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# TECHNICAL REPORT

## SINTEF Energiforskning AS

Postadresse: 7465 Trondheim  
Resepsjon: Sem Sælands vei 11  
Telefon: 73 59 72 00  
Telefaks: 73 59 72 50

www.energy.sintef.no

Foretaksregisteret:  
NO 939 350 675 MVA

SUBJECT/TASK (title)

**Thermogravimetric investigation of four fuels**

CONTRIBUTOR(S)

Judit Sandquist, Mario Ortega, Øyvind Skreiberg

CLIENT(S)

KRAV Consortium

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RESULT (summary)

The KRAV project focuses on small-scale CHP plants running on biomass, included low quality biomass fuels. In order to be more cost efficient, it is a need to be able to burn low quality fuels in small-scale CHP plants.

Four fuels (wood pellets, demolition wood, coffee waste and glossy paper) were investigated in this report, with TGA-MS technique. Two atmospheres were used, the combustion experiments were carried out in argon with 21 vol% oxygen and the pyrolysis experiments were carried out in pure argon. Three different heating rates (5, 20 and 100 K/min) were used, to investigate the influence of the heating rate on the fuel conversion.

Coffee waste releases volatiles at the lowest temperature, but the release is slowest in this case, followed by wood and demolition wood, and glossy paper releases volatiles at the highest temperature. The volatiles release temperature is not affected by the presence of oxygen but increases slightly with increasing heating rate. The volatiles release is followed by the char conversion process at higher temperatures, and this process is slow. The process is faster in the presence of oxygen. When oxygen is not available in the reactive gas, the char does not convert completely. The char conversion rate decreases with increasing heating rate and the portion of unconverted char in the ash increases.

In the combustion experiments, coffee waste ignites at 5 K/min heating rate, all fuels ignite at 20 K/min heating rate and none at 100 K/min heating rate.

The results derived in these TGA experiments will together with planned accompanying macro-TGA experiments provide useful fundamental knowledge about the characteristics of the fuels.

## KEYWORDS

SELECTED BY AUTHOR(S)	Biomass	TGA
	Combustion	Pyrolysis

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## 1 INTRODUCTION

The KRAV project focuses on small-scale CHP plants running on biomass, included low quality biomass fuels, as one of the important contributors to the Norwegian energy system. Until now, small-scale plants have been using high-quality, clean biomass fuels, because more advanced technology is costly at this scale. However, low quality fuels are of interest. In order to be more cost efficient, it is a need to be able to burn low quality fuels in small-scale CHP plants. For this purpose, the fuels need to be analysed and characterised.

The fuel composition has an important influence on the conversion process in a plant<sup>1</sup>. During biomass combustion, NO<sub>x</sub> emissions mainly originate from the nitrogen content in the fuel<sup>2</sup>. The sulphur content in the fuel is the main factor affecting the amount of SO<sub>x</sub> emissions. The Cl and S content in the fuel are responsible for corrosion and fouling, thus affecting the plant efficiency and cost effectiveness.

The volatile content in the fuel strongly influences the thermal decomposition and combustion process of biomass fuels. After being released, most of the volatiles react with oxygen, forming water and CO<sub>2</sub>. The process is followed by the char oxidation, which is a much slower process<sup>1</sup>.

The amount of Si, Ca, Mg, K, Na and P (main ash-forming minerals) present in the fuel determines the amount and type of ash formed during the combustion process and therefore its treatment, transport and storage. Moreover the ash elements can react with the pyrolysis or combustion products and influence the emissions from the process.

Pyrolysis is by definition thermal decomposition occurring in the absence of oxygen. It is always the first step of a combustion process, where it is followed by total or partial oxidation.

This report presents the results of thermogravimetric investigation of four fuels.

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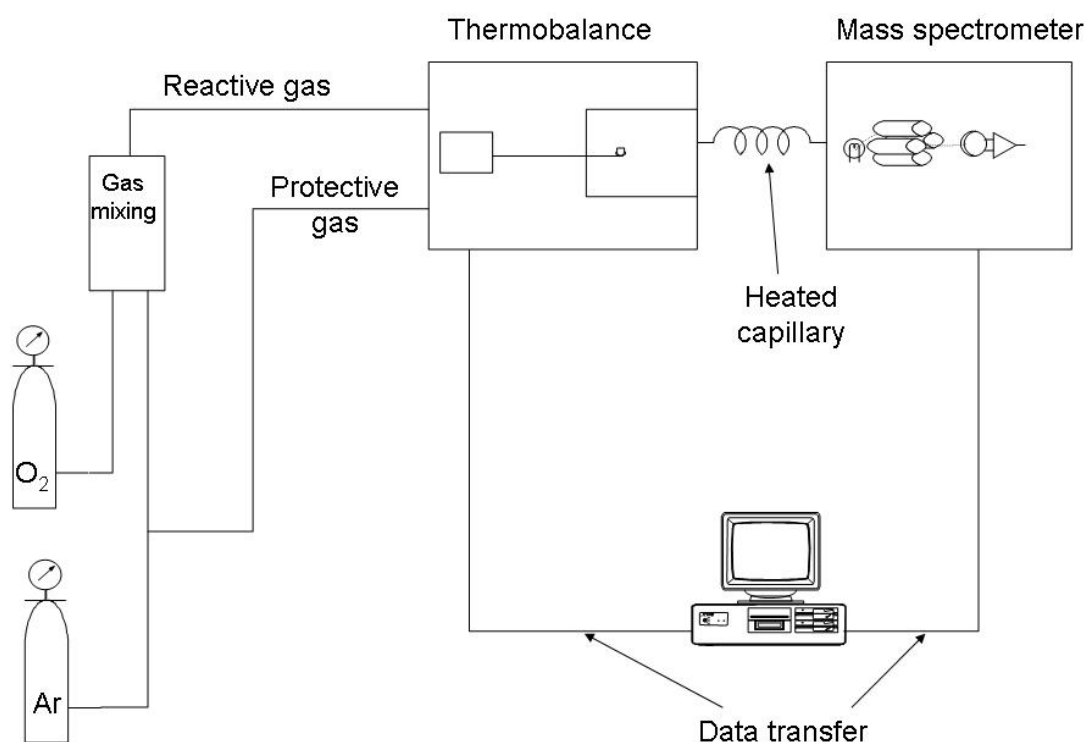
<sup>1</sup> Handbook of biomass combustion and co-firing, (ed.: Sjaak van Loo and Jaap Koppejan), Earthscan, 2008

<sup>2</sup> W. Permchart, V.I. Kouprianov: Emission performance and combustion efficiency of a conical fluidized-bed combustor firing various biomass fuels, *Bioresource Technology* 92 (2004) 83–91.



## 2 MATERIALS AND METHODS

Thermogravimetry/mass spectrometry (TG/MS) experiments were carried out in a Mettler-Toledo TGA/SDTA851e thermobalance coupled to a Pfeiffer-Vacuum GSD 301 T3, ThermoStar™ quadrupole mass spectrometer through a quartz capillary heated to 200 °C, as Figure 1 shows.



**Figure 1 TGA-MS instrumentation**

Samples were placed into an alumina pan and were heated to 900 °C. The flow rate of the reactive gas was 100 mL/min. Argon purge gas of 20 mL/min was used to protect the balance. A part of the evolved compounds were introduced into the mass spectrometer (MS), which operated in electron impact ionisation mode with 60 eV electron energy.

The experimental conditions were as follows:

- 4 fuels: wood pellets, demolition wood, coffee waste and glossy paper (see Figure 2/A)
- 3 of the fuels were grinded to powder and glossy paper was cut to pieces (see Figure 2/B)
- atmosphere/reaction gas composition:
  - 21 vol% oxygen + 79 vol% argon
  - 100% argon
- heating rate: 5 K/min, 20K/min and 100 K/min
- atmospheric pressure
- temperature range: 60-900 °C

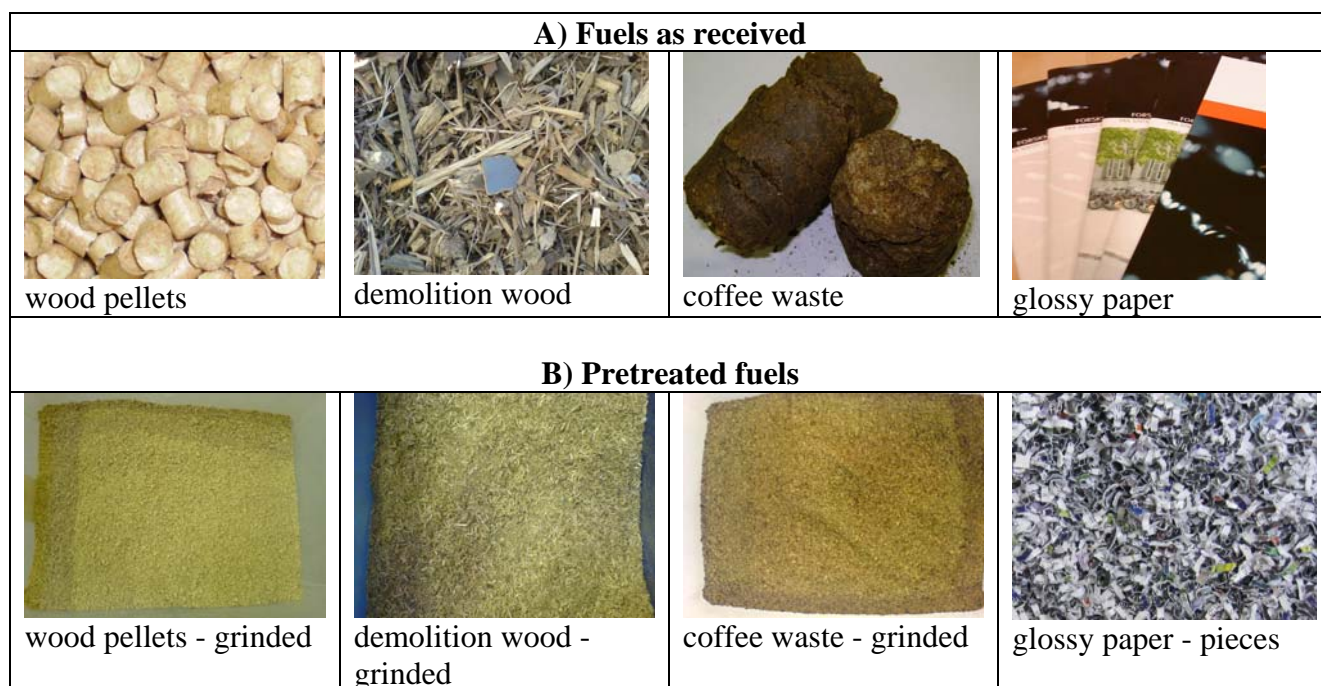


Figure 2 Fuels: A) as received, B) pretreated for the experiments

Ultimate analysis of the fuels is shown in Table 1 and proximate analysis is shown in Table 2.

**Table 1 Ultimate analysis (wt%, dry ash free basis) of the selected fuels.**

Fuel	C	H	O	N	S	Cl
Wood pellets	50.33	6.21	bd	0.11	<0.02	0.020
Demolition wood	49.29	6.08	bd	0.38	0.089	0.033
Coffee waste*	51.33	6.79	bd	3.02	0.21	0.055**
Glossy paper	41.90	5.30	bd	0.10	<0.02	0.093

bd: by difference, \* data from Becidan (2007)<sup>3</sup> \*\* new analysis

**Table 2 Proximate analysis and heating value of the selected fuels.**

Fuel	Fixed C (wt%, db)	Volatiles (wt%, db)	Ash (wt%, db)	Moisture (wt%, wb)	HHV (MJ/kg, db)
Wood pellets (as pellets)	14.34	85.58	0.08	7.0	19.95
Demolition wood	16.06	82.37	1.57	5.2	19.06
Coffee waste*	16.75	76.67	6.58	10.7	19.82
Glossy paper	4.50	70.70	24.8	3.8	10.4

wb: wet basis, db: dry basis, \* data from Becidan (2007)

During the experiments weight loss was monitored by the TGA together with a number of chosen compounds in the MS. The following chemical compounds were detected in the MS:

- Hydrogen was monitored by the intensity of its molecular ion  $m/z=2$
- Methane was monitored by the intensity of its fragment ion  $m/z=15$
- Water was monitored by the intensity of its molecular ion  $m/z=18$
- Hydrocarbons were monitored by the intensity of their common fragment ion  $m/z=26$

<sup>3</sup> Becidan M, Skreiberg Ø, Hustad JE (2007). Products distribution and gas release in pyrolysis of thermally thick biomass residues samples. J. Anal. Appl. Pyrolysis 78:207–213.

