

Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips[☆]

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Revised 21 November 2001; accepted 30 November 2001; available online 2 January 2002

Abstract

The change of mass and composition of biomass tar due to homogeneous secondary reactions was experimentally studied by means of a lab reactor system that allows the spatially separated production and conversion of biomass tar. A tarry pyrolysis gas was continuously produced by pyrolysis of wood chips (fir and spruce, 10–40 mm diameter) under fixed-bed biomass gasification conditions. Homogeneous secondary tar reactions without the external supply of oxidising agents were studied in a tubular flow reactor operated at temperatures from 500 to 1000 °C and with space times below 0.2 s. Extensive chemical analysis of wet chemical tar samples provided quantitative data about the mass and composition of biomass tar during homogeneous conversion. These data were used to study the kinetics of the conversion of gravimetric tar and the formation of PAH compounds, like naphthalene.

It is shown that, under the reaction conditions chosen for the experiments, homogeneous secondary tar reactions become important at temperatures higher than 650 °C, which is indicated by the increasing concentrations of the gases CO, CH₄, and H₂ in the pyrolysis gas. The gravimetric tar yield decreases with increasing reactor temperatures during homogeneous tar conversion. The highest conversion reached in the experiments was 88% at a reference temperature of 990 °C and isothermal space time of 0.12 s. Hydrogen is a good indicator for reactions that convert the primary tar into aromatics, especially PAH. Soot appears to be a major product from homogeneous secondary tar reactions. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Biomass tar; Pyrolysis; Gasification; Kinetics

1. Introduction

Tar as an unwanted constituent of producer gas from biomass gasification can cause severe operating problems in internal combustion engines. Today's available gas cleaning systems for biomass gasifiers are cost intensive and often do not reliably fulfil the requirements for IC engine fuel gas quality [1]. In order to provide fundamentals for primary measures against the tar problem, i.e. appropriate gasifier design and operating conditions, tar conversion during gasification process conditions is studied in the present work.

1.1. Secondary tar reactions

Tar is an extremely complex mixture of organic compounds that are produced during thermochemical

conversion processes from organic material. The term 'tar' describes a lump involving thousands of single substances. Because of its complexity, there is no consistent and generally accepted definition for tar mixtures [2]. Tar appears as a product from pyrolysis of the solid carbonaceous fuel during biomass gasification processes. This primary tar formation is not avoidable. However, after their evolution from the solid phase, the primary tar vapours are subjected to secondary tar reactions (STR) that alter both mass and composition of the tar. A partial tar conversion by STR already occurs in the pores of the 'mother' fuel particle as well as in the gas-phase and on surfaces outside the particle. According to the phases involved, STR are divided into *homogeneous* and *heterogeneous* reactions. Processes like cracking, partial oxidation, (re)polymerisation and condensation may occur in both classes.

In order to improve the design of gasifiers with regard to producer gas quality, there is a demand for kinetic data on STR, especially concerning the behaviour of important compound classes [2]. Although there is a considerable amount of literature on pyrolysis of biomass, investigations

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[☆] Published first on the web via Fuelfirst.com—<http://www.fuelfirst.com>

Nomenclature

A	frequency factor. For first-order reaction rate constants: (s^{-1})
c_{gT}	concentration of gravimetric tar in pyrolysis gas ($g\ m^{-3}$)
E_A	activation energy ($kJ\ mol^{-1}$)
$\Delta H_{298\ K}$	standard enthalpy of formation ($kJ\ mol^{-1}$)
k_h	reaction rate constant for gravimetric tar conversion (s^{-1})
k_{N1}	reaction rate constant for conversion of gravimetric tar into intermediate (s^{-1})
k_{N2}	reaction rate constant for conversion of intermediate tar into naphthalene (s^{-1})
k_{N3}	reaction rate constant for soot formation ($m^3\ kg^{-1}\ s^{-1}$). See Ref. [14]
r_h	reaction rate for gravimetric tar conversion ($g\ m^{-3}\ s^{-1}$)
R	ideal gas constant: $8.31441\ J\ mol^{-1}\ K^{-1}$
T	local reactor temperature (K)
T_R	reactor reference temperature ($^{\circ}C$)
v	gas velocity in reactor ($m\ s^{-1}$)
x	reactor length coordinate (m)

that specifically focuses on quantitative data from STR, related to clearly defined process conditions, are rare.

