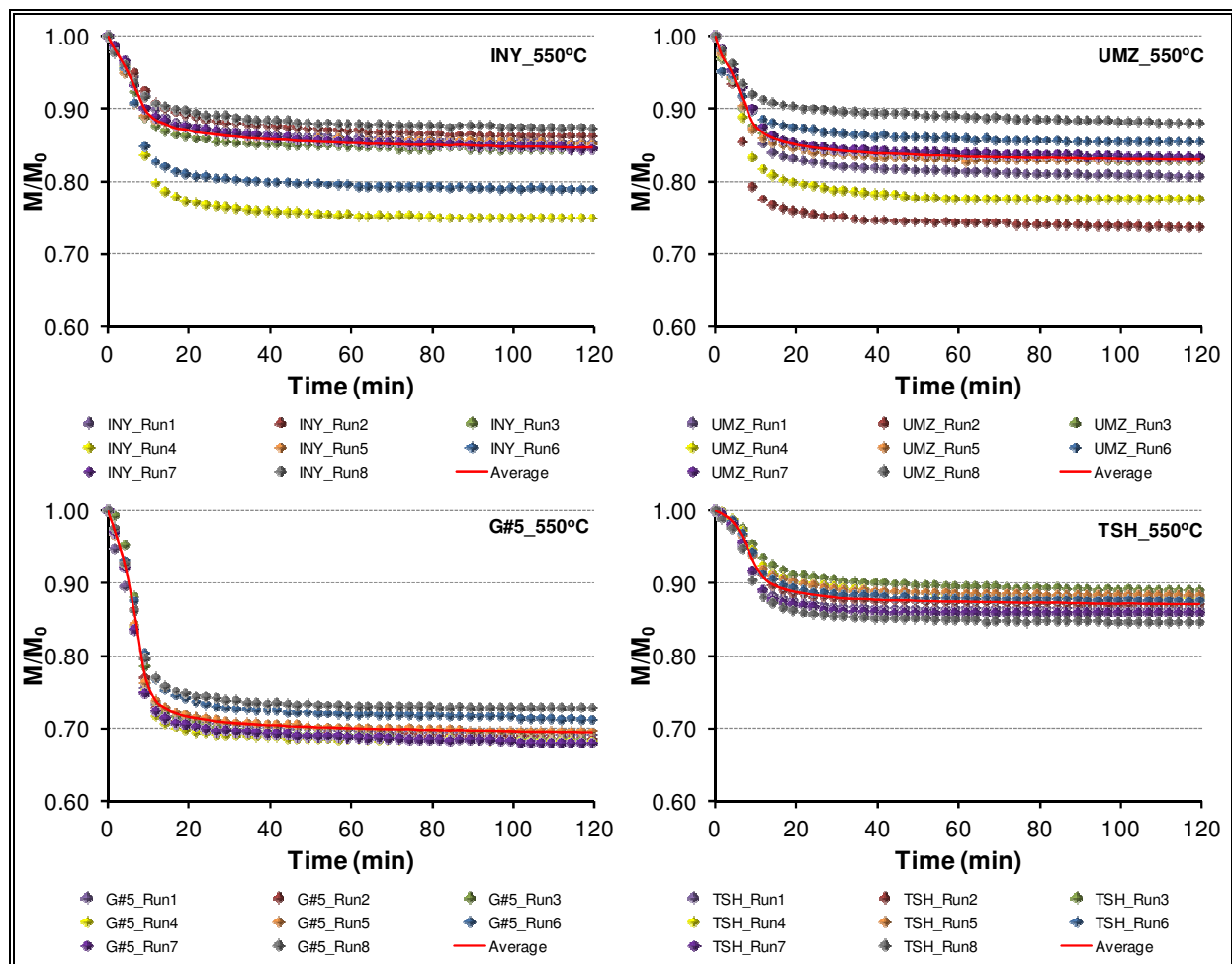


Figure D.7 Normalised devolatilization results for all four coals at 550°C.

