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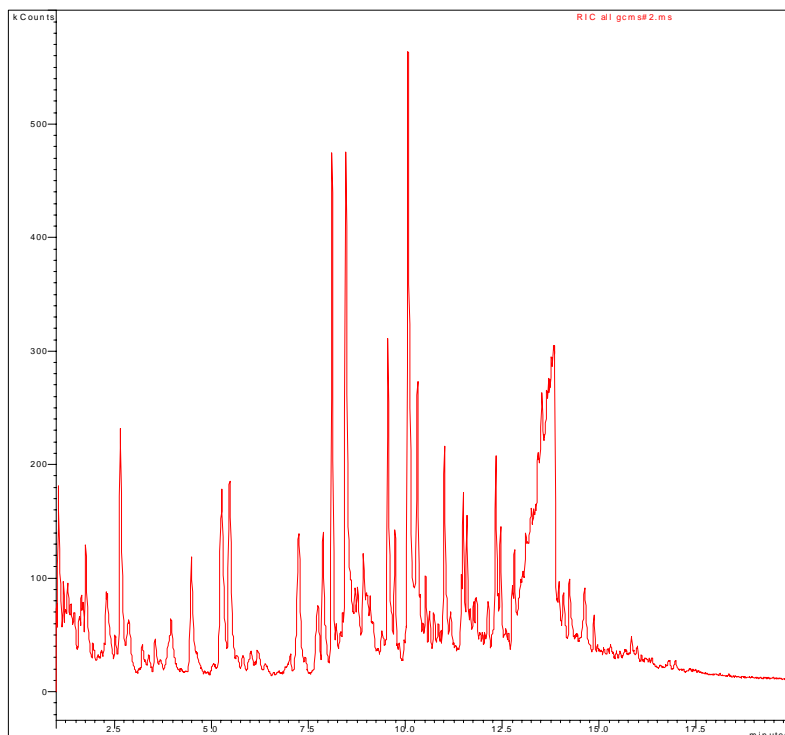
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EXPERIMENTAL CHARACTERISATION OF RESIDUAL-TAR IN WOOD CHAR



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INDEX

Introduction	5
Experiments and results	5
Pyro-oven experiments	5
Macro-TGA experiments	8
Flash pyrolysis analysis	10
Flash-pyrolysis and GC/MS analysis of residual tars	10
Flash-pyrolysis and FID analysis of residual volatile HC	14
Conclusion	15

INTRODUCTION

The pyrolysis process in staged gasifiers, where pyrolysis and gasification of relatively large particles takes place in separate reactors, can be characterised as “slow” pyrolysis meaning that the overall heating rate of the material, due to the particle size, is relatively slow (maximum 100 °C/min). This can be compared to the “fast” pyrolysis of fluid bed gasification. In a fluid bed gasifier relatively small particles are induced to heating rates that are several orders of magnitude higher than for slow pyrolysis.

One of the main advantages of staged gasification, is that by conducting the pyrolysis in a separate reactor in a controllable atmosphere and at controllable temperatures it is possible to produce char of a uniform quality. The main property with regards to the char quality, is the amount of “residual” tar in the char, meaning the amount of tar that will be released by further thermal treatment of the char. This property is very dependent on the temperature history of the char and in particular the pyrolysis end-temperature.

In order to make any conclusions about the residual tar volatiles from wood char it is very important to know the history of the char. In the experiments, wood char has been produced in the laboratory under controlled conditions, different char qualities have been produced by pyrolysing wood chips at similar heating rates with varying end-temperatures. To determine the relationship between char quality and residual tar volatiles, char has been produced at end-temperatures ranging from 250 to 1000 °C, and the char samples have been analysed for the content of tar volatiles.

For producing the char, wood chips from French pinewood have been used.

EXPERIMENTS AND RESULTS

PYRO-OVEN EXPERIMENTS

Experiments have been conducted with pyrolysis of wood chips samples at varying end-temperatures. Before the pyrolysis, the wood chips were dried in an oven for 24 hours at 100 °C. The dry wood chips were then pyrolysed in a special oven, batches of 20 g were heated at rates of 6 °C/min, and the atmosphere in the oven was kept inert by flushing with a constant flow of nitrogen. Picture 1 shows an example of a sample before and after pyrolysis. The end-temperature was kept constant for two hours, before cooling down, in order to achieve a uniform temperature of the char. Figure 1 shows an example of a temperature evolution during the pyrolysis.