- Carbon dioxide was monitored by the intensity of its molecular ion  $m/z=44$

Carbon monoxide was also monitored by its molecular ion ( $m/z=28$ ) but the results could not be evaluated, probably due to nitrogen leakage in the system. Nitrogen and carbon-monoxide has the same molecular ion, therefore it is advisable to use helium or argon as a carrier gas when MS is used.

It must be noted, that a mass spectrometer has different selectivity for the different compounds, thus limited quantitative possibilities. The used mass spectrometer was not calibrated, therefore the quantitative values should not be considered. Furthermore, interferences between the different compounds are not taken into account (different compounds might have the same fragment ions), therefore only large enough peaks should be considered.

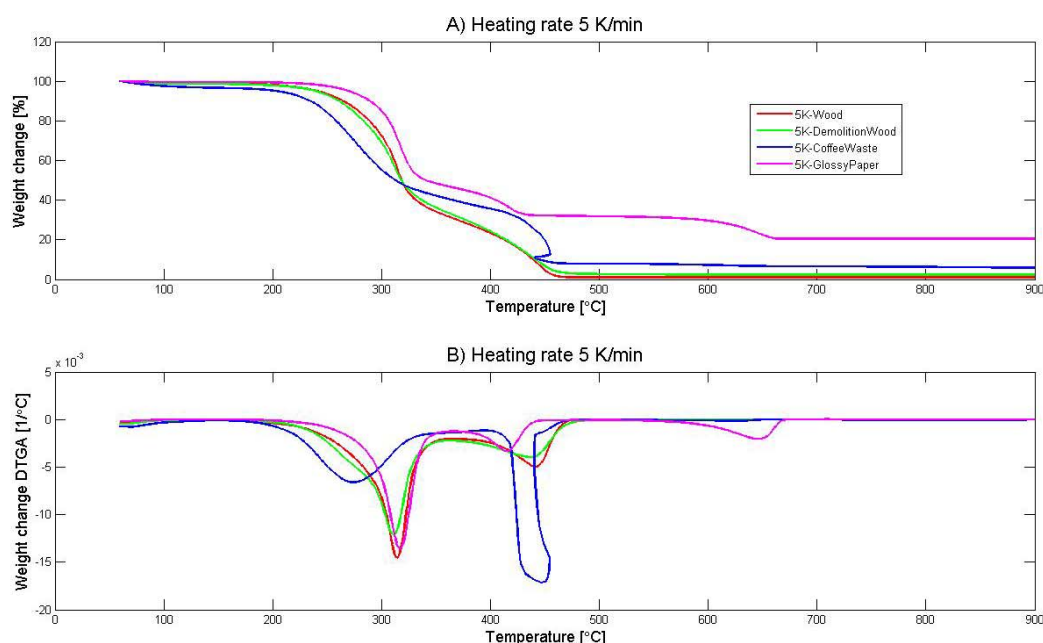
The MS results are presented in the Appendix.

### 3 RESULTS AND DISCUSSION

#### 3.1 Combustion experiments

Combustion experiments were carried out with a reactive gas that contains 21 vol% oxygen and 79 vol% argon.

Figure 3 shows the thermal decomposition of the samples between 60 and 900 °C at a low (5 K/min) heating rate when 21% oxygen is available in the reactive gas.

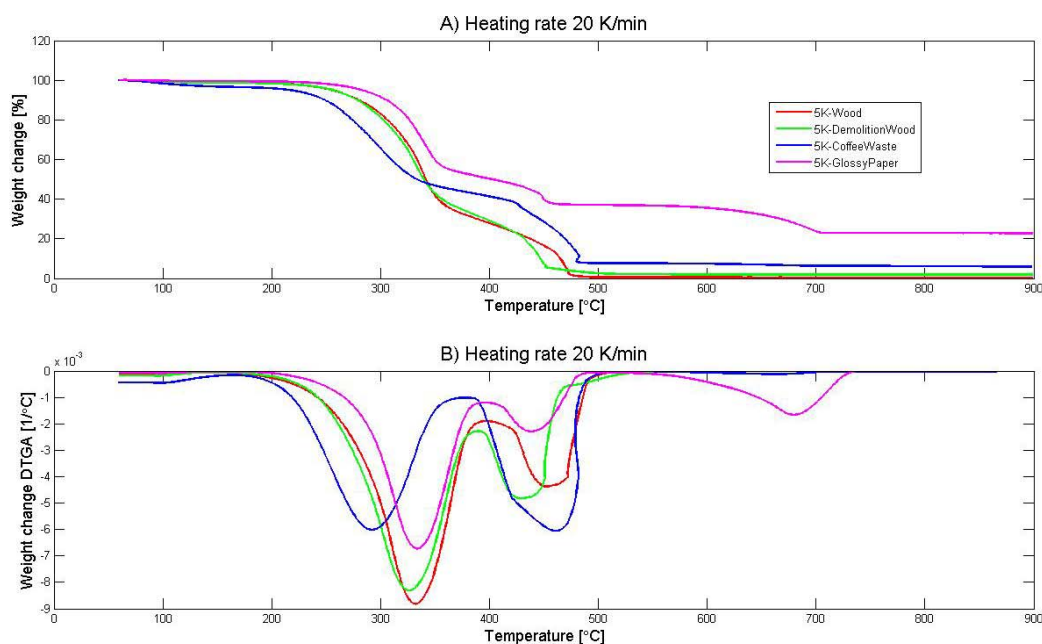


**Figure 3 Weight loss A) and weight loss rate B) at 5 K/min when 21% oxygen is available**

Coffee waste starts to release volatile compounds already below 200 °C, wood and demolition wood starts to lose weight slightly over 200 °C followed by glossy paper, which does not decompose until it reaches approximately 250 °C. The weight loss rate increases until 280 °C in case of coffee waste and approximately until 310 °C in case of the other fuels. At the same time, coffee waste is the fuel which releases volatiles slowest. The volatile release rate is the same for the other fuels. Most of the volatiles react with oxygen, and is converted to water and CO<sub>2</sub> (see Appendix for MS results). Only a small amount of volatiles leave the TGA unreacted or partly reacted as the small peaks of the hydrocarbons indicate. Between 410 and 430 °C the figure shows char conversion which is a slower process. In case of the coffee waste fuel the figure shows ignition followed by powerful cooling by the TGA (the curve 'moves backwards'). TGA is an instrument with powerful heating and cooling capability in order to keep the temperature precisely at the programmed value. Ignition is not clear in case of the other three fuels, and it is not sure that there was an ignition during these experiments. The MS curves show water and CO<sub>2</sub> release in large amounts only in case of the coffee waste fuel. The combustion of the coffee waste is so violent that the fuel cannot combust completely and there are emissions of all the other measured compounds as well. The fuel conversion finishes at around 500 °C and ashes remain. In case of

the glossy paper sample a weight loss can be seen between 600 and 650 °C, which is probably due to CaCO<sub>3</sub> to CaO conversion. Glossy paper contains large amounts of filler materials (around 40%) and most of those is calcium-carbonate. This conversion releases carbon dioxide, which can be seen in the CO<sub>2</sub> figures (see Appendix for MS results). It must be noted that the MS curves are normalised, and there is always the same amount of CO<sub>2</sub> released between 600 and 700 °C from the glossy paper sample, thus it can be considered as an internal standard. Therefore, the quantities in the CO<sub>2</sub> curves are comparable.

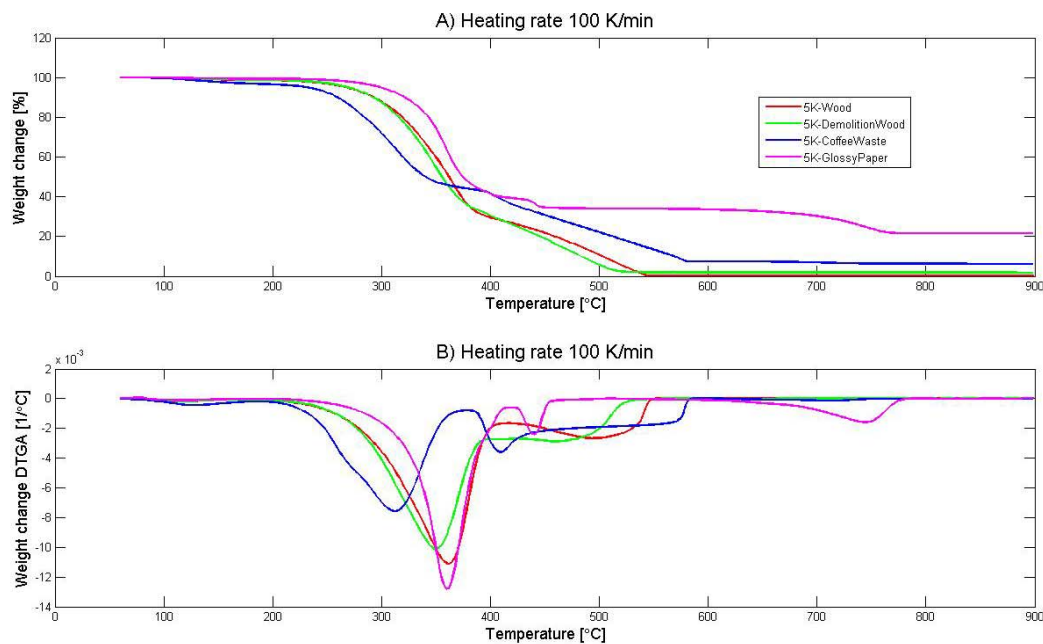
Figure 4 shows the thermal decomposition of the samples between 60 and 900 °C at a medium (20 K/min) heating rate when 21% oxygen is available in the reactive gas.



**Figure 4 Weight loss A) and weight loss rate B) at 20 K/min when 21% oxygen is available**

The decomposition at 20 K/min is very similar to decomposition at 5 K/min, but there are some differences. The temperatures of volatiles release move slightly higher. The MS figures show (see Appendix for MS results) that at 20 K/min heating rate the volatiles cannot convert fully to water and CO<sub>2</sub> by reaction with oxygen, there are unreacted compounds left. Both methane and hydrocarbons evolve, which is a clear effect of the increased heating rate. The temperatures of char conversion at around 400 °C remain the same. The char conversion rate increases considerably apart from coffee waste. Coffee waste ignites clearly in this case as well. The other fuels ignite as well, as it is shown in the MS figures. The ignition is not violent, three of the fuels are converted mostly to water and CO<sub>2</sub> with only a small amount of unburned compounds released. The combustion of coffee waste is the most violent but not as violent as in case of 5 K/min heating rate. This is shown in the CO<sub>2</sub> curve, the height of the peak is much lower in the latter case.

Figure 5 shows the thermal decomposition of the samples between 60 and 900 °C at a high (100 K/min) heating rate when 21% oxygen is available in the reactive gas.



