An analysis and experimental investigation of the cracking and polymerisation of tar

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Tar production is one of the major problems for the introduction of gasifiers for biomass. Before the gas can be introduced into the gas engine the tar content has to be reduced to low values. One way to diminish the tar content of gas obtained from a gasifier is by thermal cracking. This research is part of a larger research on thermal cracking and partial oxidation in an external recycle-loop of pyrolysis gas. Knowledge about the influence of process parameters (temperature, residence time, gas composition and the influence of catalysts like charcoal) on the cracking of tar is still scarce [e.g. 1,2].

Thermal cracking is performed in an external reactor. An experimental set-up at ECN is built to determine the effect of two parameters (temperature and residence time). This set-up is shown in Figure 1.

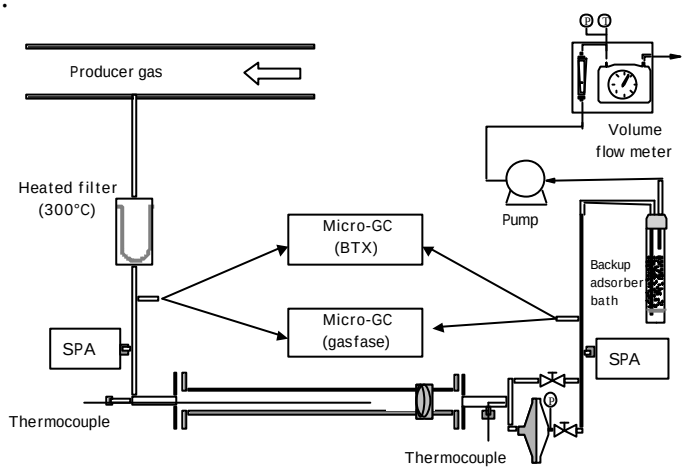

Figure 1: Experimental set-up

Producer gas (coming from a fluidised bed gasifier) is lead through a heated filter. After this filter the gas flows through an electrically heated tubular reactor. The tar content is analysed by the SPA (Solid Phase Absorption) method. The smaller components (like benzene) are analysed by a Gas Chromatograph. Experiments on the cracking of tar are performed in a temperature range of 900 to 1150?C and residence times of 1 to 12 s.

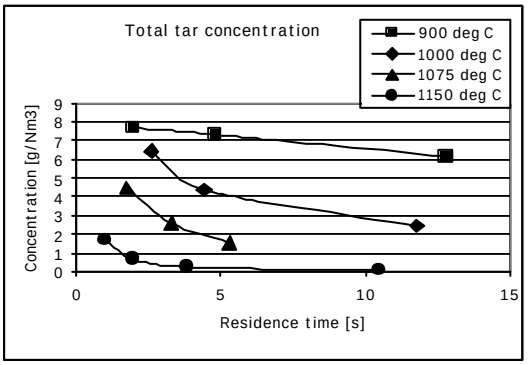

Figure 2a: Tar concentration as a function of the residence time at four temperatures

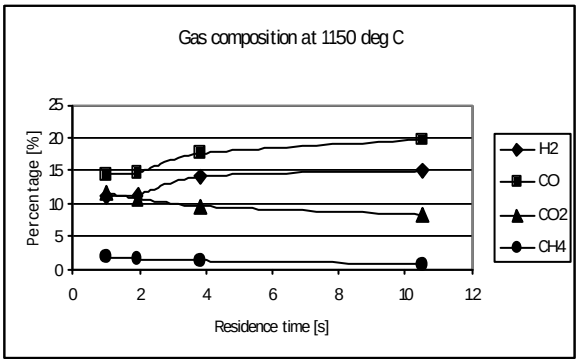

Figure 2b: Gas composition as a function of the residence time at 1150?C

Raising the temperature as well as the residence time turns out be favourable (figure 2a). In both cases a decline in tar concentration is obtained. For a temperature of 1150?C and residence times between 4 and 10 sec the tar concentration drops below 0.2 g/Nm^3 (a limit often used for gasmotors). The effect on the gas composition (figure 2b) shows a slight increase in CO en H_2, while the CO_2 and CH_4 concentration drop.

Table 1 shows that the 'total' input and output agree well; 99.5% of the carbon in the input is found back in the products (output). The amount of C_1 and C_2 compounds (CO, CO_2, CH_4, C_2H_4 and C_2H_6) in the product gases ("output") almost equals the amount of C_1 and C_2 compounds in the input. Furthermore, the carbon balance shows that a large part of the tars and smaller C_xH_y compounds are converted by polymerisation into soot. The amount of soot plus tar in the output comes very close to the amount of tar plus benzene plus toluene in the input. This also follows from the SPA results which show the formation of larger tar compounds (4-, 5- and > 5- ring compounds) and eventually the formation of soot. At higher temperatures lighter compounds like benzene and toluene disappear. However, this effect seems not to be caused by cracking reactions. Polymerisation of light hydrocarbons to heavy aromatic compounds seems to take place. Therefore, a plausible explanation for the high amounts of soot formed is that soot is not only formed from tar polymerisation, but also from polymerisation of one-ring aromatics.

Table 1: The carbon balance at 1075?C and a residence time of 3.29 s

Input of C [gr/h]				**Output of C [gr/h]**
CO	69	?	CO	91
CO_2	87	?	CO_2	82
CH_4	20	?	CH_4	17
C_2H_4	15	?	C_2H_4	1
C_2H_6	1	?	C_2H_6	--
Benzene (C_6H_6)	11	?	Benzene (C_6H_6)	7
Toluene (C_7H_8)	3	?	Toluene (C_7H_8)	--
Xylene (C_8H_{10})	--	?	Xylene (C_8H_{10})	--
Tar	5	?	Tar	2
Soot	--	?	Soot	11
HCN	--	?	HCN	--
Total	212		**Total**	211

[1] Boroson ML, Howard JB, Longwell JP, Peters WA. Product yields and kinetics from the vapor phase cracking of wood pyrolysis tars. AIChE J. 35 (1), 1989, p. 120-128.
[2] Brandt P, Henriksen U. Decomposition of tar in pyrolysis gas by partialoxidation and thermal cracking. Part 2. In: Biomass for energy and industry. Proc. 10th European conference and technology exhibition (Eds. Kopetz H, et al.), C.A.R.M.E.N., Rimpar, 1998, p. 1616-1618.