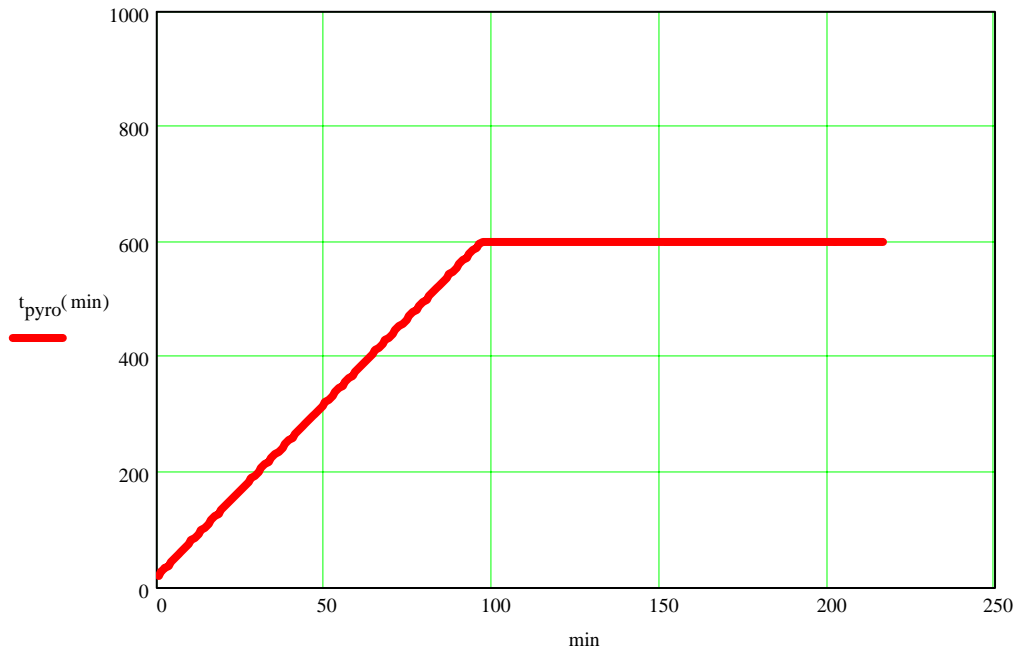


Figure 1 Example of the temperature for the pyrolysis experiments



Picture 1 A wood sample before and after pyrolysis.

After cooling down the char samples were weighed again in order to determine the weight-loss due to the pyrolysis, Figure 2 shows the result of the pyrolysis experiments, in the figure the release of volatiles is depicted as percent weight loss of the initial wood sample. Two test series are depicted, the initial test series (run 1) showed that in the interval from 250 to 400 °C there was a very high weight loss from the char, in the interval from 400 to 600 °C the degree of weight loss is reduced significantly and from 600 to 800 °C no weight loss is observed. In order to verify the observations from the first test run a second series of experiments was conducted, in this test run some of the samples were repeated in order to determine repeatability for the experiments. Samples were also made at three new end-temperatures in order to verify the characteristic curve of the volatilisation of the wood. In Figure 3 all the measurements are depicted as well as an exponential model curve for the volatilisation of the wood.

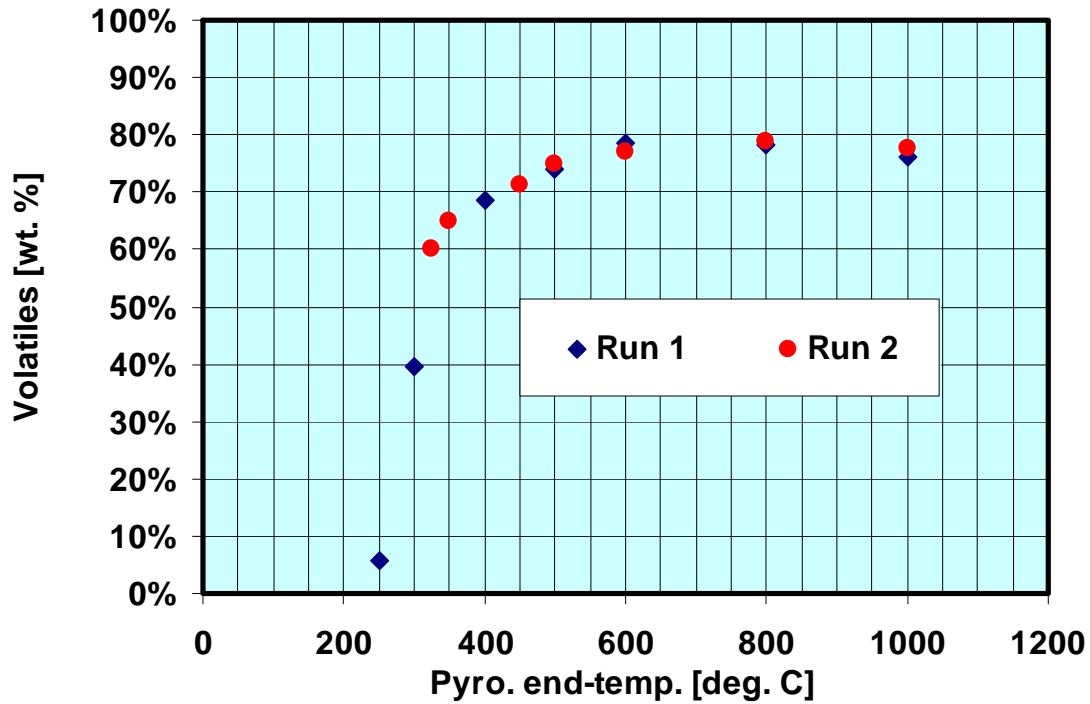


Figure 2 The two test runs for the release of volatiles in wt.% depicted as a function of the pyrolysis temperature.