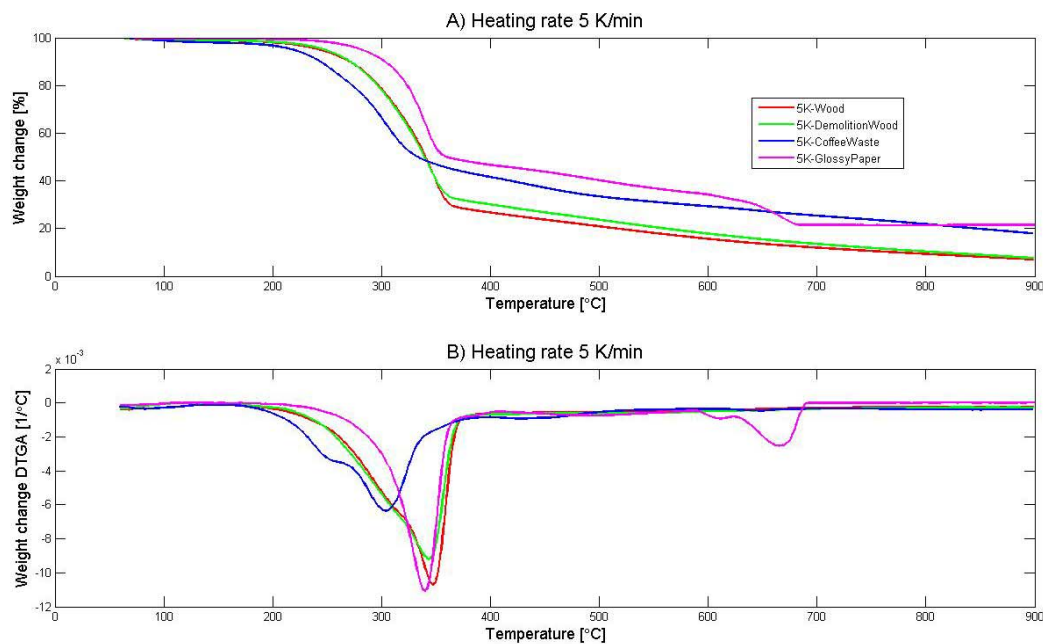
**Figure 5 Weight loss A) and weight loss rate B) at 100 K/min when 21% oxygen is available**

Figure 5 is also similar to the previous figures, and with increased heating rate the volatiles release temperature increases in this case as well. The conversion rate is somewhat lower than in the case of heating with low heating rate and higher than in the case of 20 K/min. The MS curves (see Appendix for MS results) show further decrease in the volatiles conversion to water and CO<sub>2</sub>. The amount of hydrocarbons and methane seem to be increased (compared to the noise level, which is assumed to be constant) as well. The high temperature carbon conversion is carried out at a much lower reaction rate. No ignition is seen at high heating rate for the samples, nor in the MS figures. The CO<sub>2</sub> peaks are small compared to the previous ones.

### 3.2 Pyrolysis experiments

Pyrolysis experiments were carried out with a reactive gas that contains 100 % argon.

Figure 6 shows the thermal decomposition of the samples between 60 and 900 °C at a low (5 K/min) heating rate when no oxygen is available in the reactive gas.

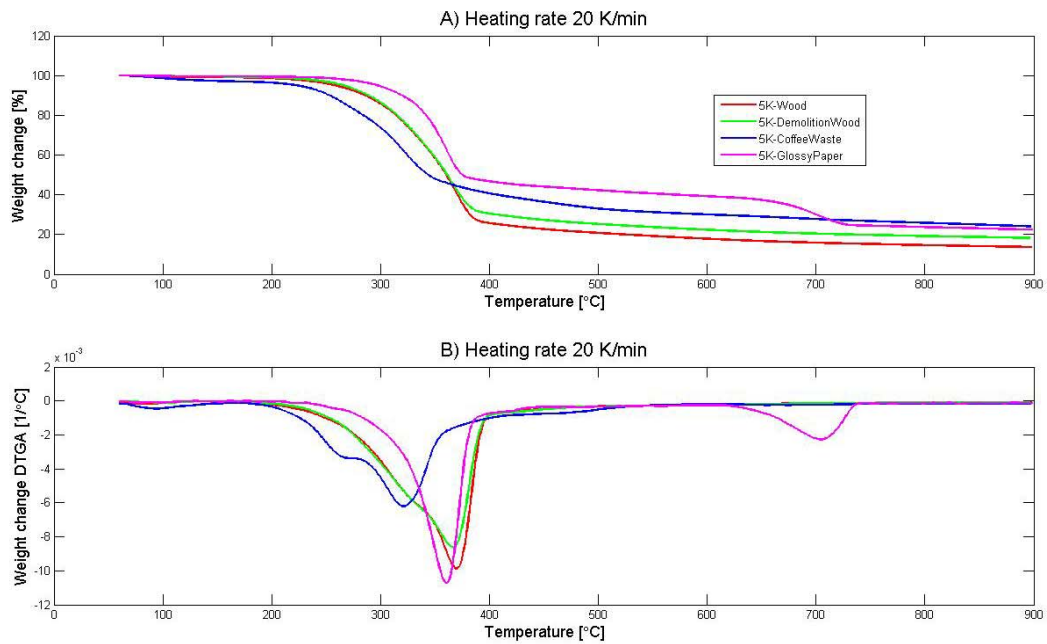


**Figure 6 Weight loss A) and weight loss rate B) at 5 K/min when no oxygen is available**

The release of the volatiles starts at the same temperature as at the previous experiment with 5 K/min heating rate, even if there is no oxygen available for the reaction. The conversion rates are somewhat lower than in the case when oxygen is available. Coffee waste starts to release volatiles earliest, followed by the wood samples. The typical wood pyrolysis DTGA curves can be seen, with a high cellulose peak and a hemicellulose shoulder at the low temperature side. Glossy paper has only the cellulose peak, it contains no hemicellulose and lignin. The cellulose peaks of these three fuels are overlapping, which makes the hemicellulose shoulder more visible in case of wood and demolition wood curves. The released volatiles react to water and  $\text{CO}_2$  in this case as well, due to the oxygen content of the fuel used. There are some other compounds released as well, as the MS curves show (see Appendix for MS results), but at a much less degree, than expected. The following char conversion is very slow, and as the curves indicate that not all the carbon converts without oxygen. The  $\text{CO}_2$  release curve show continuous release of  $\text{CO}_2$  in smaller amounts. The exception is the glossy paper sample, it has only a low amount of fixed carbon and a high amount of ash. The  $\text{CaCO}_3$  to  $\text{CaO}$  conversion seems clear in the figure. The reaction needs only heat, no external oxygen, and proceeds regardless of the atmosphere.

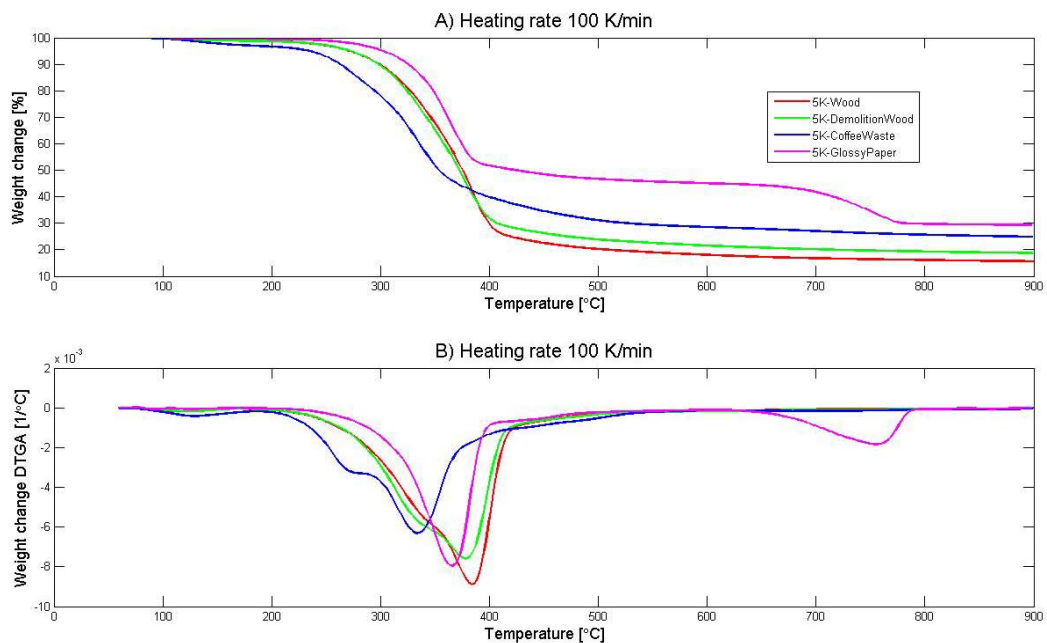
Figure 7 shows the thermal decomposition of the samples between 60 and 900 °C at a medium (20 K/min) heating rate when no oxygen is available in the reactive gas.





**Figure 7 Weight loss A) and weight loss rate B) at 20 K/min when no oxygen is available**

Figure 8 shows the thermal decomposition of the samples between 60 and 900 °C at a high (100 K/min) heating rate when no oxygen is available in the reactive gas.



**Figure 8 Weight loss A) and weight loss rate B) at 100 K/min when no oxygen is available**

Figure 7 and Figure 8 shows that there is only a slight difference between the experiments with different heating rate. The volatile release temperature increases slightly without oxygen available in the reaction gas as well. The conversion rate decreases with increased heating rate. The MS curves reveal that there is less CO<sub>2</sub> released during volatiles release. There are probably more unreacted compounds released (compared to the noise level, which is assumed to be constant),

more hydrocarbons and methane release is shown in the MS curves. The carbon conversion rate decreases as well. This is probably due to the fact that this reaction is time-consuming. With less time available (with increasing heating rate) less char reacts. The total weight loss decreases as well with increased heating rate.

## 4 CONCLUSIONS

Four fuels were investigated in this report, with TGA-MS technique. Two atmospheres were used, the combustion experiments were carried out in argon with 21% oxygen and the pyrolysis experiments were carried out in pure argon. Three different heating rates were used, to investigate the influence of the heating rate on the fuel conversion.

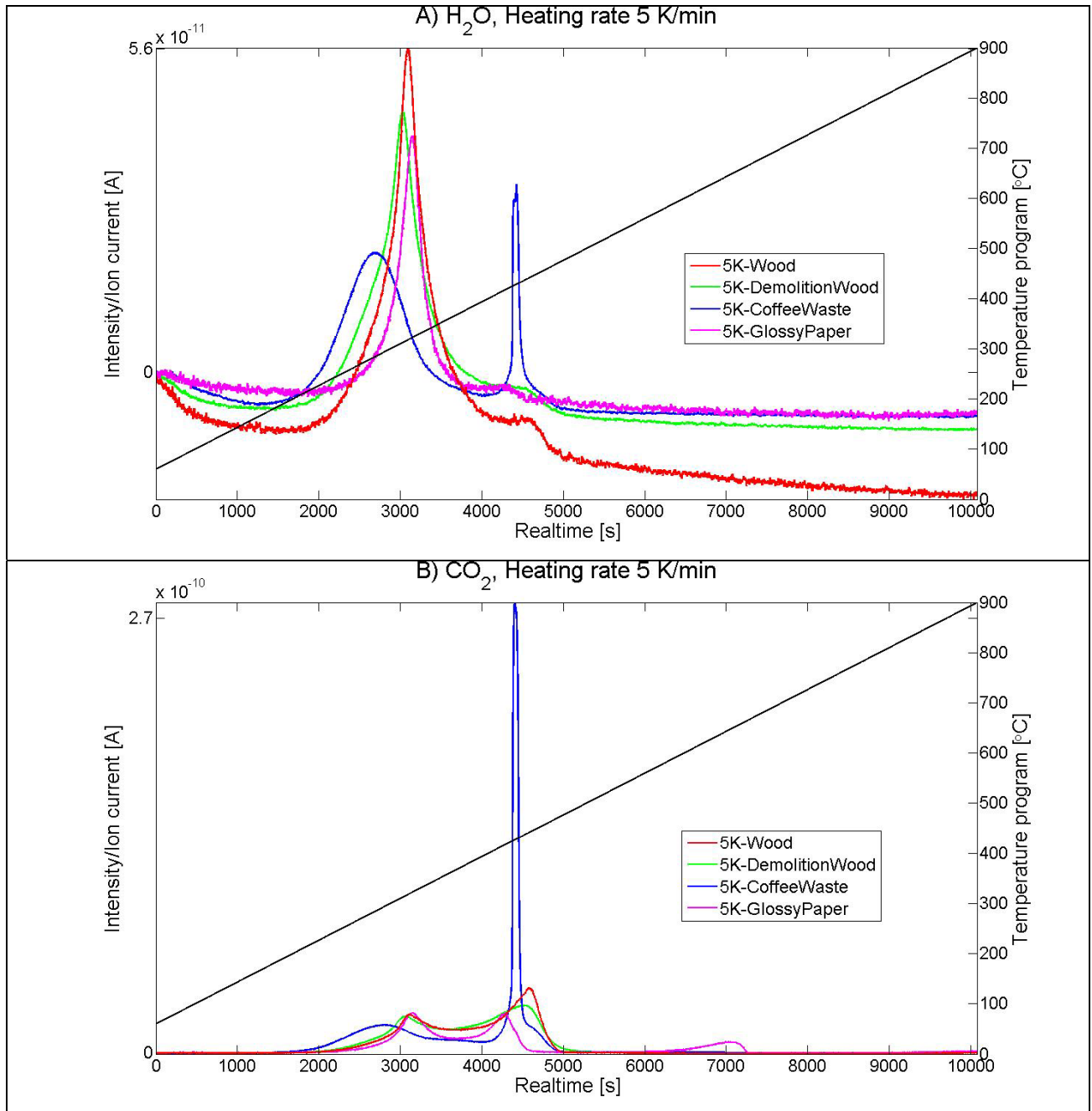
The fuel conversion starts with volatiles release. Coffee waste releases volatiles at the lowest temperature, but the release is slowest in this case. Wood and demolition wood release volatiles at a higher temperature, followed by the glossy paper sample which releases volatiles at the highest temperature of the four fuels. The volatiles release temperature is not affected by the presence of oxygen but increases slightly with increasing heating rate. The volatiles convert to water and carbon-dioxide. The conversion is fastest if oxygen is available in the reactive gas, and decreases with increasing heating rate. With decreasing volatiles conversion, the amounts of the unburnt compounds are increasing. The volatiles release is followed by the char conversion process at higher temperatures, and this process is slow. The process is faster in the presence of oxygen. when oxygen is not available in the reactive gas, the char conversion is so slow that there are no second peaks visible in the DTGA curves. The char does not convert completely, and char and ashes remain in those cases. The char conversion rate decreases with increasing heating rate and the portion of unburnt in the ash increases.