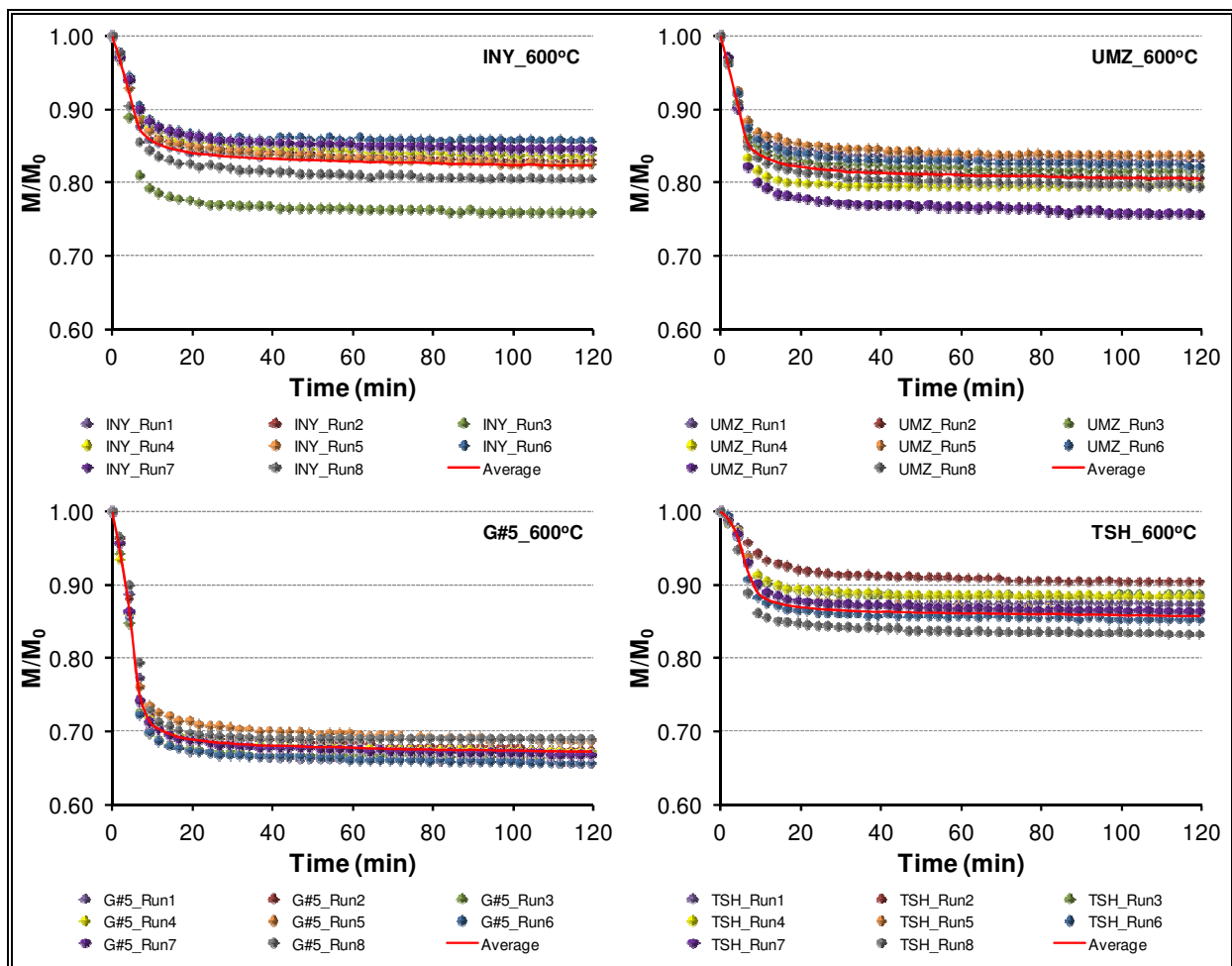


Figure D.8 Normalised devolatilization results for all four coals at 600°C.

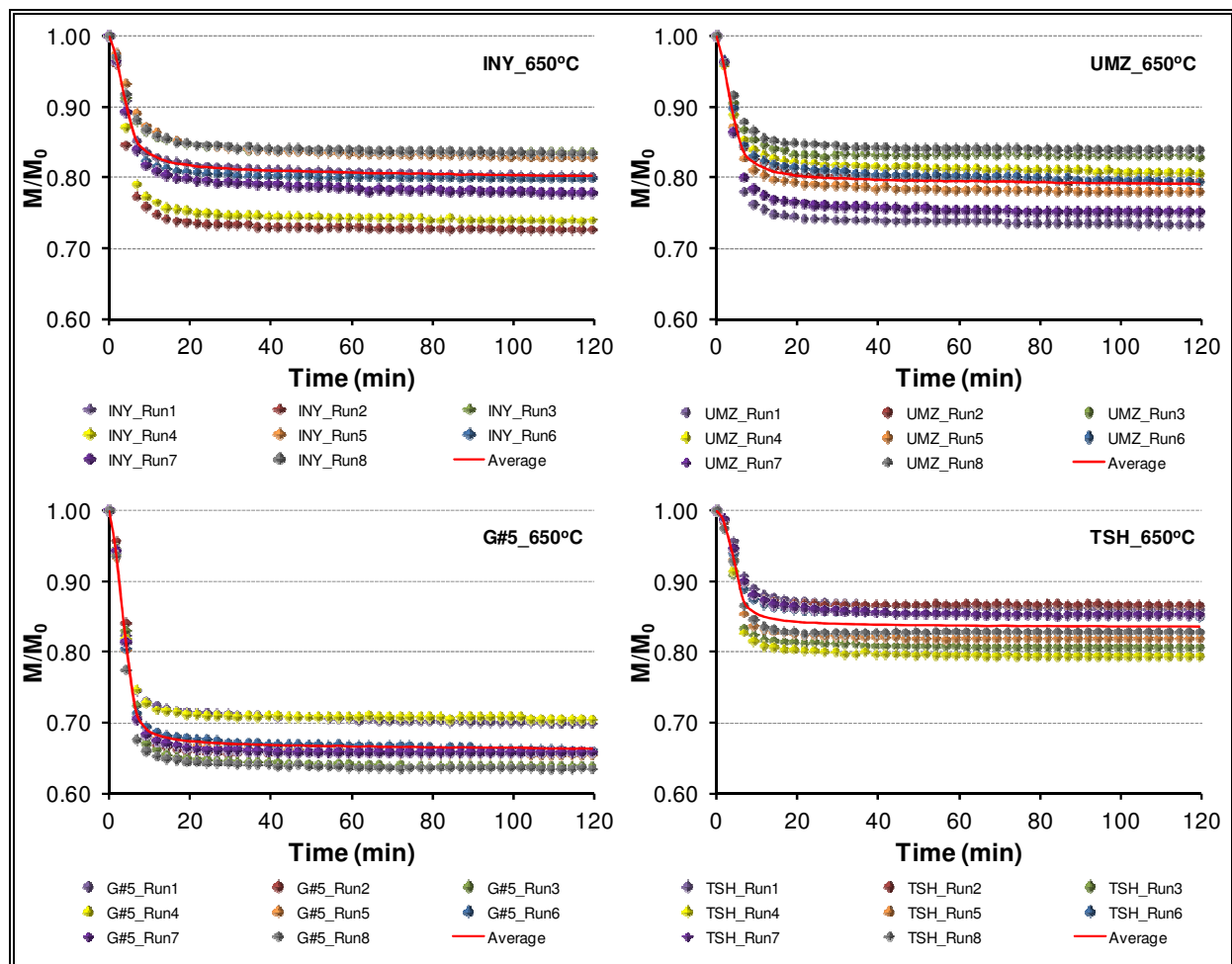


Figure D.9 Normalised devolatilization results for all four coals at 650°C.

