

VAPOUR PHASE CRACKING OF TAR FROM PYROLYSIS OF BIRCH WOOD

by

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The vapour phase cracking of tar from pyrolysis of birch wood (particles, 0.5–1.0 mm) was studied in a thermogravimetric analyser (TGA) and in a coupling of the TGA with a consecutive tubular reactor. The TGA was heated from 100 to 1000 °C at a heating rate of 5 K/min in all experiments and the tubular reactor was operated at constant temperatures of 600, 700, and 800 °C at different residence times. Kinetic parameters for tar cracking and yield coefficients for the production of different gases from tar cracking were calculated.

Introduction

The tar content of gases from thermochemical conversion of biomass has an important influence on the operation of any downstream equipment 1–3 . Although knowledge of the tar cracking kinetics is of major importance for finding optimal operating conditions and an optimal reactor design (e. g. of gasifiers, ...) only few papers have been presented dealing with kinetics for tar cracking [4–9]. And this despite the fact that hundreds of papers have been presented dealing with kinetics for primary pyrolysis of different types of biomass (e. g. 10–14).

The objective of the present paper was to investigate vapour phase cracking of tar from pyrolysis of birch wood. Besides the determination of kinetic parameters for tar cracking and that of yield coefficients for the formation of product gases, variation of these parameters with temperature of tar formation was also found. This finding could be of importance for the upgrading of the tars.

Sample preparation

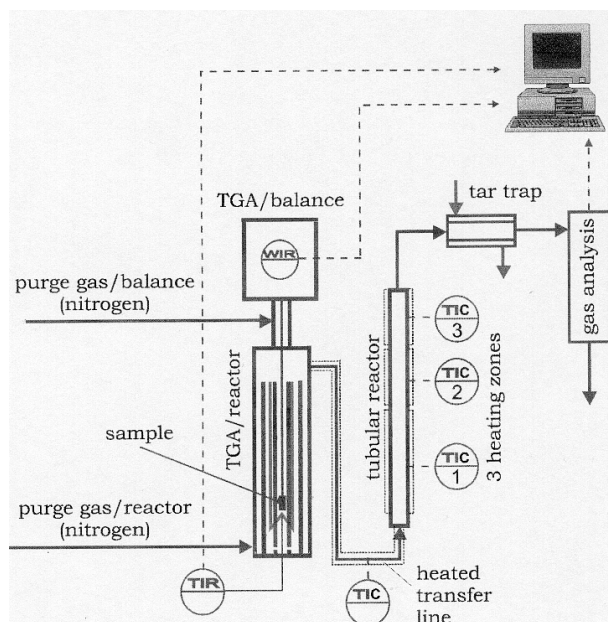
For each experiment about 250 mg of birch wood particles (size fraction 0.5–1.0 mm) were filled in a sample basket (25 mm in length and 10 mm in diameter) made of Incoloy 800 wire mesh. The preparation of the particles was done by means of a rasp and sieving. Before the experiments all samples were dried for 2 hours at a temperature of 105 °C in a drying oven. Table 1 shows the proximate and ultimate analysis of the birch wood used.

Table 1. Proximate and ultimate analysis of birch wood

wt.-%, dry	
Volatiles	88.6
Fixed C	11.1
Ash	0.3
wt.-% dry and ash free	
C	50.7
H	6.3
O	42.3
N	0.7

Experimental set-up

Figure 1 shows a diagram of the experimental set-up used for this work. It is a coupling of a thermogravimetric analyser (TGA) and a tubular reactor, where experiments both with the TGA alone and with the coupling were carried out. The tubular re-

**Figure 1. Thermogravimetric analyser combined with a tubular reactor for investigation of tar cracking reactions**

actor ($\varnothing 16 \text{ mm} \times 2.2 \text{ m}$) is made of quartz-glass (for avoidance of possible catalytic effects of metallic compounds 15) and is provided with three independent heatable zones in order to achieve different residence times of the volatiles. A detailed description of this experimental set-up can be found in 16.