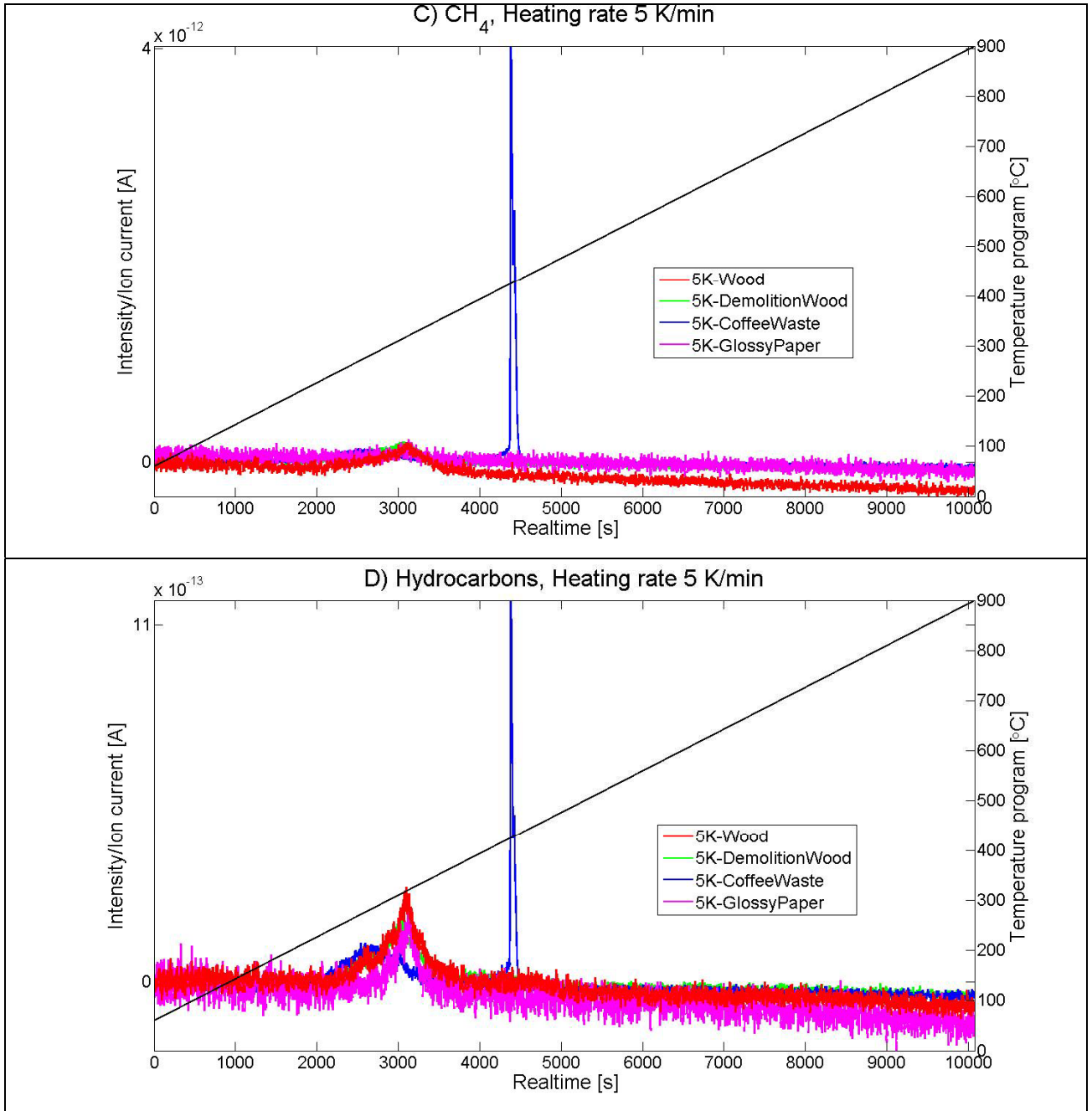
In the combustion experiments, coffee waste ignites at 5 K/min heating rate, all fuels ignite at 20 K/min heating rate and none at 100 K/min heating rate.

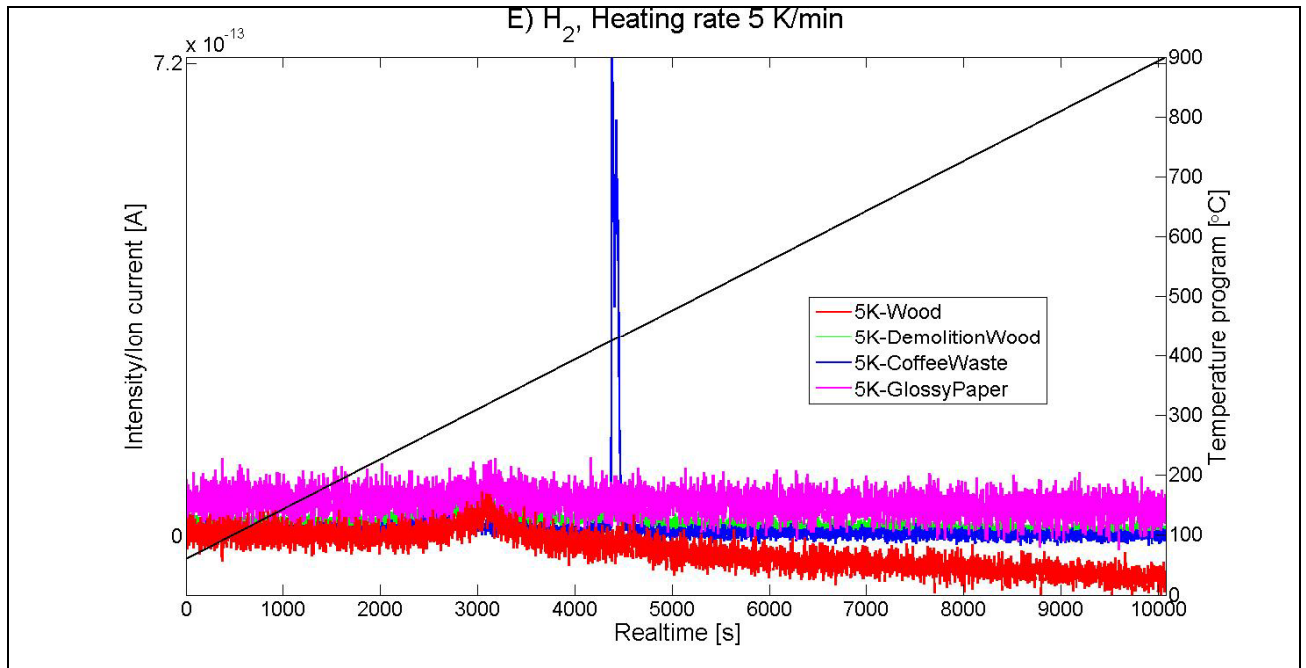
The results derived in these TGA experiments will together with planned accompanying macro-TGA experiments provide useful fundamental knowledge about the characteristics of the fuels.

**APPENDIX – MASS SPECTROMETRY (MS) RESULTS**

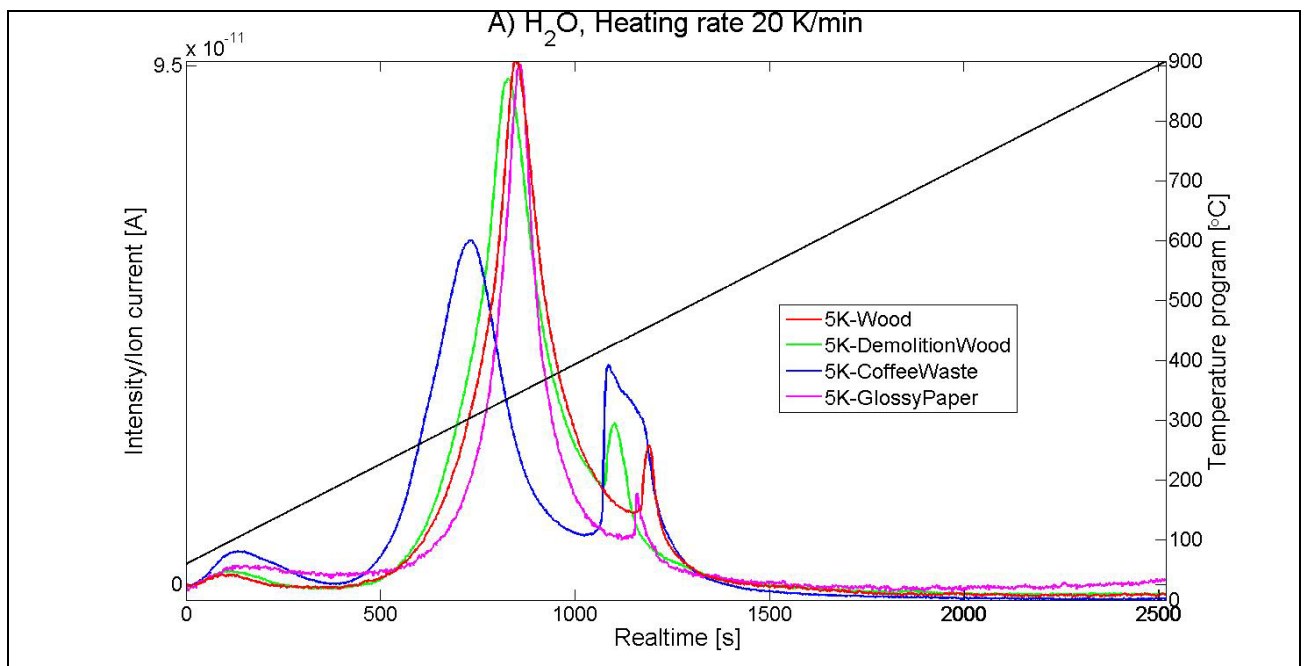
**Combustion experiments, reactive gas: 21% oxygen, 79 % argon**