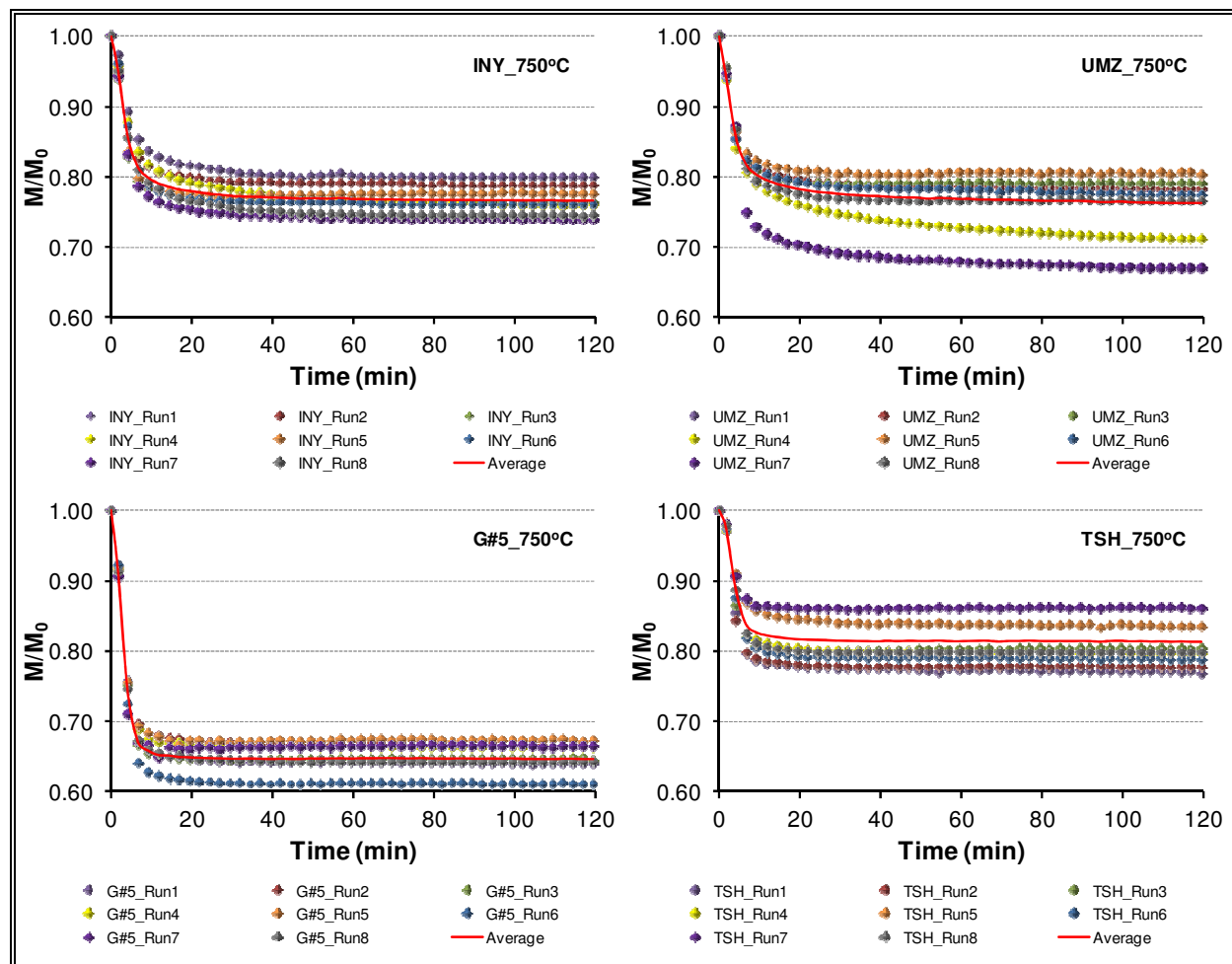


Figure D.10 Normalised devolatilization results for all four coals at 750°C.

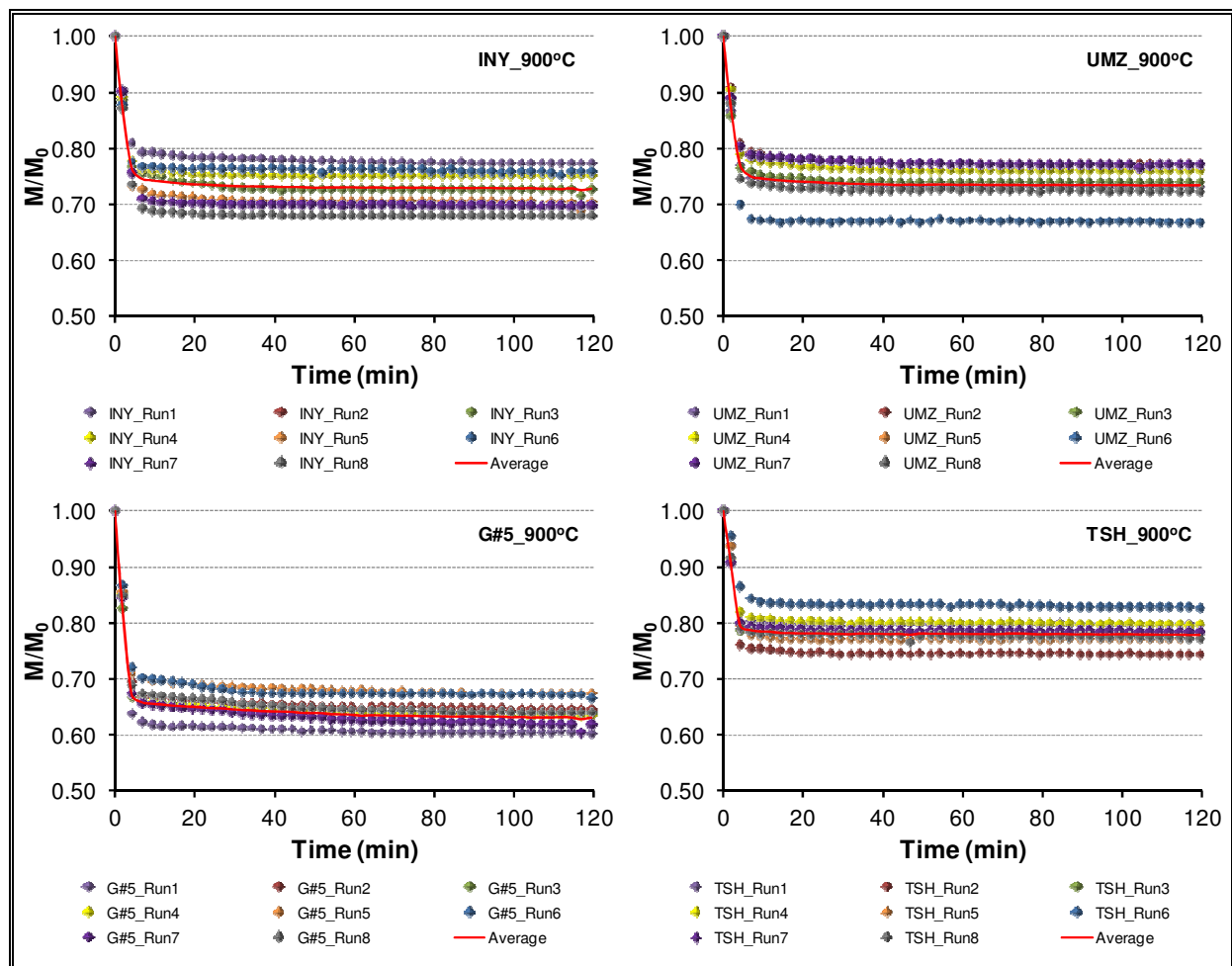


Figure D.11 Normalised devolatilization results for all four coals at 900°C.