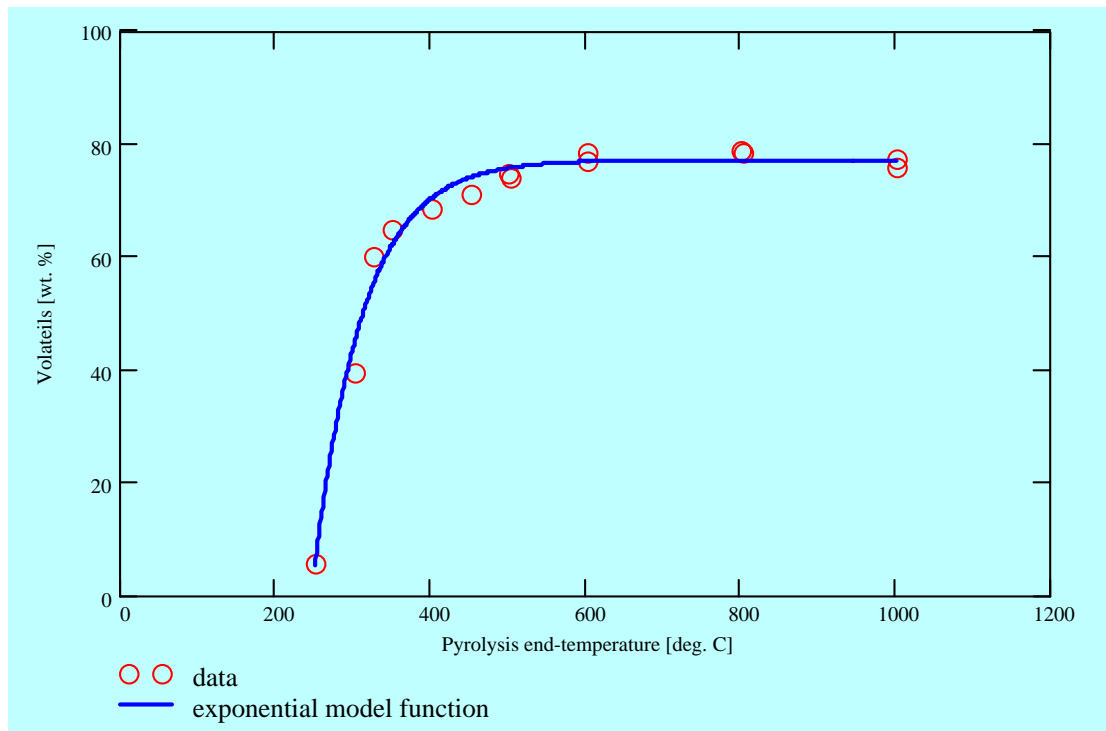


Figure 3 The volatilisation curve shown as an exponential model function.

That there is no measurable weight loss of the char at pyrolysis temperatures above 600 °C does not mean that volatiles are not released in this interval, the predominate volatile component released from the char at these elevated temperatures will though be hydrogen and the weight loss due to this is not detectable with the equipment used. The curve for the release of volatiles during pyrolysis corresponds well with what is seen in the literature [1].

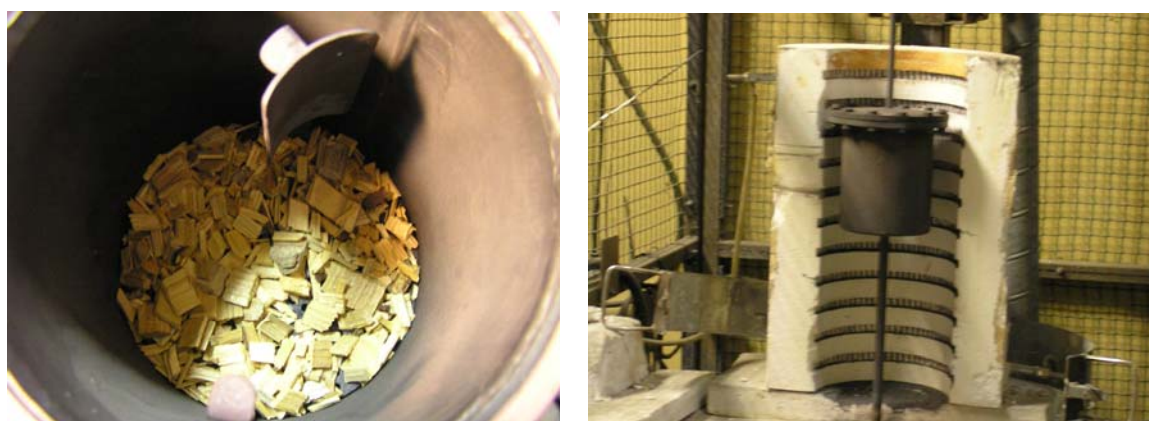
MACRO-TGA EXPERIMENTS

In order to verify the volatilisation of the woodchips during pyrolysis a parallel experiment was conducted where a 20 g woodchip sample was pyrolysed in a macro-TGA (see Picture 2) at a constant heating rate of 4 °C/min from 20 to 1000 °C (see Figure 4), the weight loss of the sample was measured continuously. The sample was flushed by nitrogen during the experiment.