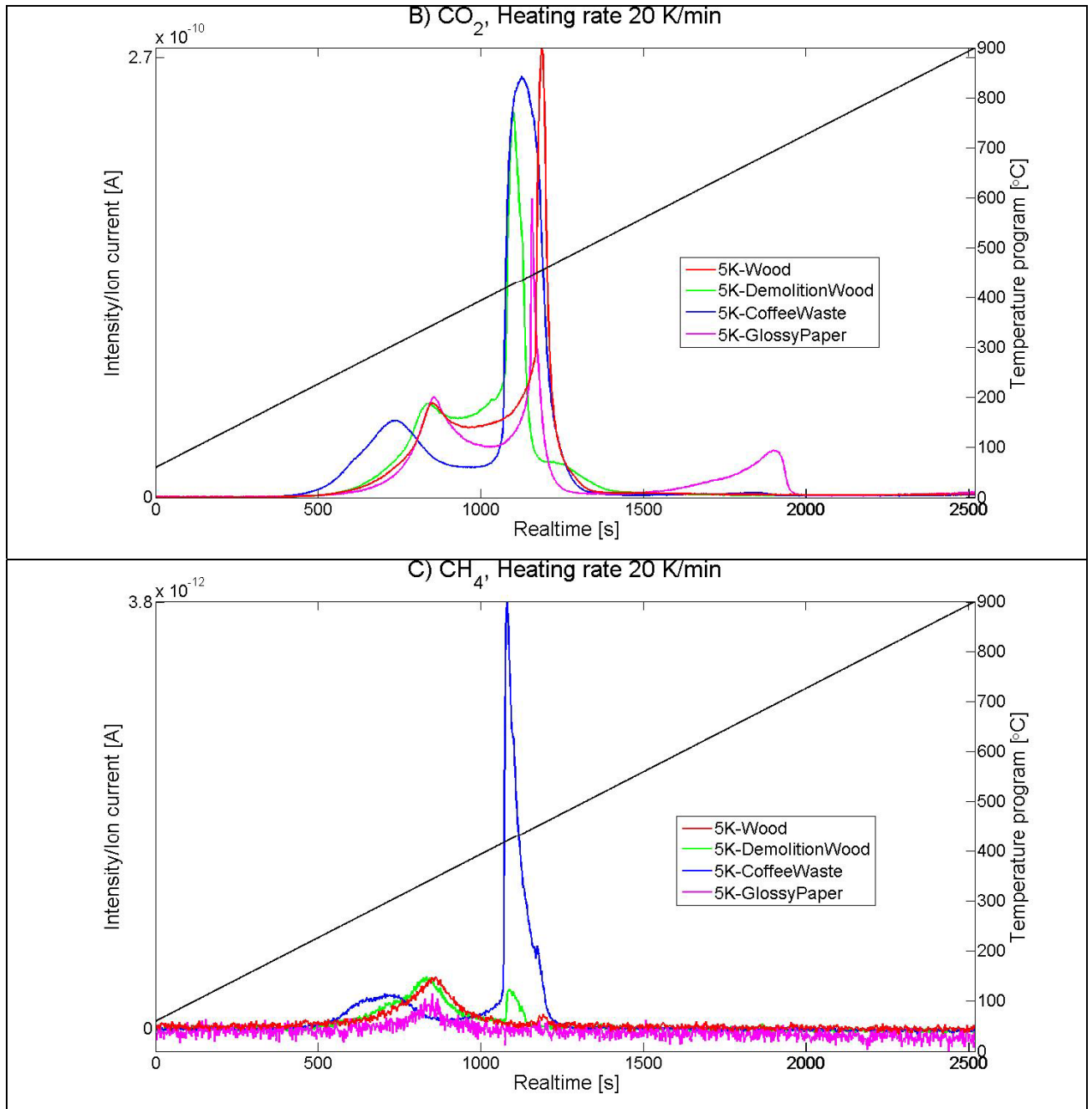




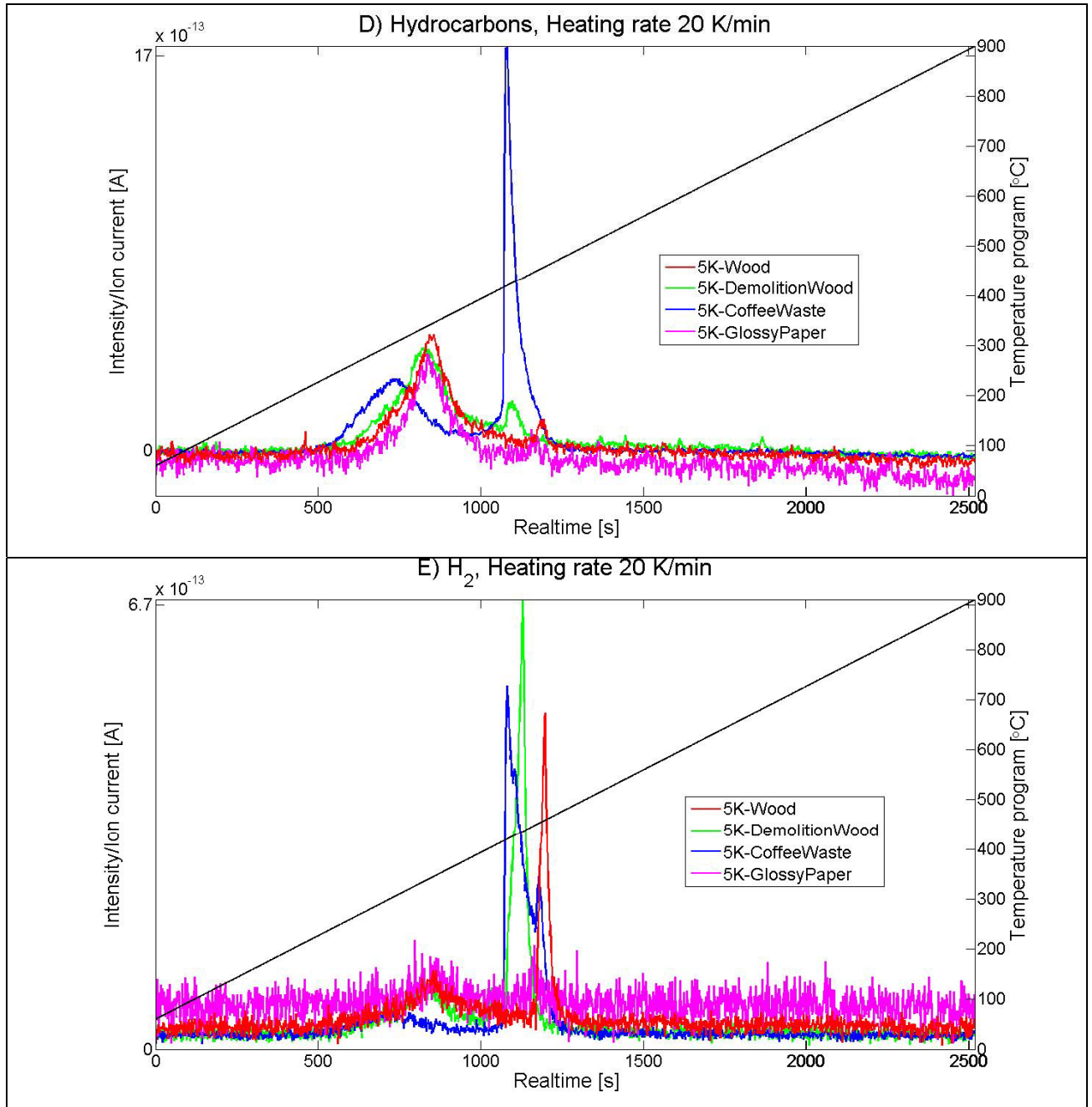


**Figure 9**

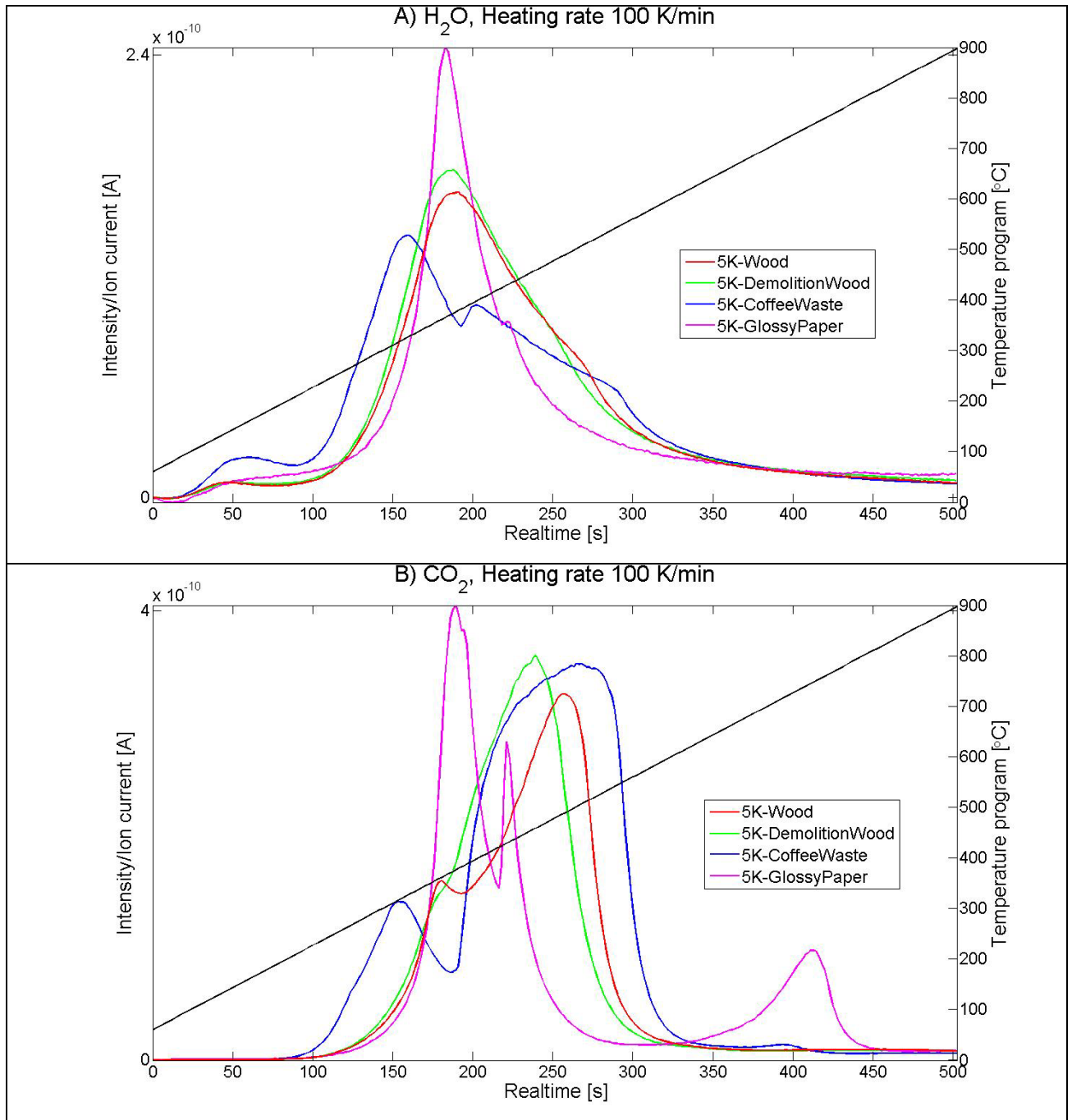


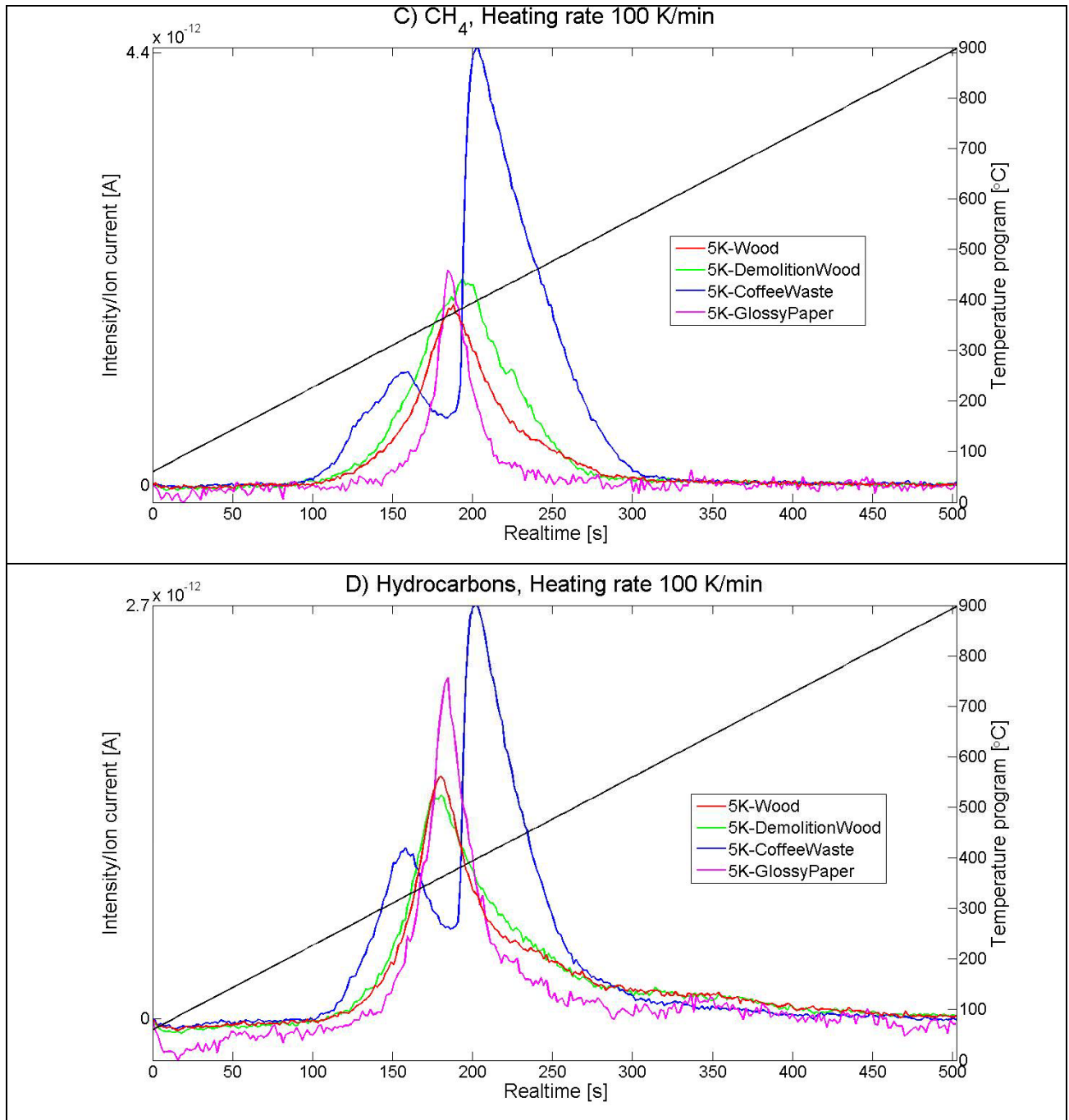


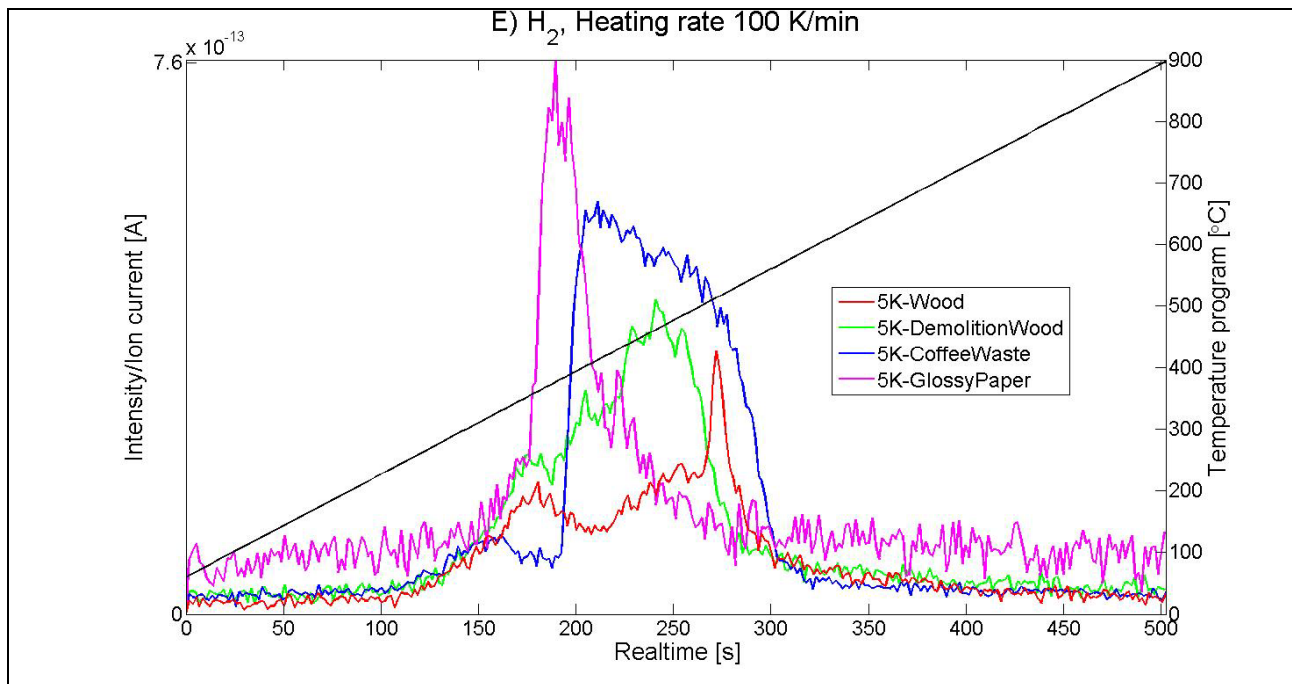