D.6 Comparison between modelled and experimental DTG and TG curves

This appendix provides a comparison between modelled and experimental DTG and TG results obtained from the non-isothermal TG analysis of pulverized coal samples. Only the model validations assuming three, four, five and eight pseudo-components, of the 25 and the 40K/min experiments of coals INY and TSH have been included for illustrative purposes in Figures D.12 and D.13, while comparisons of the modelled TG curves, at the four heating rates, assuming 3 and 8 pseudo-components can be found in Figures D.14 and D.15 for coals UMZ and G#5.

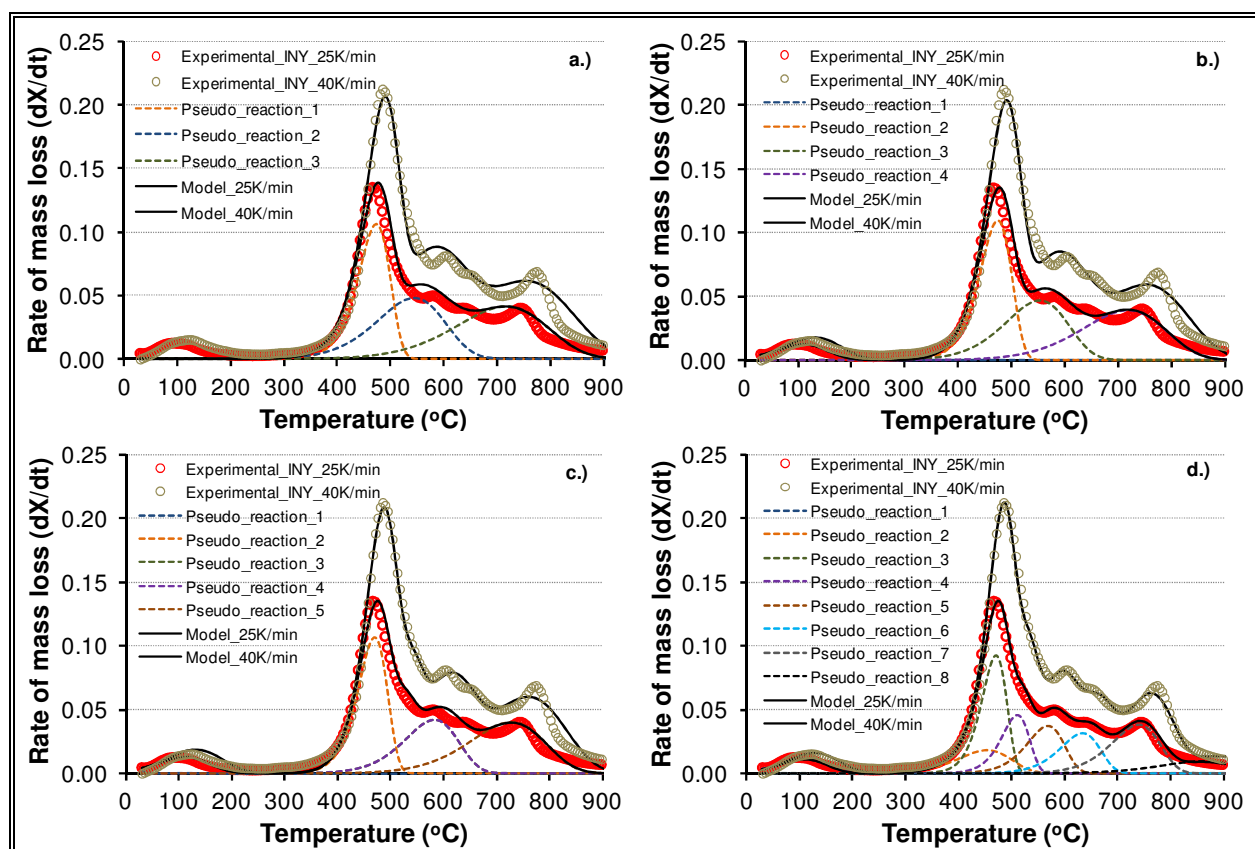


Figure D.12 Simulated reaction rate curves for coal INY based on the first order model of a.) 3, b.) 4, c.) 5 and d.) 8 pseudo-components.