The volatilisation curve from the TGA experiment is shown in Figure 5, as it is seen the curve is significantly different from the curve from the pyro-oven experiments. There is an apparent delay in volatilisation with regards to temperature and the magnitude is also reduced compared to the pyro-oven curve. After the experiment it was observed that some of the tar released during the pyrolysis had condensed in outlet pipe thus giving an error in the weight measurement, this is seen as part of the reason for the disparity of the TGA curve compared to the pyro-oven curve.

The particle size of the wood chips is of such that they are defined as being thermally thick [1], this implies that there can be a temperature gradient through the particle. This factor will result in a disparity in the results of the two experiments, since for each sample in the pyro-oven experiments the end-temperature was kept constant for two hours before cooling the sample down while in the TGA experiment the sample was continuously heated from room temperature to 1000 °C, thus the two heating approaches are not directly comparable. This could, in the temperature interval from 250-400 °C, explain the delay in volatilisation versus temperature for the TGA experiment compared to the pyro-oven experiment. Whereas the delay is apparent in this interval the slope of the two curves are comparable. In the interval 400-1000 °C the disparity becomes more significant, properly due to an increasing build up of tar in the outlet pipe.

It was decided that the existing TGA reactor, which is normally used for gasification of char, is not applicable for pyrolysis of wood due to the relative high amount of tars released.



Picture 2 The wood sample and the macro-TGA set-up.

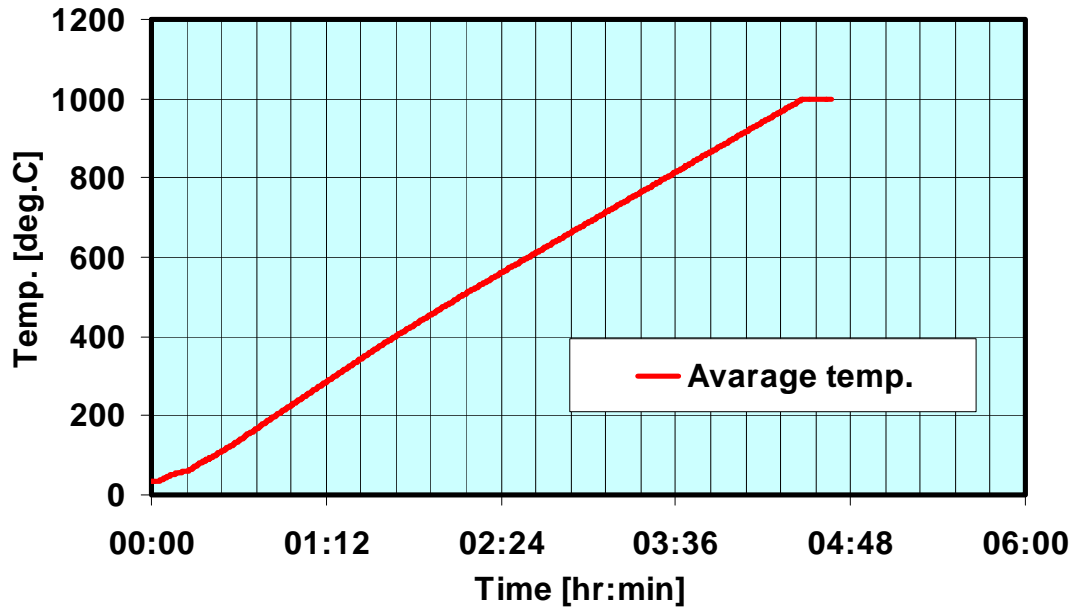


Figure 4 The measured temperature during the TGA experiment.