In all experiments the TGA was operated at the same conditions. The wood samples inside the TGA-reactor were heated from 100 to 1000 °C at a heating rate 1 of 5 K/min. During the heating, the reactor of the TGA was purged with $2.4 \text{ l}\cdot\text{min}^{-1}$ (s.t.p.) of nitrogen. In order to protect the balance of the TGA from the pyrolysis gases, it was purged separately with $1.2 \text{ l}\cdot\text{min}^{-1}$ (s.t.p.) of nitrogen during the experiments. In the experiments with the tubular reactor, the latter was operated at temperatures of 600, 700 or 800 °C, however those zones which were not needed for experiments with short residence times were kept at 250 °C in order to avoid tar condensation. The tubular reactor was purged with the total flow of gas ($3.6 \text{ l}\cdot\text{min}^{-1}$ (s.t.p.) nitrogen + volatiles) coming from the TGA. The pressure in the experimental set-up (TGA and tubular reactor) was atmospheric in all experiments. Table 2 gives an overview of the operating conditions in the TGA and in the tubular reactor during the experiments.

Downstream of the tubular reactor, the product gas was cleaned in a water cooled tar trap at a temperature of 15 °C. The non-condensable gas mixture was analysed with regard to the contents of carbon monoxide, carbon dioxide, methane, ethane, ethene, acetylene, hydrogen and water. The gas analysis was done by a BOMEM MB 100 FTIR-spectrometer (Hartmann & Braun), a BINOS 1000 carbon monoxide analyser (Fisher & Rosemount) and a CALDOS hydrogen analyser (Hartmann & Braun). Tar was assumed to be the difference between the differential mass loss (from the TGA) and the sum of the gases found.

Table 2. Operating conditions in the TGA and in the tubular reactor

Run	TGA	Tubular reactor					
		Zone	Entrance	1	2	3	Experimental average residence time in heated zone $\tau \text{ s}$
		Length m	0.13	0.95	0.5	0.62	
#2	Temperature: 105–1050 °C Heating rate: 5 K/min	Temperature °C	250	600	600	600	2.12
#4			250	250	250	600	0.64
#5			250	700	700	700	1.82
#6			250	250	700	700	0.99
#7			250	250	250	700	0.55
#8			250	800	800	800	1.63
#9			250	250	250	800	0.49
#1		Without tubular reactor					

Results and discussion

Results from the tar cracking experiments

Figures 2 to 10 show the experimentally found rates of formation of tar, carbon monoxide, carbon dioxide, methane, ethane, ethene, acetylene, hydrogen and water over the TGA-temperature (= sample temperature) from the different runs (see Table 2). It must be noted that the rates of formation shown in figures 2 to 10 are overall rates

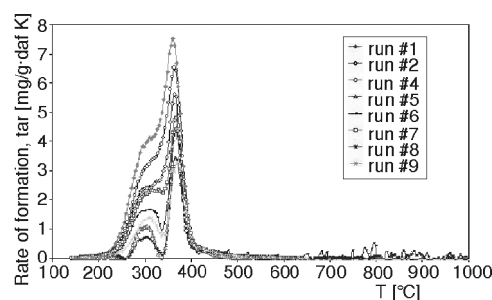


Figure 2. Rate of tar formation from different runs, as difference form differential mass loss and sum of rates of formation of all detected gases

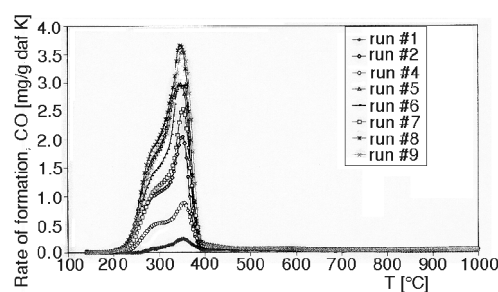


Figure 3. Rate of formation for carbon monoxide from different runs

of formation. This means that they represent the amounts formed in the total system "TGA + tubular reactor". Since the tar produced by primary pyrolysis in the TGA does not completely crack in the tubular reactor, the overall rates of tar formation from the different runs are always positive. The same applies for the different gas components. These rates of formation are again overall rates of formation (formed in the total system