**Figure 10**

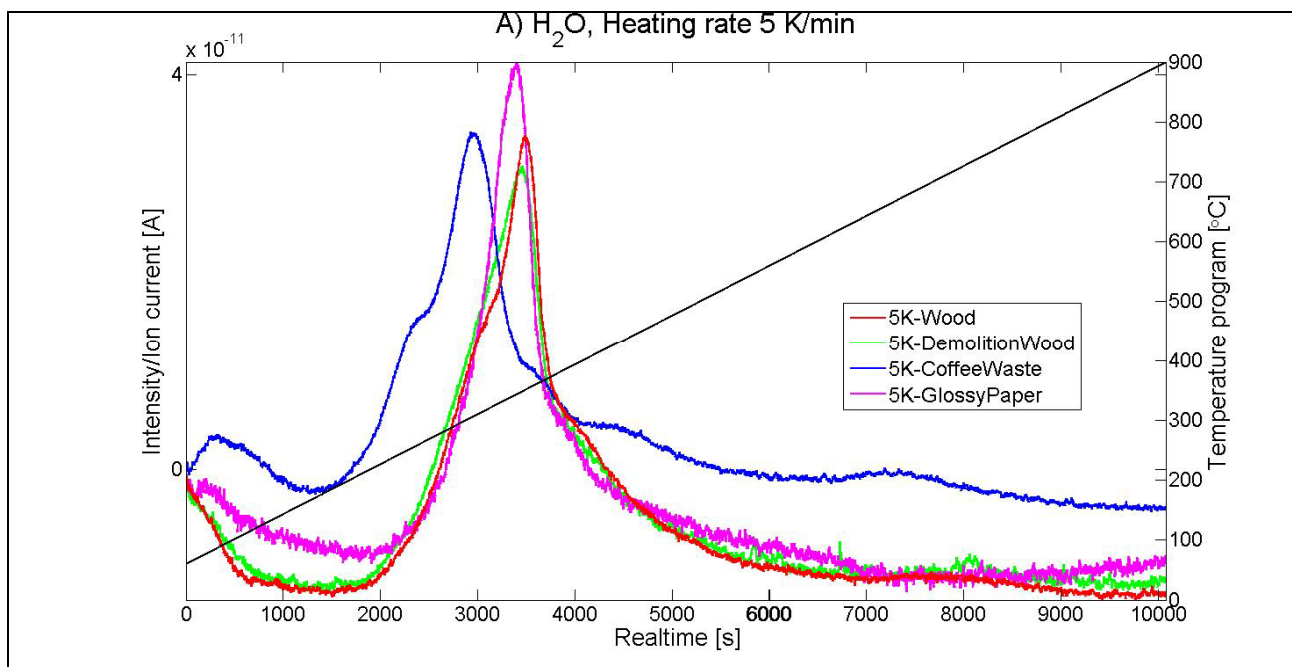


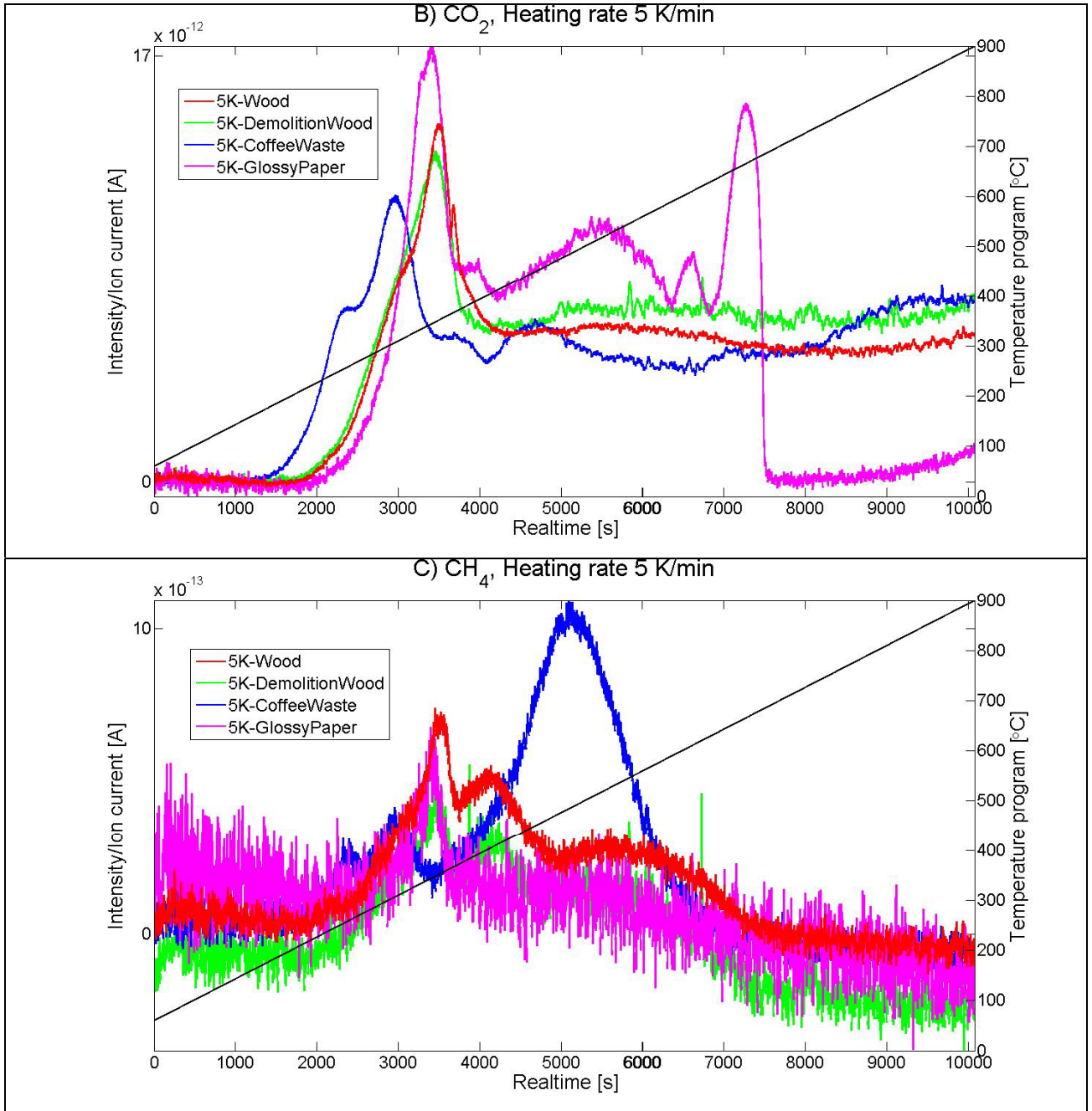




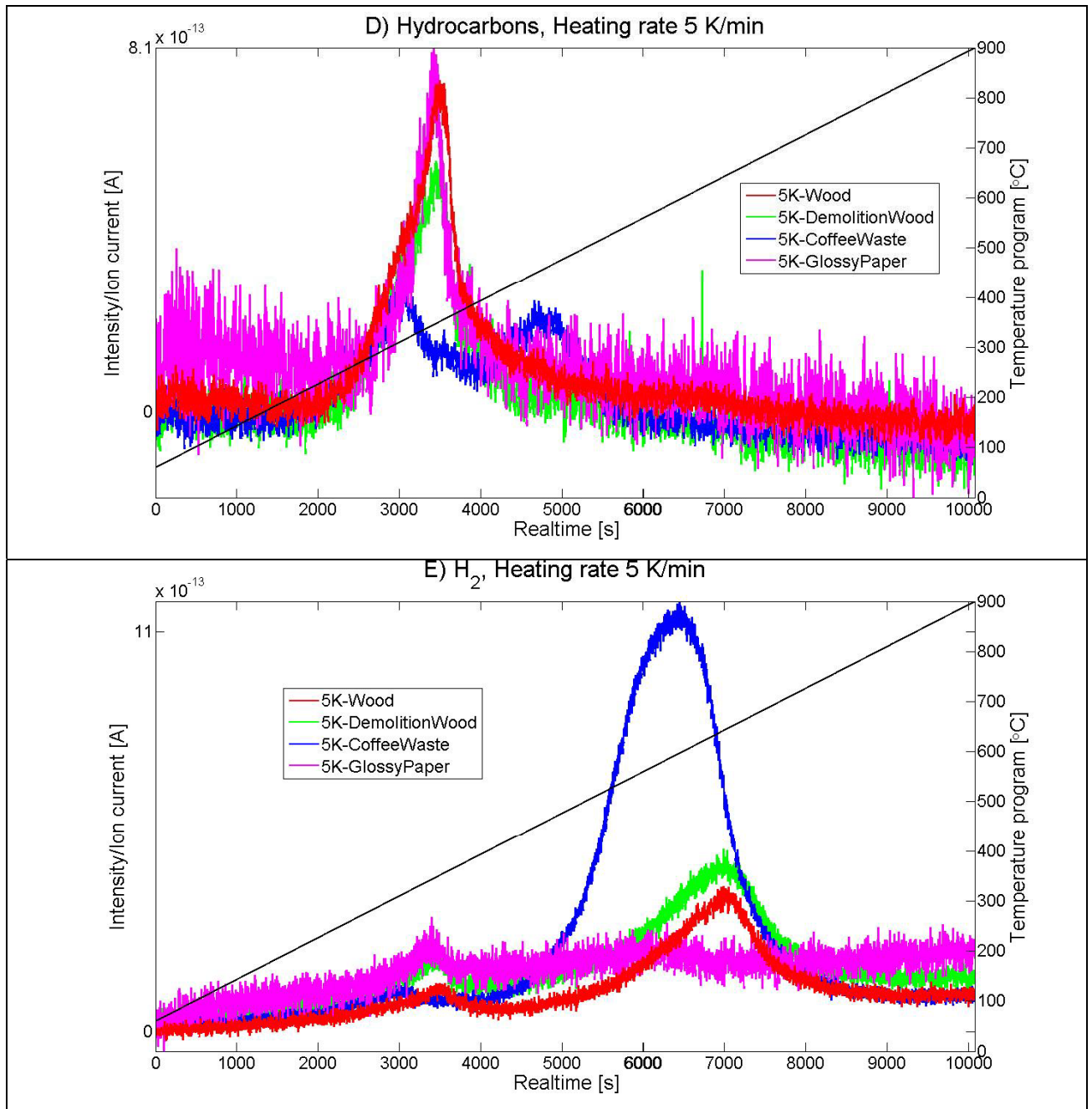
**Figure 11**

**Pyrolysis experiments, reactive gas: 100 % argon**

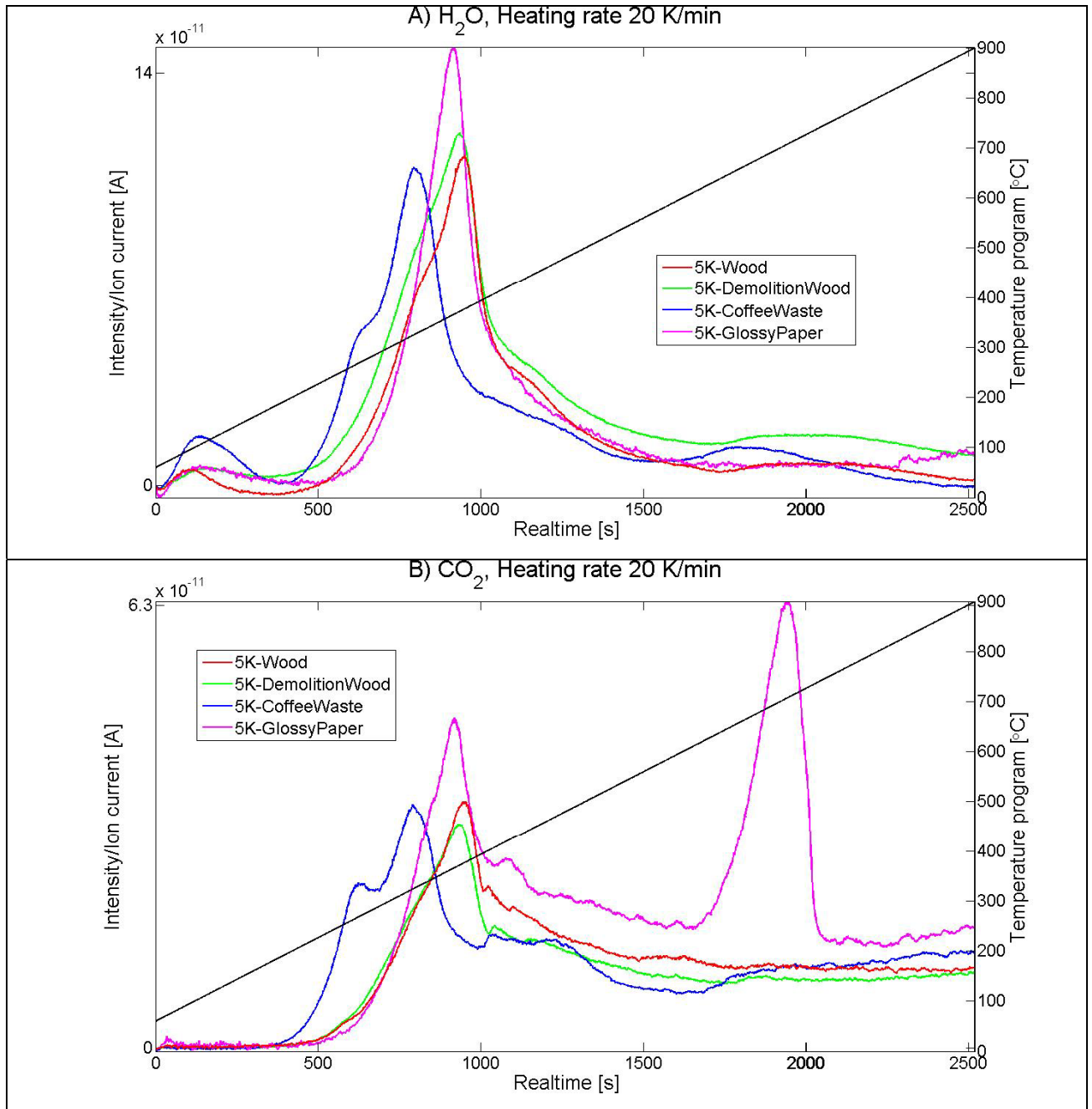