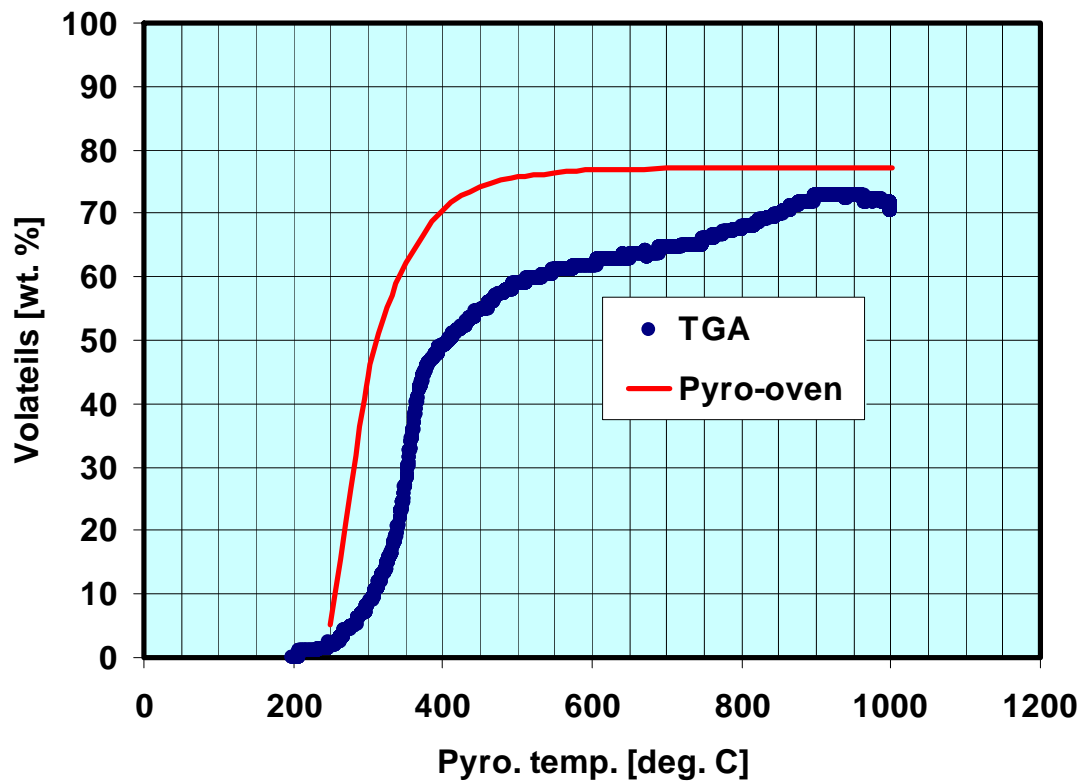


Figure 5 The volatilisation curve for the pyro-oven and TGA experiments

FLASH PYROLYSIS ANALYSIS

In order to characterise the quality of the char samples from the pyro-oven experiments, the residual tar volatiles in the char were analysed.

By combining analytical flash-pyrolysis of the char and GC/MS analysis of the produced volatiles, a qualitative determination of the composition of the tar was performed. By analysing the spectra of the tar volatiles from the different char samples it was possible to determine a relationship between degree of pyrolysis and the quality of the volatiles. Flash-pyrolysis followed by FID detection was used in order to quantify the organic volatiles.

Flash-pyrolysis and GC/MS analysis of residual tars

Flash-pyrolysis was performed by instantaneously heating up a small sample of char to a temperature of 800 °C. Figure 6 shows the measured heating curve for the flash-pyrolysis. Samples, of the quantity of 25-100 µg, were placed on a platinum foil and heated by inducing a high current to the foil. Picture 3 shows the char sample, and the foil on which the sample is placed. The volatiles produced by the flash-pyrolysis are directly induced on to the GC column followed by MS detection and can thus be evaluated. Analysis by flash-pyrolysis has been conducted on the following char samples from the pyro-oven experiments: 250, 300, 400, 500 and 600 °C.

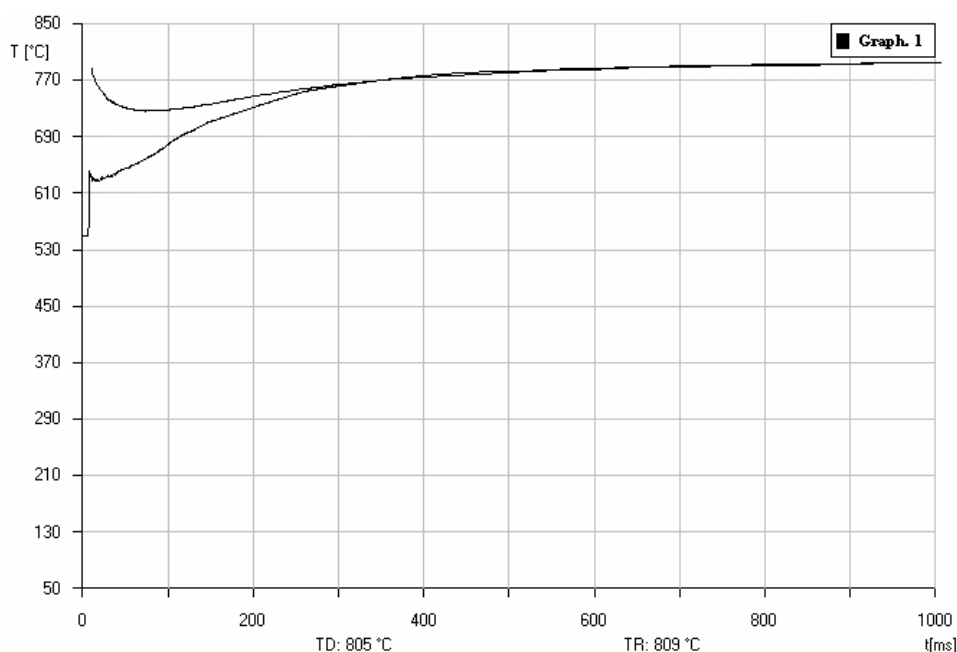
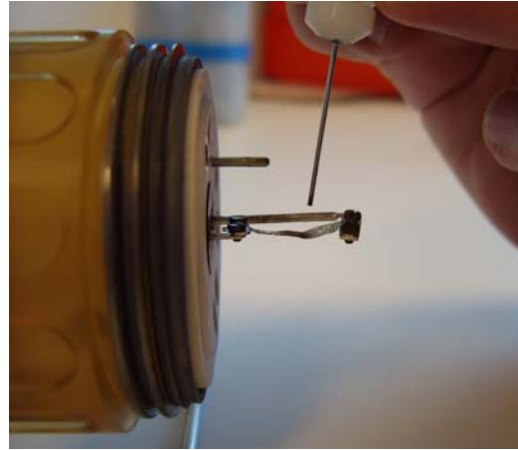


Figure 6 The heating curve for the flash-pyrolysis.