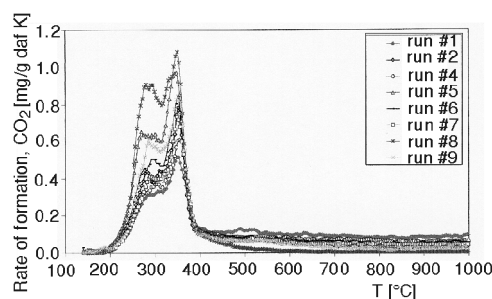


Figure 4. Rate of formation for carbon dioxide from different runs

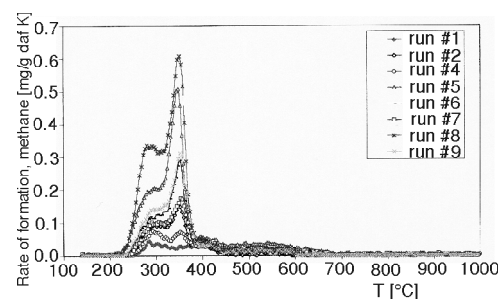


Figure 5. Rate of formation for methane from different runs

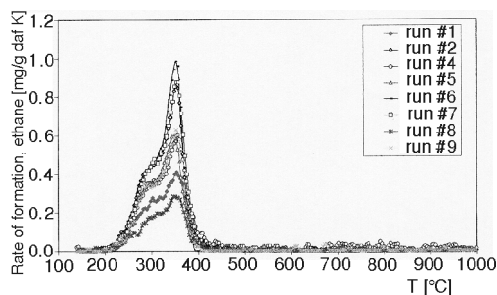


Figure 6. Rate of formation for ethane from different runs

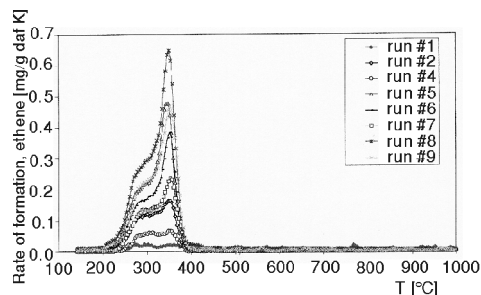


Figure 7. Rate of formation for ethene from different runs

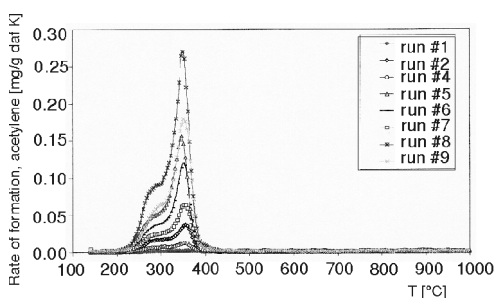


Figure 8. Rate of formation for acetylene from different runs

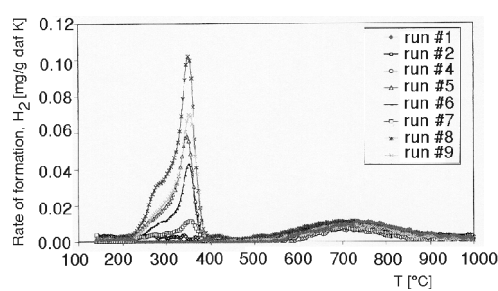


Figure 9. Rate of formation for hydrogen from different runs

”TGA + tubular reactor”). And these overall rates of formation for the different gas components result from primary pyrolysis reactions (in the TGA) and the contribution from tar cracking (in the tubular reactor).

Run #1 represents the result obtained from a TGA experiment without the tubular reactor. Because of the low heating rate in the TGA, the volatiles leaving the wood particles inside the reactor of the TGA are only exposed to temperatures almost equal to the temperature of their formation. Since most of the volatiles were formed at low temperatures (250–450 °C) where the extent of vapour phase tar cracking reactions can be neglected [4, 16], in the TGA only primary pyrolysis reactions are considered. Besides tar the main products from primary pyrolysis of birch wood are char, carbon monoxide, carbon diox-

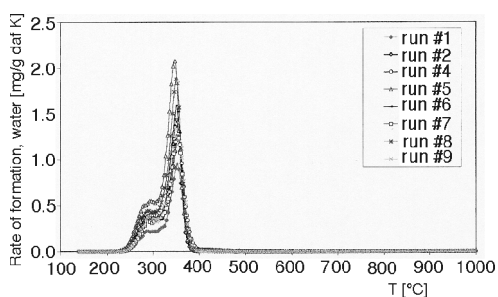


Figure 10. Rate of formation for water from different runs

ide, ethane and water. Further from primary pyrolysis of birch wood low amounts of methane, ethene, acetylene and hydrogen are obtained.