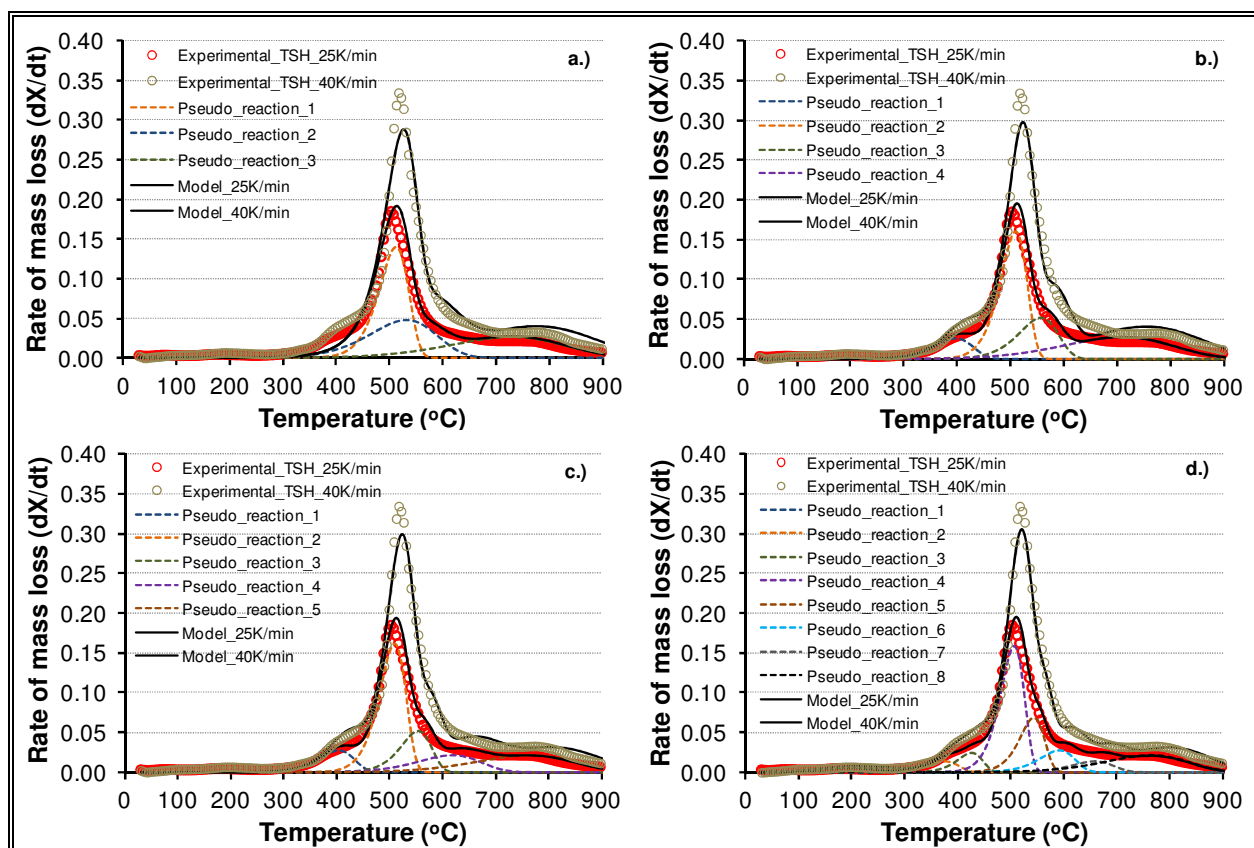


Figure D.13 Simulated reaction rate curves for coal TSH based on the first order model of a.) 3, b.) 4, c.) 5 and d.) 8 pseudo-components.

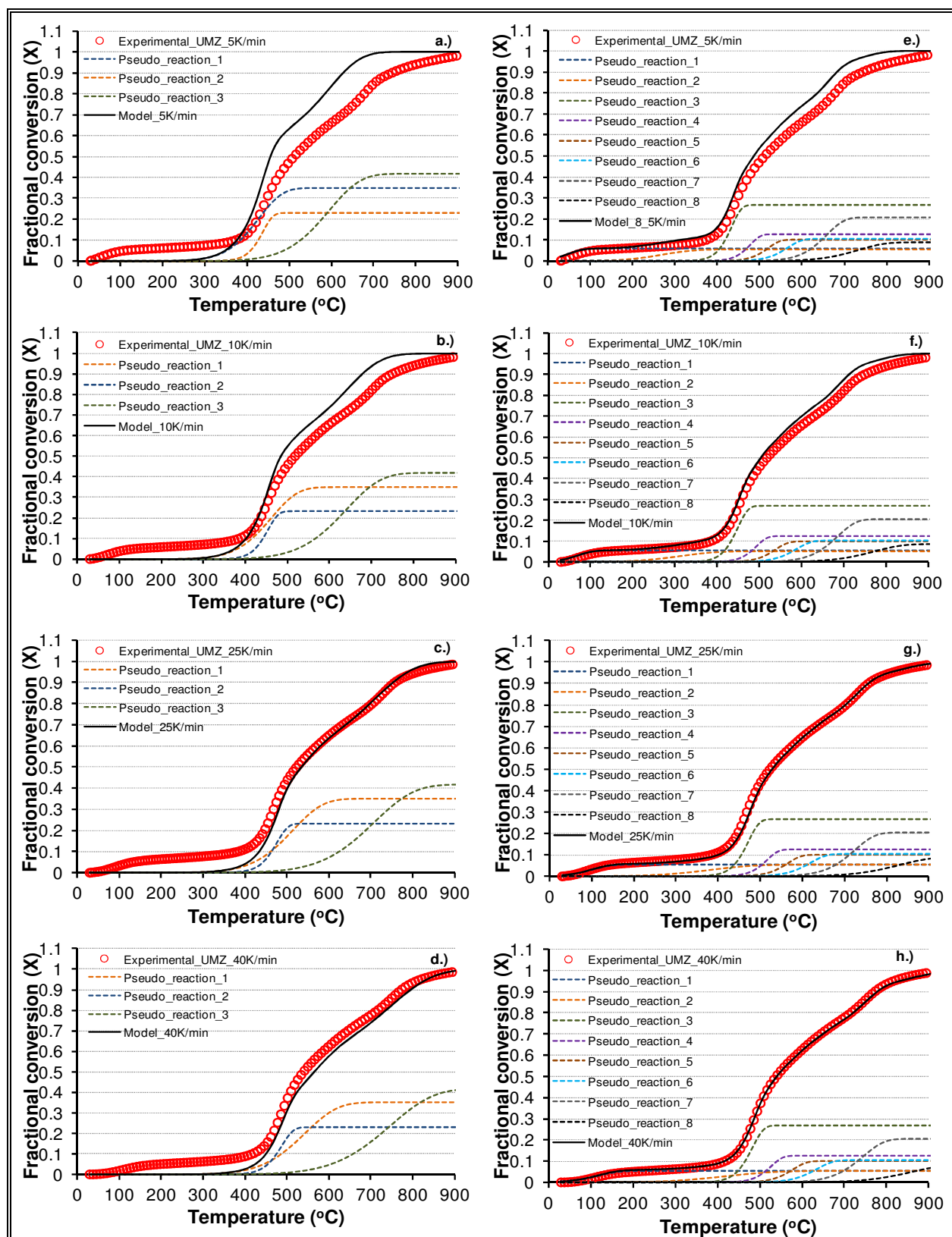


Figure D.14 Comparison between experimental and modelled TG curves for coal UMZ, assuming a-d.) 3 reactions and e-h.) 8 reactions.