Picture 3 The char sample and the pyrolysis filament

In Figure 7 two chromatograms are shown, one for char that has been pyrolysed to an end-temperature of 250 °C and one that has been pyrolysed to 300 °C. The chromatograms depict the residual tar compounds that are released from the char through the flash pyrolysis, it is seen that a large range of tar volatiles, in significant quantities, are released from the low quality chars.

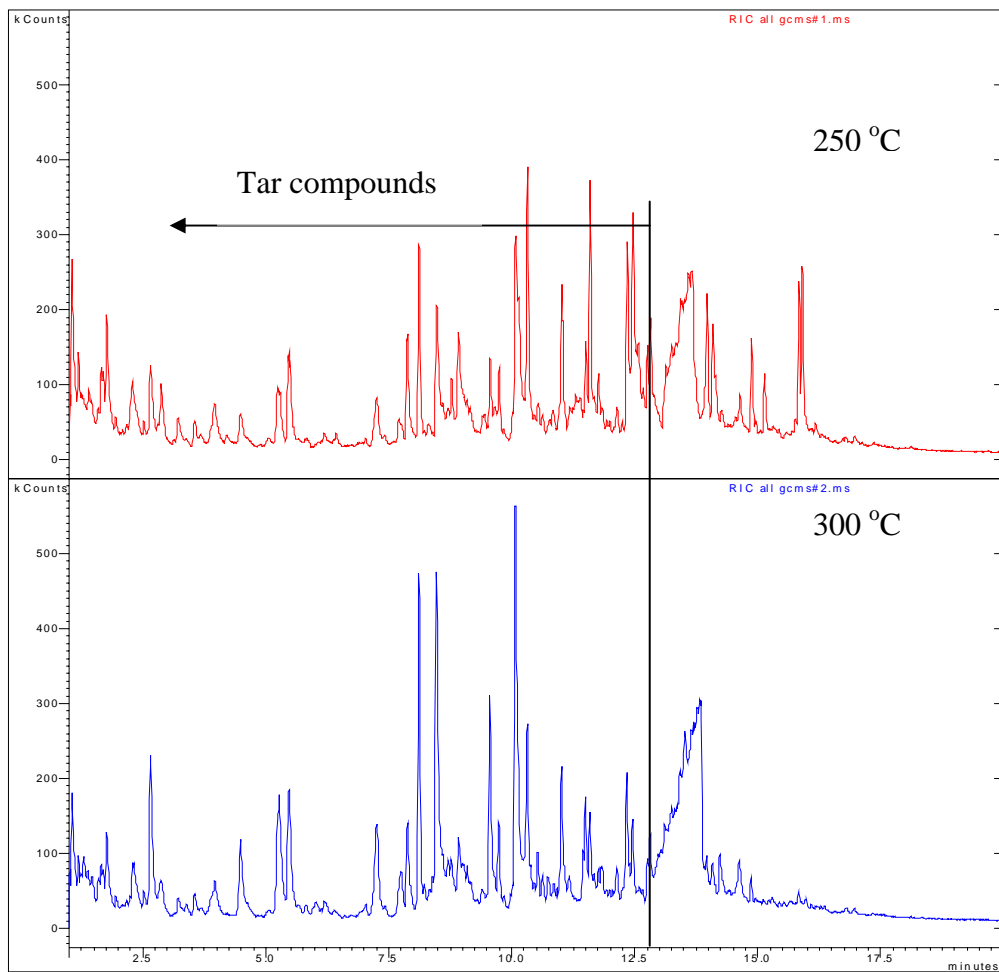


Figure 7 The chromatograms for the char samples that have been pyrolysed to 250 and 300 °C

Apparently there is no significant reduction in the residual tar for the 300 °C char compared with the 250 °C char, thus very low amounts of tar are release in this temperature interval, this relates to a significant release of volatiles as seen in Figure 3 were 43% of the total volatilisation takes place in this interval. The volatile compounds that are released from the char in this temperature interval are primarily CO, CO₂ and water.

In Figure 8 the tar release from 300 °C char is compared with the release from the 400 and 500 °C char, it is evident that there is significant difference in char quality when the pyrolysis temperature is increased from 300 °C to 400 °C. From these chromatograms it is apparent that for pyrolysis end-temperatures above 400 °C residual tar from the char is hardly detectable. In this interval were 37% of the volatiles are released also the major part of the tars are released, see Figure 3. A difference in residual tar for the 500 °C char compared to the 400 °C char is hardly detectable in these chromatograms.

Increasing the intensity of the chromatograms by a factor 67 it is possible to depict the very small amounts of tar volatiles that are released from the ≥ 400 °C char. Figure 9 shows the chromatograms for the 400, 500 and 600 °C char. It is seen that hardly any volatiles are detectable. For the 400 °C char a relatively large peak is though seen, this has been identified as being an anhydro-sugar which is a derivative from the breakdown of the celluloses in the char, this very characteristic peak is also seen for the lower temperature chars (Figure 7) while for the 500 °C the peak has disappeared, indicating the final breakdown of celluloses. The smaller peak, which is seen both for the 400 and 500 °C is also a breakdown product of celluloses. The breakdown of celluloses through pyrolysis has been proposed to go via anhydro-sugars and the end product is either low MW volatile products or solid carbonised products. The anhydro-sugar and its derivatives are proven to have a high affinity to oxidation and will thus decompose if exposed to an oxidation zone as in staged gasifiers. This implies that char that has been pyrolysed at temperatures above 400 °C will not contain any significant residual tars when it reaches the char bed in the gasifier.