Runs #2 to #9 represent the results obtained from experiments using the TGA coupled with the tubular reactor where the tubular reactor was operated at different conditions (see Table 2). In all runs the TGA was operated at the same conditions as in run #1. Because of this it is assumed that in the TGA also in runs #2 to #9 only primary pyrolysis takes place and the products leaving the TGA are the same as in run #1. A fact which supports this assumption is that the sample weight loss curves from runs #1 to #9 are identical. Therefore the differences in the experimentally found rates of formation for tar, carbon monoxide, carbon dioxide, methane, ethane, ethene, acetylene, hydrogen and water (see Figs. 2–10) from the different runs are only from tar cracking reactions in the tubular reactor downstream of the TGA.

As can be seen in Fig. 2, the differences in the rates of tar formation between run #1 (only primary pyrolysis) and runs #2 to #9 (experiments using the tubular reactor) are large up to a temperature of 370 °C and decrease with higher tar formation temperature (= sample temperature). As already found from pyrolysis of spruce wood [16] also from pyrolysis of birch wood different types of tar are produced, depending on the momentary sample temperature. The conversion of these tars by tar cracking is dependent on the temperature of tar formation. For example, tar which was produced by primary pyrolysis in the temperature range up to 350 °C (see run #1) is mostly converted in run #8 (by tar cracking in the tubular reactor). The same overall rate of formation was found in all runs for tar which was produced at temperatures above 380 °C.

Kinetic modelling

The employed approach was presented in our previous study on the vapour phase cracking of tar from pyrolysis of spruce wood [16]. It is assumed that three different types of tars are produced from primary pyrolysis each having its own cracking characteristics.

Production of primary tars

The production of primary tars was modelled according to eq. (1). It assumes that three independent parallel reactions produce three different types of primary tar, types 1, 2 and 3. But since besides tar also other products are obtained from primary pyrolysis, eq. (1) is not a complete kinetic model for primary pyrolysis. Figure 11 shows the result for the rate of tar formation during run #1. In this run the TGA was used without the tubular reactor and only primary pyrolysis is considered. The individual rates of tar formation of the three independent parallel reactions and the sum of these reactions according to equation (1) are also presented in Fig. 11. Table 3 contains the kinetic parameters for these three independent parallel reactions.

$$\frac{dV}{dT}_{tar,total} = \frac{1}{m_{i-1}} \frac{dV}{dt}_{tar,i} = \frac{1}{m_{i-1}} C_{tar,i} Q = \frac{1}{m_{i-1}} k_{0,i} e^{\frac{E_{a,i}}{RT}} (V_{tar,i}^* - V_{tar,i})^{n_i} \quad (1)$$

Figure 11. Formation of primary tar in a TGA experiment and modelling results using three independent parallel reactions

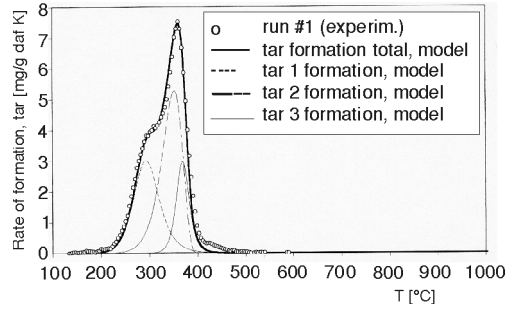


Table 3. Kinetic parameters of the three independent parallel reactions for the formation of primary tar from pyrolysis of birch wood

	Tar 1, formation	Tar 2, formation	Tar 3, formation
k_0	$10^8 \text{ g} \cdot \text{mg}^{-1} \cdot \text{s}^{-1}$	$4 \cdot 10^9 \text{ s}^{-1}$	$10^{24} \text{ g} \cdot \text{mg}^{-1} \cdot \text{s}^{-1}$
$E_a \text{ kJ} \cdot \text{mol}^{-1}$	138	144	346
$V^* \text{ mg} \cdot \text{g}^{-1}$	210	290	106
n	2	1	2

Vapour phase cracking of tar

A good description of the experimental results presented in Fig. 2 was possible when for the cracking of the three different primary tars the following was assumed: Primary tars 1 and 2 crack according to a simple first order overall kinetic model (see eq. (2)). Primary tar 3 does not crack.