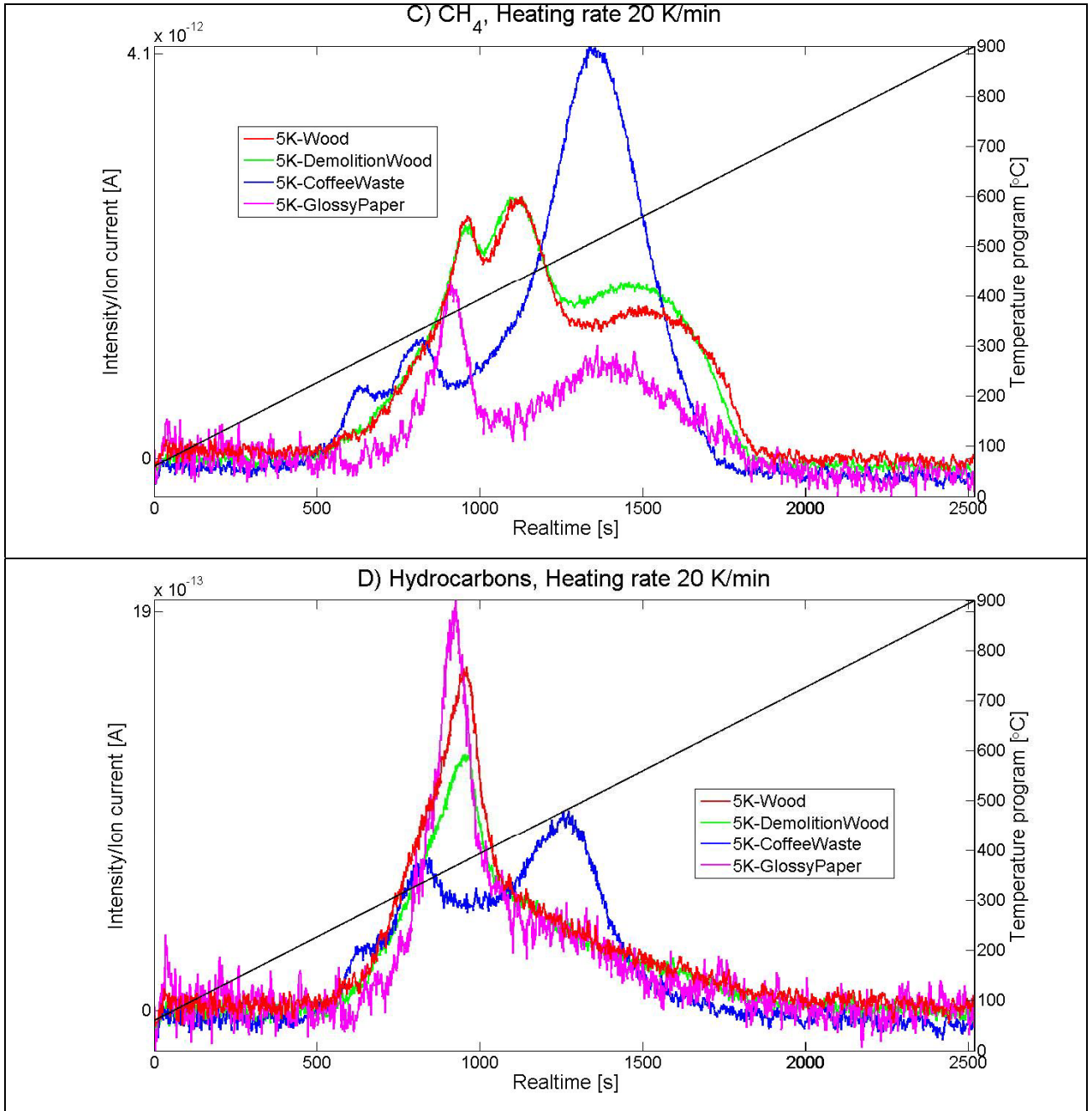




**Figure 12**







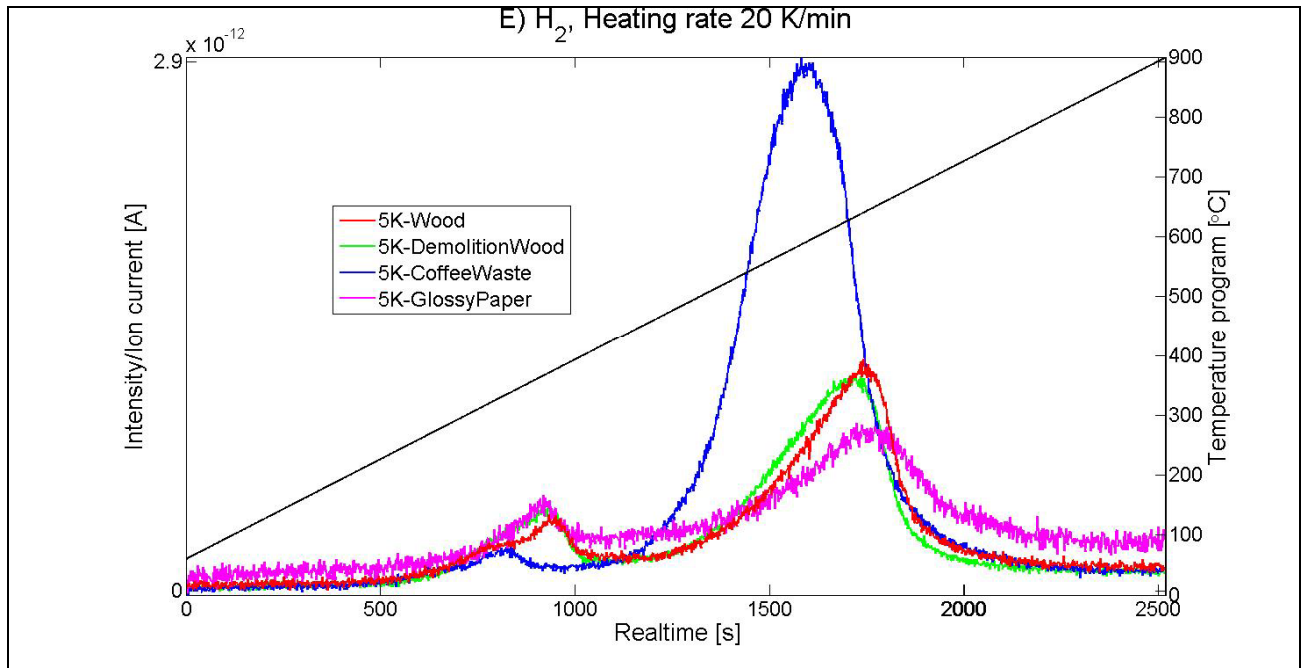
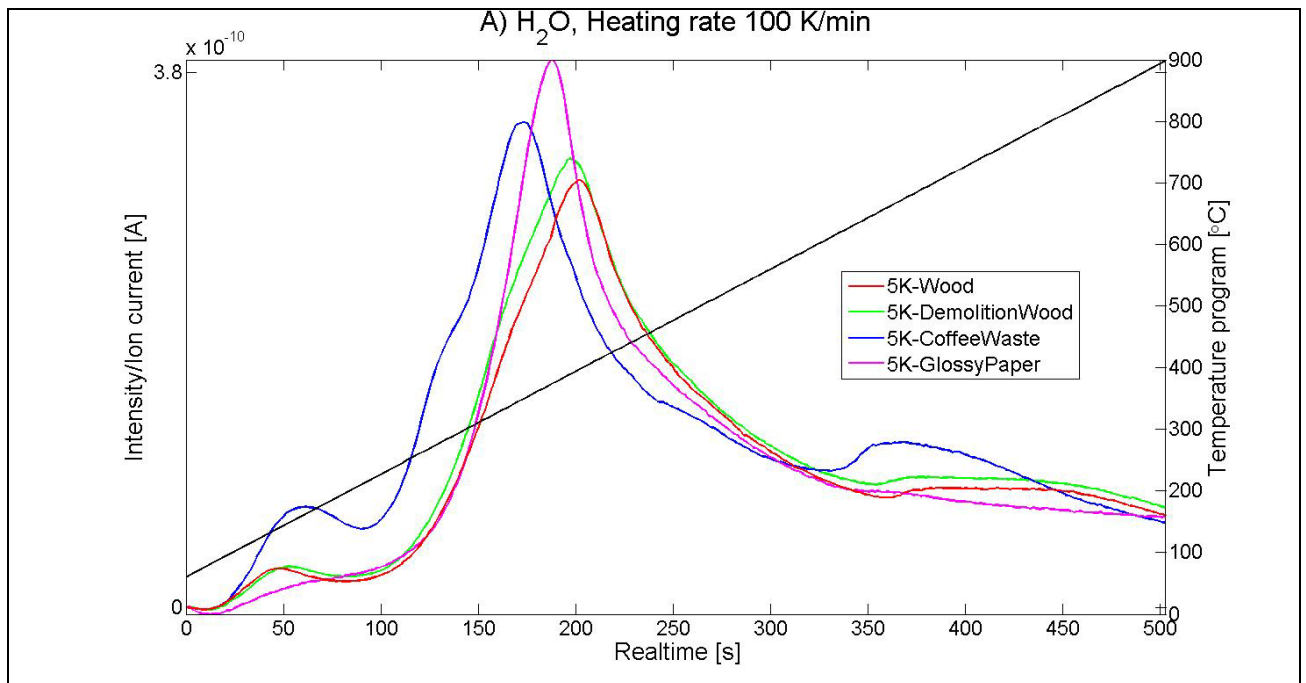
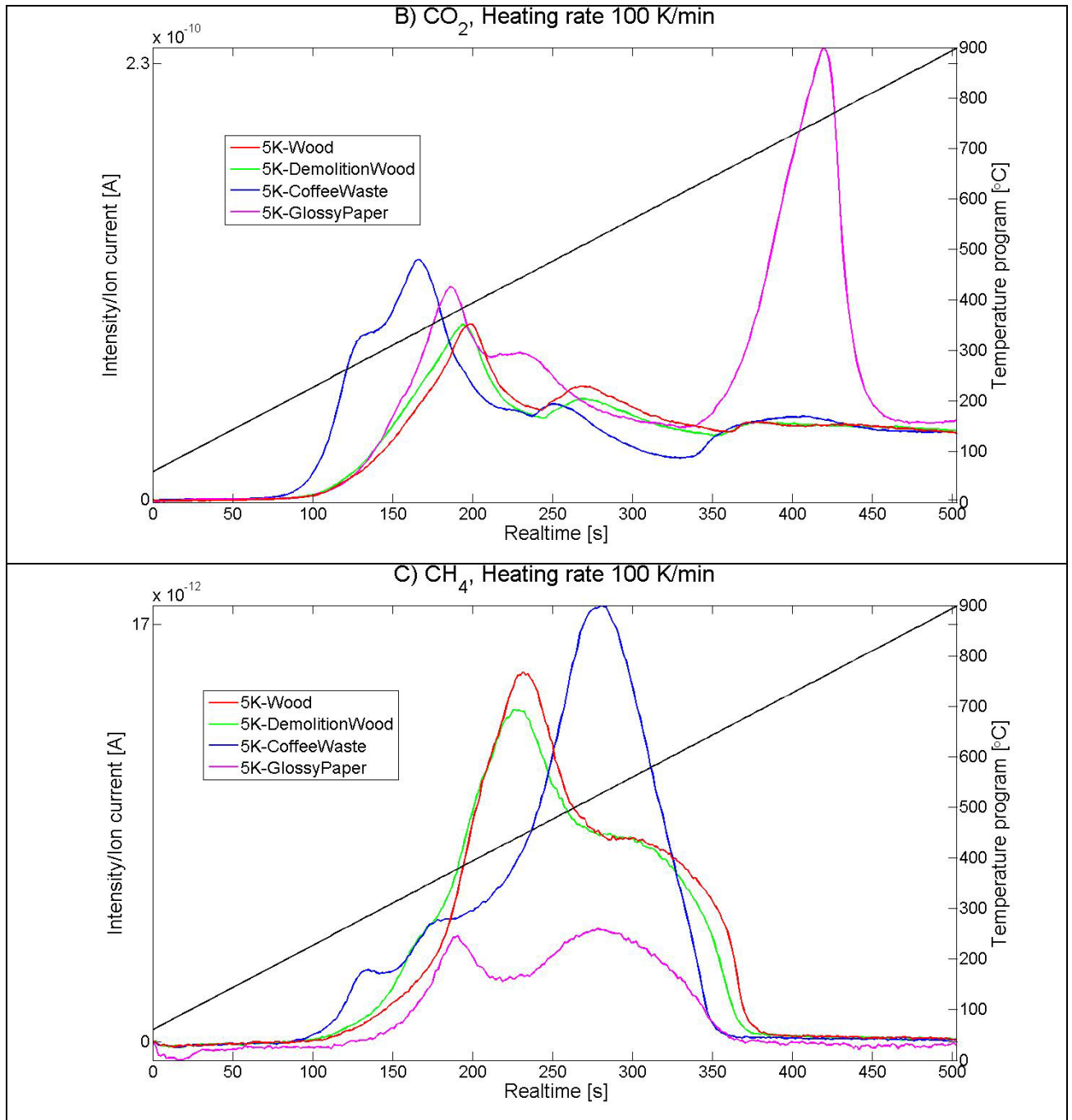