In the 600 °C chromatogram no detection of any volatiles are seen, only noise. This proves that at pyrolysis end-temperatures of this magnitude there will be no residual tar in the char and thus the char will not contribute to any further tar formation in a subsequent gasification of the char.

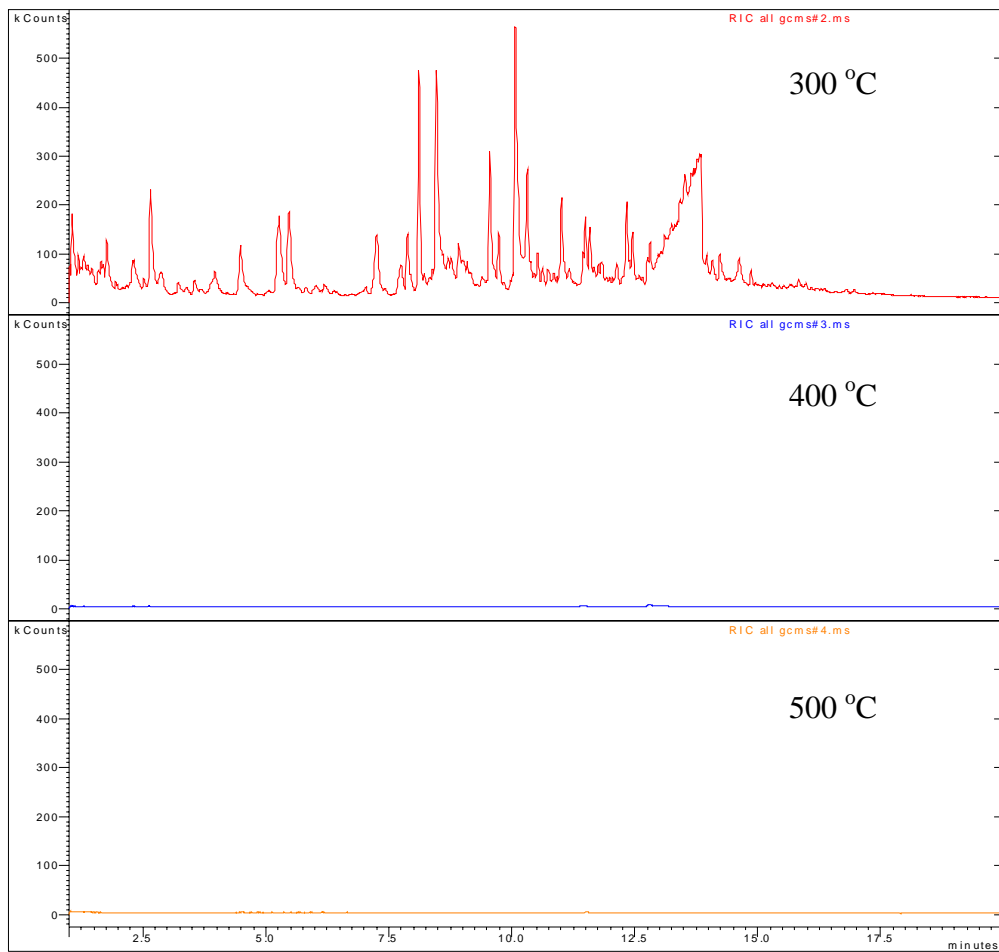


Figure 8 The chromatograms for the char samples that have been pyrolysed to 300 and 500 °C