$$r_{tar,i} = k_{0,i} e^{\frac{E_{a,i}}{RT}} C_{tar,i} \quad (2)$$

The kinetic parameters for the cracking of primary tars 1 and 2 were calculated applying a flow model which considers the non-isothermal conditions as well as the axial dispersion inside the tubular reactor [see 16]. Table 4

Table 4. Kinetic parameters for the vapour phase cracking of tar from pyrolysis of birch wood

Substance	$E_a \text{ kJ} \cdot \text{mol}^{-1}$	$k_0 \text{ s}^{-1}$
Birch wood, tar 1	55.32	576.2
Birch wood, tar 2	136.60	$6.343 \cdot 10^7$
Birch wood, tar 3	No cracking	No cracking

shows the kinetic parameters calculated for the vapour phase cracking of the tars from pyrolysis of birch wood determined within this work.

Figure 12 shows a comparison between experimental results for the rate of tar formation and predictions from the tar cracking model for different runs. As can be seen from Fig. 12, the cracking model is well able to describe the dependency of tar conversion on the tar formation temperature. Models which are just based on different tar yields (which are only integral values) obtained from different experimental conditions 4–9 are not able to consider such effects.

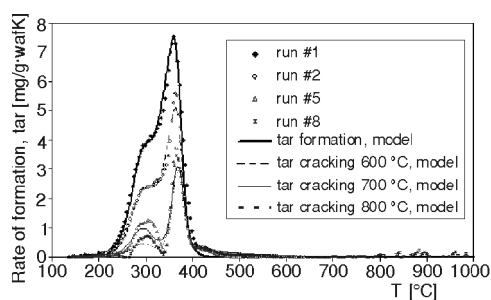


Figure 12. Rate of formation of tar from different runs, comparison between experimental results and predictions from the tar cracking model

Stiles and Kandiyoti [7] also investigated the thermal cracking of tar from pyrolysis of birch wood (silver birch) and they assumed a cracking of tar through a set of parallel and independent first order reactions which are described by one common frequency factor k_0 and a statistical distribution of activation energies (E_a and σ). Stiles and Kandiyoti [7] determined the following kinetic parameters: $E_a = 73$ kJ/mol, $\sigma = 6.2$ kJ/mol and $k_0 = 5.3 \cdot 10^3$ l/s.

A comparison of these kinetic data with the parameters determined within this work (see Table 4) shows that the parameters (E_a and k_0) determined for "birch wood, tar 1" within this work are lower than those determined by Stiles

and Kandiyoti and the parameters determined for "birch wood, tar 2" are higher than those determined by Stiles and Kandiyoti. It seems that if the cracking of two different types of tars (type 1 and 2) is modelled only by one set of parameters then these parameters are more or less mean values of those which are obtained when the two different tars are modelled separately.

Gas formation from tar cracking

As can be seen from Figs. 3 to 10 the overall rates of formation of the different pyrolysis gases are strongly dependent on the operating conditions of the tubular reactor (see Table 2).

The main product from tar cracking is carbon monoxide. A comparison of the runs #1 (primary pyrolysis) and #8 (tubular reactor: 800 °C, $\tau = 1.63$ s) in Fig. 3 show that the rate of formation of carbon monoxide increases by about the factor 7. Since there exists such a strong dependency of the rate of formation of carbon monoxide on the experimental conditions inside the tubular reactor (temperature and residence time), the yield of carbon monoxide (or the rate of formation of carbon monoxide) can

be considered as an indicator for the extent of tar cracking reactions. This was also suggested by Boroson *et al.* 4 . However Morf 18 suggests to use the hydrogen yield as an indicator for the extent of tar cracking reactions. But since the determination of hydrogen usually bases on heat conductivity measurements which are very sensitive to the presence of other components in the gas and further since the hydrogen yields are much lower than the carbon monoxide yields, carbon monoxide seems to be the more suitable indicator for the extent of tar cracking reactions.