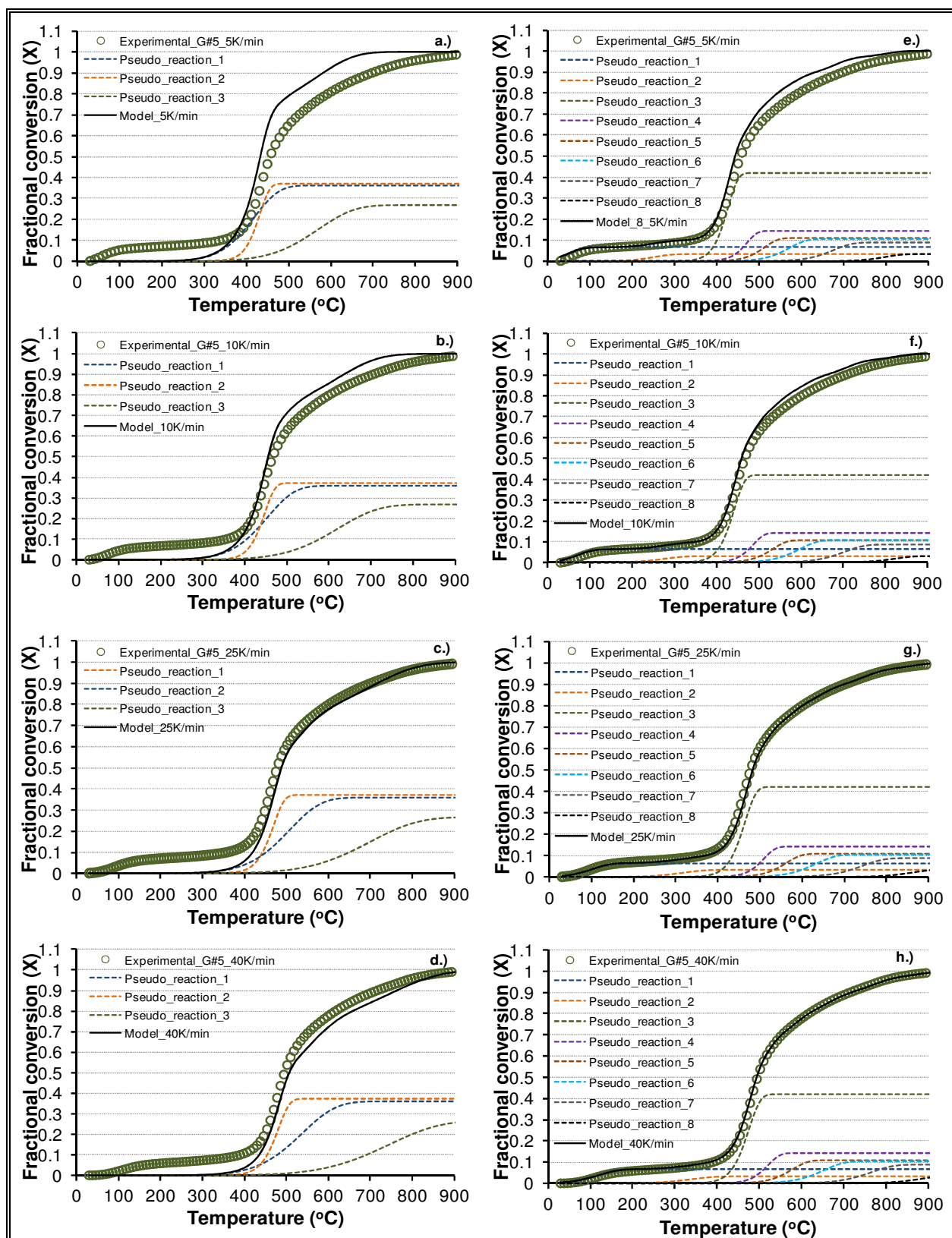


Figure D.15 Comparison between experimental and modelled TG curves for coal G#5 assuming, a-d.) 3 reactions and e-h.) 8 reactions.