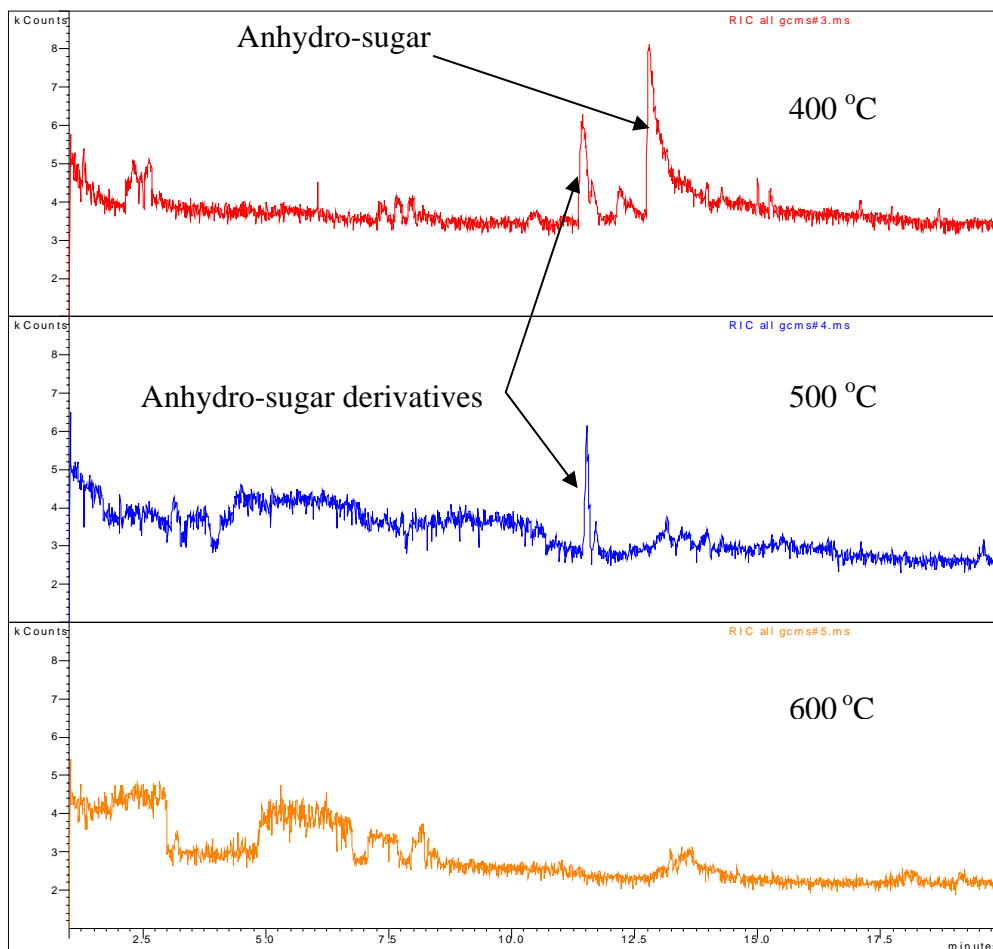


Figure 9 The chromatograms for the char samples that have been pyrolysed to 400-600 °C.

Flash-pyrolysis and FID analysis of residual volatile HC

Experiments with analytical flash-pyrolysis followed by flame ionisation detection (FID) of the organic volatiles have been conducted on tree of the char samples: 250, 300 and 500 °C. The flash-pyrolysis was conducted in the same way as described above, the amount of released volatiles was detected by an FID which only detects the volatile hydrocarbon compounds that are released by the pyrolysis.

Table 1 shows the results of the experiments were HC denotes the total amount of volatile hydrocarbons that has been released from the char by the pyrolysis. The total amount of HC also includes low MW compounds such as CH₄ and C₂H₆. From experiments with pyrolysis of straw [2] it is known that CH₄ constitute a significant amount of the volatile HC released by pyrolysis. The contribution of low MW compounds on the total volatile HC amount has not been investigated in this project. The work regarding characterisation of char will be continued in the scope of the *Green Fuel Cell* [3] project.

From the second column in Table 1 it is seen that the amount of volatiles in the 250 °C char is the same as for the 300 °C char which corresponds very well with the results of the GC/MS measurements as seen in Figure 7. Likewise the significant drop in HC volatiles from 300 °C to 500 °C corresponds with what is seen from Figure 8.

Only 0.7 g of residual volatile HC pr. Kg of wood chips is present in the 500 °C char, and the HC will predominantly consist of anhydro-sugar derivatives and CH₄.

Pyro. End-temp. [°C]	Volatiles [g HC/kg char]	Volatiles [g HC/kg wood chips]
250	87.2	82.2
300	88.7	53.7
500	2.7	0.7

Table 1 Results of the flash-pyrolysis/FID analysis, HC denotes the total amount of the volatile hydrocarbons.

CONCLUSION

An experimental investigation of wood-char quality with regards to the “residual” tar content has been conducted.

To determine the relationship between char quality and residual tar volatiles, char has been produced at end-temperatures ranging from 250 to 1000 °C, and the char samples have been analysed for the content of tar volatiles.

The char samples were produced by slow pyrolysis of wood chips from pine, at a heating rate of 6 °C/min in nitrogen. The volatilisation curve for the wood chips showed that at 600 °C more than 97% wt. of the volatiles has been released.

In order to determined and characterise the residual tar content in the char, flash pyrolysis combined with GC/MS analysis has been applied. The qualitative analyses of the char showed that at a pyrolysis end-temperature of 600 °C no residual volatile tar compounds were detectable. This implies that pyrolysis of wood char at temperatures above 600 °C will not result in further release of tar compounds from the char.

It was shown that the almost all of the tar produced by slow pyrolysis of wood chips is released in the temperature interval between 300 and 400 °C, only small amounts of anhydro-sugar and its derivatives is released at elevated temperatures.

[1] *Pyrolyse af træflis*. Søren Thaaning Pedersen, Stig Møller Andersen. Master thesis, Technical University of Denmark MEK-ET-EP 2001-04.

[2] *Eksperimentel og beregningsmæssig undersøgelse af forhold ved pyrolyse og forgasning af halm* Ulrik Henriksen, Erik Kofoed, Ole Christensen, Søren Gabriel, Thomas Koch. Department of Energy Engineering. DTU. RE 91-3. 178 pages. 1991

[3] [GFC website http://www.dk-teknik.dk/cms/site.asp?p=2408](http://www.dk-teknik.dk/cms/site.asp?p=2408)

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