Due to the strong dependency of the rate of formation of carbon monoxide on the experimental conditions inside the tubular reactor it was assumed that there exists a linear correlation between the rate of tar cracking and the rate of carbon monoxide formation from tar cracking. This assumption was extended to all gaseous components. Therefore the formation of the individual product gases j from tar cracking can be described according to eq. (3) using the rates of tar cracking (cracking of tars $i=1$ and $i=2$, tar 3 does not crack) and constant yield coefficients $Y_{j,i}$

$$r_j = \sum_{i=1}^2 (r_{tar,i}) Y_{j,i} \quad (3)$$

A comparison of experimental results and model predictions (eq. 3) showed that a reasonable accordance could only be obtained for the components carbon monoxide, carbon dioxide and water. For the components acetylene, ethane, ethene, hydrogen and methane the model was not able to predict the experimental results in any case. For example, the rates of formation of ethane (see Fig. 6) obtained from run #6 (tubular reactor: 700 °C, $\tau = 0.99$ s) are always much higher than from run #1 (only primary pyrolysis) but those from run #8 (tubular reactor: 800 °C, $\tau = 1.63$ s) are significantly lower than those from run #1. A possible explanation seems to be the occurrence of additional homogeneous gas-phase reactions between the different hydrocarbons and hydrogen (which cause *e. g.* a reduction of ethane and with that a related production of ethene and hydrogen at high temperatures) 17 .

But when the components acetylene, ethane, ethene, hydrogen and methane are put together to one product group "hydrocarbons and hydrogen (HC + H₂)" the model was again able to predict a reasonable accordance with the experimental results. The yield coefficient for the product group "HC + H₂" was calculated on the basis of the law of conservation of mass and the yield coefficients for carbon monoxide, carbon dioxide and water. For each type of tar the sum of all yield coefficients must be one ($Y_{CO,tar,i} + Y_{CO_2,tar,i} + Y_{H_2O,tar,i} + Y_{HC+H_2,tar,i} = 1$).

The determined yield coefficients $Y_{j,i}$ for the production of gases from cracking of tars from pyrolysis of birch wood are presented in Table 5. These coefficients are constant with respect to the investigated temperature range (600–800 °C). Further the composition of the product group "HC + H₂" is constant. For "HC + H₂" from cracking of tar 1 a C/H-ratio of 1/3.09 (mol/mol) and for "HC + H₂" from cracking of tar 2 a C/H-ratio of 1/3.29 (mol/mol) was determined. Figures 13 to 16 show a comparison of experimental results for carbon monoxide, carbon dioxide, water and "HC + H₂" from

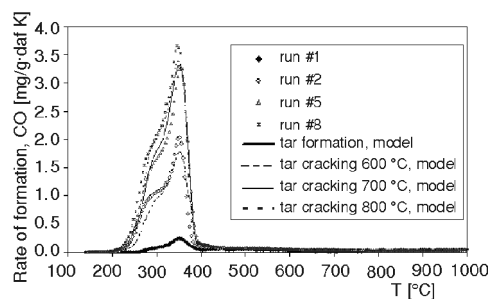


Figure 13. Rate of formation of carbon monoxide from different runs, comparison between experimental results and predictions from the tar cracking model

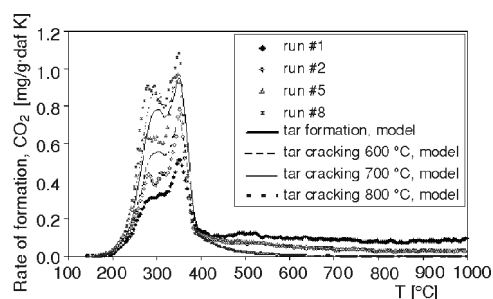


Figure 14. Rate of formation of carbon dioxide from different runs, comparison between experimental results and predictions from the tar cracking model

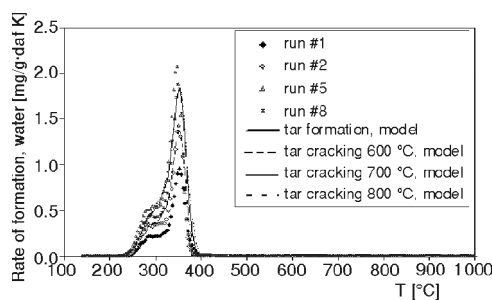


Figure 15. Rate of formation of water from different runs, comparison between experimental results and predictions

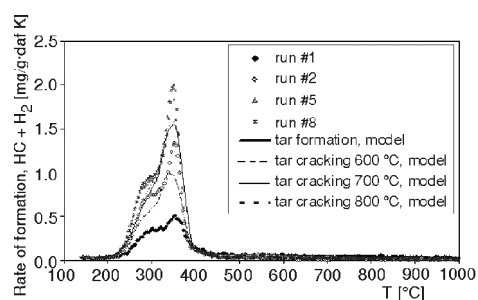


Figure 16. Rate of formation of "HC + H₂" from different runs, comparison between experimental results and predictions

different runs and predictions from the model (see eq. 3) using the yield coefficients presented in Table 5.