D.7 Modelling comparison using two different thermal conductivity models

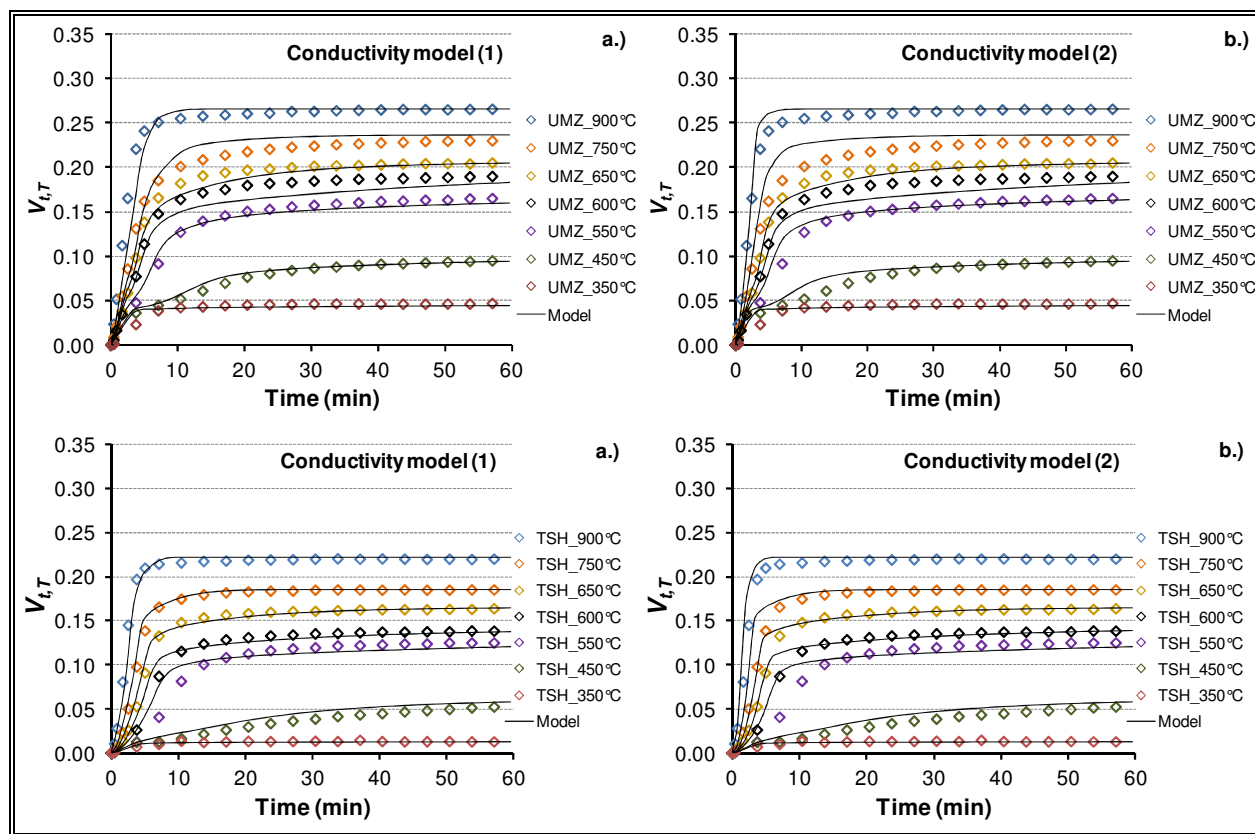


Figure D.16 Comparison between model predictions for coals UMZ and TSH using a.) thermal conductivity model (1) and b.) thermal conductivity model (2).

D.8 Experimental temperature profiles of 20 mm coal particles

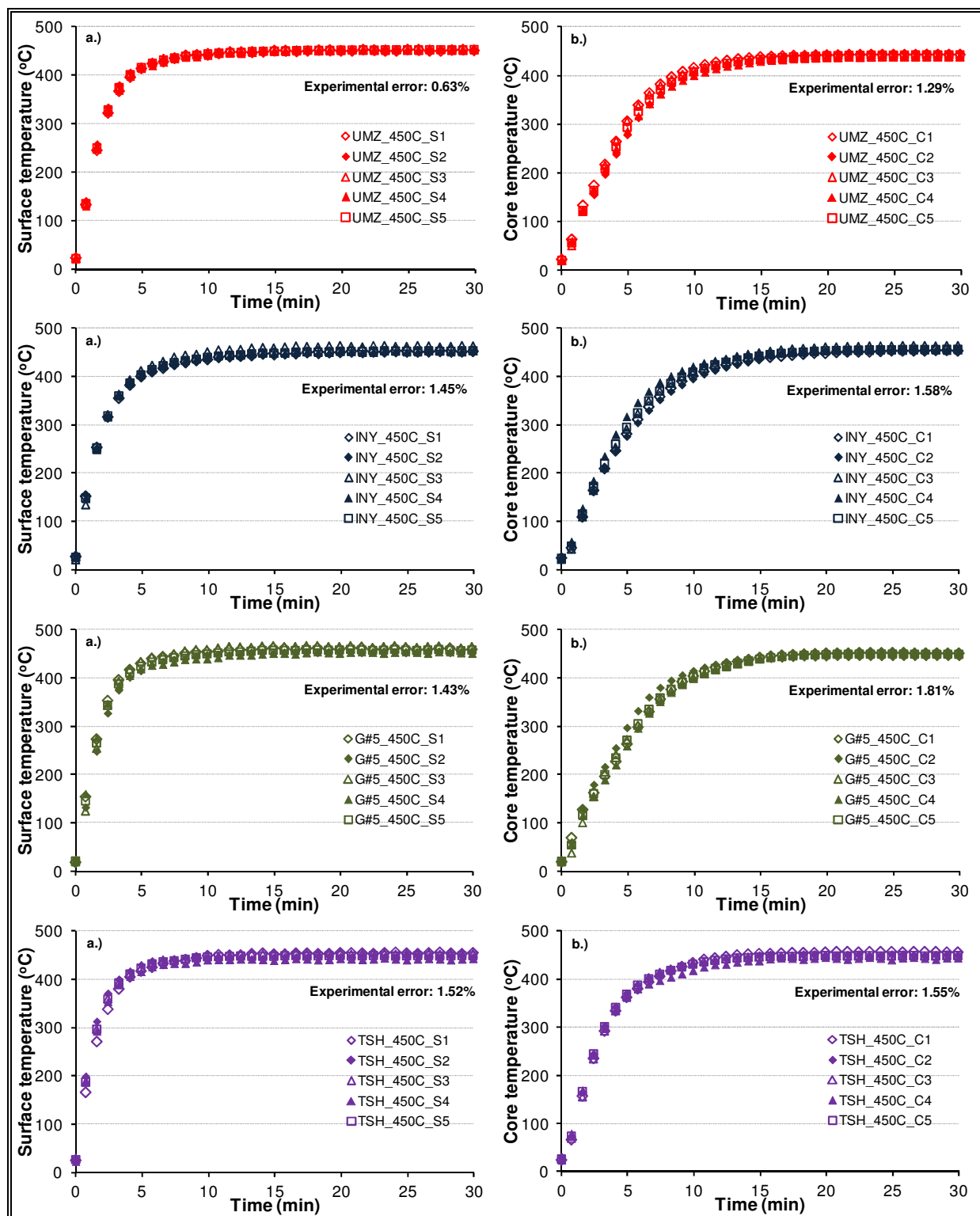


Figure D.17 Reproducibility profiles for a.) surface temperature and b.) core temperature determined from the devolatilization of all four coals at 450°C.