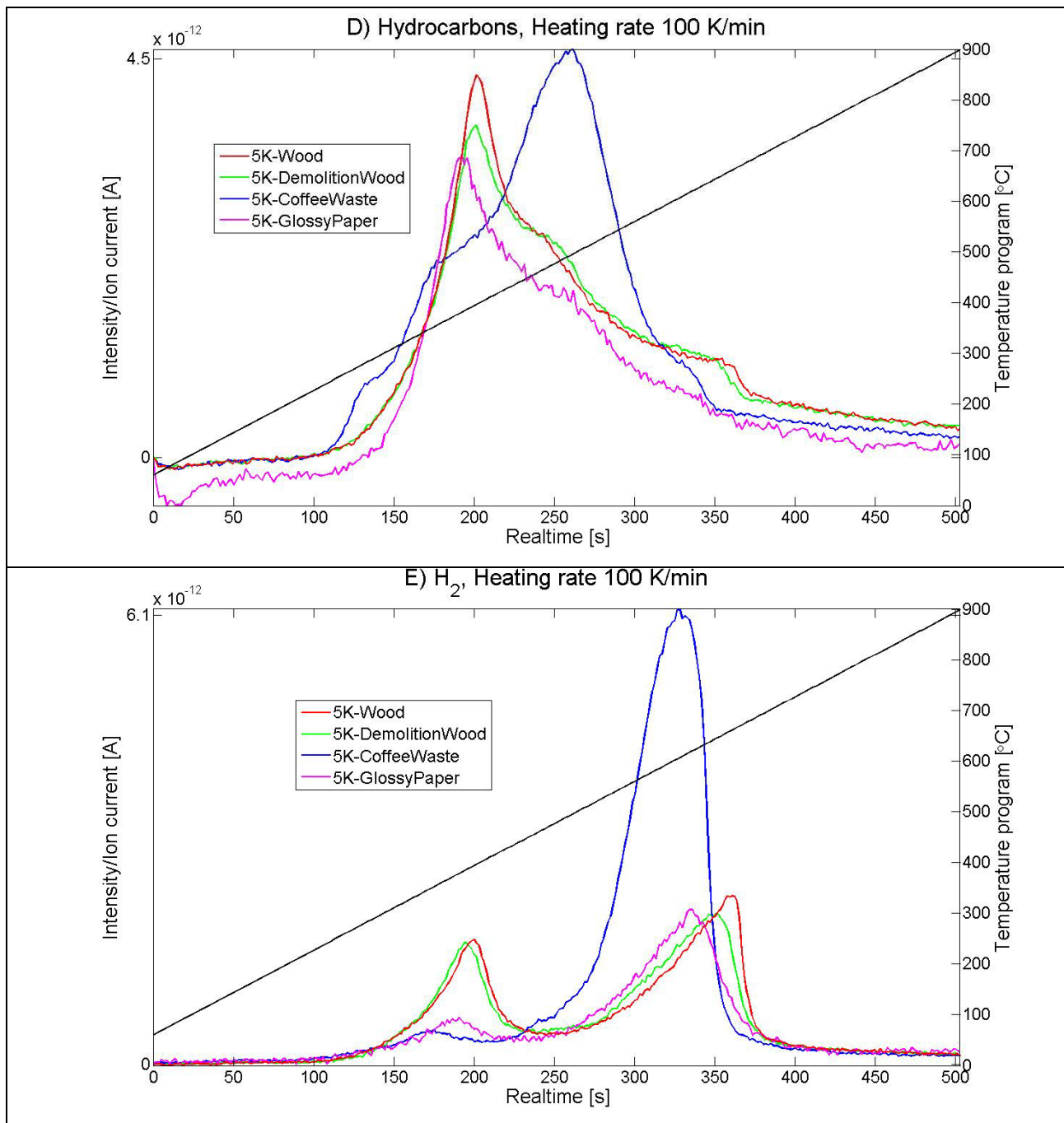


Figure 13







**Figure 14**

**SINTEF Energiforskning AS**  
Adresse: 7465 Trondheim  
Telefon: 73 59 72 00

**SINTEF Energy Research**  
Address: NO 7465 Trondheim  
Phone: + 47 73 59 72 00