Table 5. Yield coefficients for the production of gases from cracking of tar from pyrolysis of birch wood

Component j	$Y_{j,tar1}$ g/g	$Y_{j,tar2}$ g/g
Carbon monoxide	0.60	0.55
Carbon dioxide	0.20	0.07
Water	0.075	0.16
HC + H ₂	0.125	0.22
Σ	1.00	1.00

Conclusion

The cracking of tar from pyrolysis of birch wood particles was investigated by applying a experimental set-up consisting of a TGA and a tubular reactor. The experimental results showed that the extent of tar cracking is not only dependent on the conditions in the cracking reactor (temperature and residence time) but also on the temperature at which the tar was formed. Applying a model which was presented in a previous study, kinetic parameters for tar cracking and yield coefficients for the production of gases from tar cracking were determined.

Nomenclature

C_{tar}	mg/g·m ³	– tar concentration
daf		– dry and ash free
E_a	J/mol	– activation energy
k_0	1/s , g/mg·s	– pre-exponential factor
m	K/s	– TGA heating rate
n		– reaction order
Q	m ³ /s	– flow rate of purge gas
r	mg/g·m ³ ·s	– rate of reaction
R	J/mol·K	– universal gas constant
σ	J/mol	– standard deviation of activation energy
t	s	– time
T	K , °C	– temperature
τ	s	– average residence time of gas in the tubular reactor
V_{tar*}	mg/g	– tar yield
V_{tar}	mg/g	– ultimate tar yield
Y	g/g	– yield coefficient

References

- [1] Brage, C., Yu, Q., Chen, G., Sjöström, K., *Biomass and Bioenergy*, 18 (2000), p. 87
- [2] Moersch, O., Spliethoff, H., Hein, K. R. G., *Ibid* , p. 79
- [3] Hasler, P., Nussbaumer, Th., *Biomass and Bioenergy*, 16 (1999), p. 385
- [4] Boroson, M. L., Howard, J. B., Longwell, J. P., Peters, W. A., *AIChE Journal*, 35 (1989), p. 120
- [5] Diebold, J. P., The Cracking of Depolymerized Biomass Vapors in a Continuous Tubular Reactor, Master Thesis, Colorado School of Mines, 1985
- [6] Liden, A. G., Berruti, F., Scott, D. S., *Chem. Eng. Comm.*, 65 (1988), p. 207
- [7] Stiles, H. N., Kandiyoti, R., *Fuel*, 68 (1989), p. 275
- [8] Caballero, J. A., Font, R., Marcilla, A., *J. Anal. Appl. Pyrol.*, 38 (1996), p. 131
- [9] Rath, J., Steiner, G., Wolfinger, M., Staudinger, G., *J. Anal. Appl. Pyrol.*, 62 (2001) 83
- [10] Antal, Jr., M. J., Varhegyi, G., *Ind. Eng. Chem. Res.*, 34 (1995), p. 703
- [11] Milosavljević I., Suuberg, E. M., *Ibid.*, p.1081
- [12] Conesa, A., Caballero, J. A., Marcilla, A., Font, R., *Thermochimica Acta*, 254 (1995), p. 167
- [13] Órfao, J. J. M., Antunes, F. J. A., Figureido, J. L., *Fuel*, 78 (1999), p. 349
- [14] Di Blasi, C., *J. Anal. Appl. Pyrol.*, 47 (1998), p. 43
- [15] Courson, C., Makaga, E., Petit, C., Kiennemann, A., *Catalysis Today*, 63 (2000), p. 427
- [16] Rath, J., Staudinger, G., *Fuel*, 80 (2001), p. 1379

- [17] Sundaram, K. M., Froment, G. F., *Chem. Eng. Sci.*, 32 (1977), p. 609
- [18] Morf, P., Secondary Reactions of Tar During Thermochemical Biomass Conversion, Dissertation, ETH Zürich, 2001

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