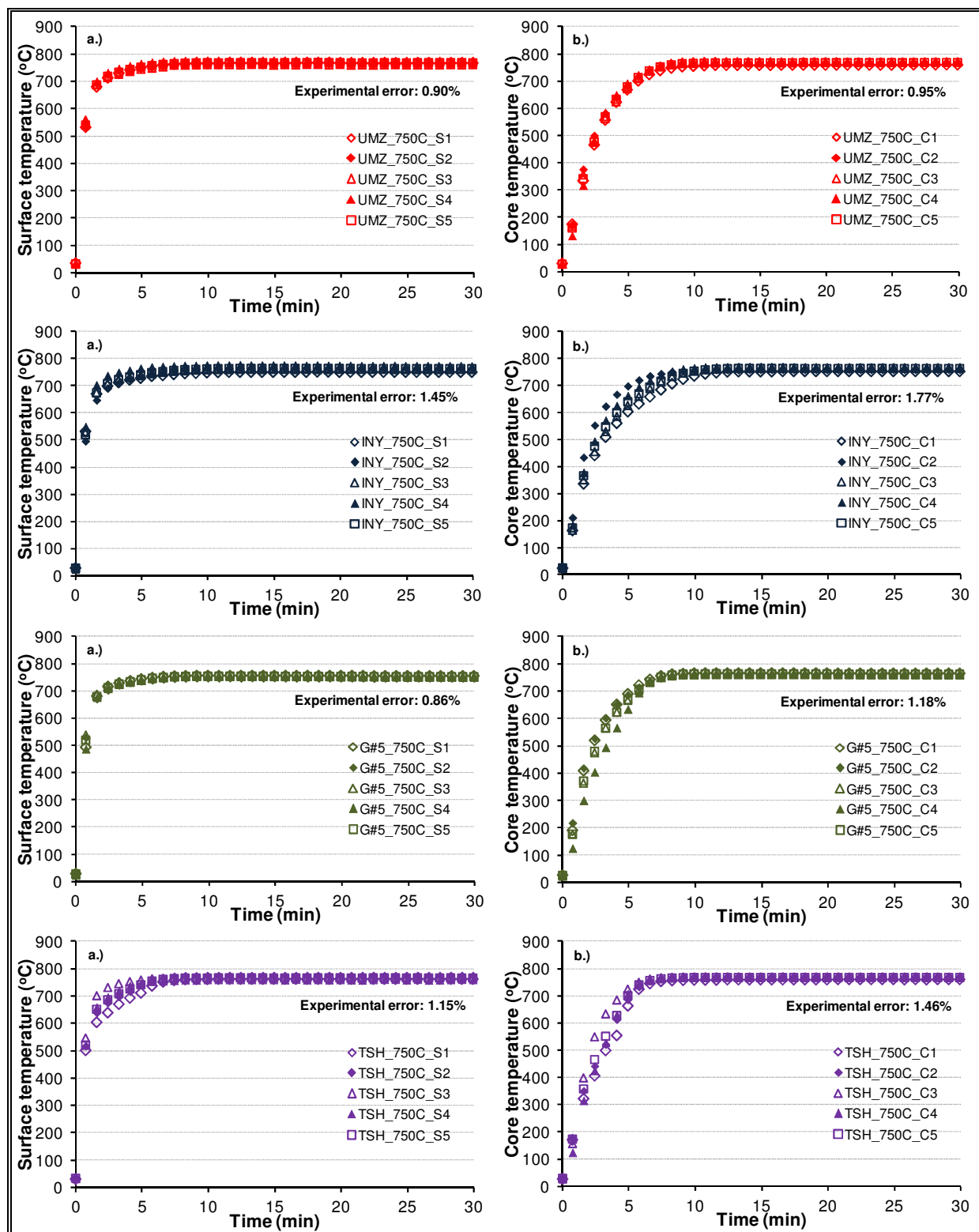


Figure D.18 Reproducibility profiles for a.) surface temperature and b.) core temperature determined from the devolatilization of all four coals at 750°C.

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Curriculum Vitae

EDUCATION (NORTH WEST UNIVERSITY, SOUTH AFRICA):

Ph.D in Chemical Engineering

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Thesis title: Product evaluation and reaction modelling for the devolatilization of large coal particles.

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Thesis title: The determination of the reaction mechanisms involved in the CO₂ gasification of inertinite-rich, high ash coal.

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November 2007

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- Hattingh, B.B*., Everson, R.C., Neomagus, H.W.J.P. & Bunt, J.R. 2011. Assessing the effect of coal ash constituents on the CO₂ gasification rate of high ash, South African coal. *Fuel Processing Technology*, 92(10): 2048-2054.
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- Burgert Hattingh*, Raymond Everson, Hein Neomagus, John Bunt and Daniel van Niekerk. Tar and gas evolution from the devolatilization of large South African coal particles, 29th Annual International Pittsburgh Coal Conference, 15-18 October 2012, Pittsburgh, PA, USA.
- Burgert Hattingh*, Raymond Everson, Hein Neomagus, John Bunt, Daniel van Niekerk, Johan Jordaan and Andre Joubert. Structural features of tars and chars derived from South African large coal particles, 29th Annual International Pittsburgh Coal Conference, 15-18 October 2012, Pittsburgh, PA, USA.

Quick reference

Table Q.1 Quick reference of coal properties.

<i>Property</i>	<i>INY</i>	<i>UMZ</i>	<i>G#5</i>	<i>TSH</i>
General information				
Coal field origin	Witbank	Witbank	Witbank	Venda-Pafuri
Seam origin	2	4	5	1 and 2
Supplier	Exxaro	Anglo	Anglo	Exxaro
Chemical properties				
Ash content (wt.%, d.b.)	18.6	14.8	13.5	17.8
Volatile matter (wt.%, d.b.)	25.5	25.2	34.1	20.5
Fixed Carbon (wt.% d.b.)	55.9	59.6	52.4	61.7
Atomic H/C ratio	0.69	0.62	0.83	0.66
Atomic O/C ratio	0.09	0.08	0.11	0.01
Free swelling index	1.0	0.5	0.5	9.0
Petrographical properties				
Rank	Bituminous Medium C	Bituminous Medium C	Bituminous Medium C	Bituminous Medium B
Vitrinite content (vol.%, m.m.f.b.)	36.7	24.4	60.2	69.2
Liptinite content (vol.%, m.m.f.b.)	3.3	3.3	9.7	1.1
Inertinite content (vol.%, m.m.f.b.)	60.0	72.2	30.1	29.7
Molecular properties				
Fraction Aromatics	0.74	0.77	0.66	0.81
Number of bridges and loops per cluster	4.4	3.9	2.8	0.2
Number of side chains per cluster	1.1	0.7	1.7	2.1
Amorphous fraction of carbon	0.58	0.59	0.67	0.52
Degree of disorder index	0.69	0.69	0.78	0.61
Highest aromatic fringe distribution	2x2	2x2	2x2	3x3
Average molecular weight (g/mol)	467.1	426.8	411.7	506.0