An overview of the composition of primary tar from fast pyrolysis processes is provided by chemical analysis presented by a number of authors [3–5]. Semiquantitative analysis of tar compounds in function of the (pyrolysis) process temperature was conducted in order to investigate the general sequence of classes of tar constituents during homogeneous STR [6]. These analytical methods were also used for the characterisation and analysis of tar from applied systems for gasification and pyrolysis of biomass [7]. Other studies related the process temperature to physical and biological properties of the formed tar [8]. Only a few studies provide kinetic data of homogeneous biomass tar conversion processes [9–12]. In a recently published work [12], the homogeneous secondary reactions of tar from the pyrolysis of spruce wood were investigated. By using a thermogravimetric analyser (TGA, for performing the primary pyrolysis) coupled to a tubular reactor, Rath and Staudinger [12] used an experimental set-up similar to the one used by Boroson [11]. In both these works, pyrolysis was performed as a batch process with regard to the fuel, for which reason there must have been a sequential release of tar compounds into the gas phase according to the compound's volatility or chemical bonds involved in the pyrolysis process. Thus, using batch pyrolysis reactors for the fuel, it is impossible to produce the whole tar matrix with a constant composition as input for the adjacent tar conversion reactor. This drawback is overcome in the present work by using a continuously fuel-fed pyrolysis process (see the

following description). Moreover, in the work by Rath and Staudinger [12], the tar was assumed to be the difference between the mass loss of the original fuel and the sum of the gases found. However, since it is known from previous works [6] that there is a formation of tar compounds (tertiary tar compounds such as polyaromatic hydrocarbons) during the vapour-phase reactions of tar, investigations on STR should include the determination of the tar composition. Therefore, the present investigation on homogeneous STR is based on an experimental program that includes tar sampling and extensive tar analysis.

Studies on heterogeneous STR involving pyrolytic formed wood chars as catalytically active surfaces are also rare [13–15]. No kinetic models for heterogeneous STR involving fresh wood char are reported in the literature. A detailed work on mechanisms and kinetics of conversion of hydrocarbons from pyrolysis was based on homogeneous conversion experiments with tar model compounds [16].

Systematic studies that report the behaviour of the tar composition during STR with quantitative data are missing in the literature. Therefore, the objective of the present work is to contribute to an improvement of the knowledge in this field by conducting a quantitative investigation of homogeneous STR without external supply of oxidising agents.

1.2. Classification of tar compounds

The classification of tar compounds used in this study is based on the work by Evans and Milne [6]. They used molecular beam mass spectrometry (MBMS) to identify different reaction regimes during thermal processes like pyrolysis and gasification. Three major product classes were identified as a result of thermal gas-phase tar conversion reactions. The primary products, found in a reactor temperature range of 400–700 $^{\circ}C$, are characterised by the presence of oxygenated compounds. The secondary products include phenolics and olefins, the formation temperature range here is 700–850 $^{\circ}C$. Tertiary products appear in the reaction regime of 850–1000 $^{\circ}C$ and are characterised by aromatics. Sometimes, this class is further subdivided into the classes 'alkyl tertiary products', like methyl-naphthalene, toluene and indene, and the 'condensed tertiary products', which include the polyaromatic hydrocarbons (PAH). A list of important single tar compounds and their classification according to Evans and Milne [6] is given by Milne et al. [2].

The classification of the quantitatively analysed tar compounds from this study according to Ref. [2] is shown in Table 1.

It should be noted that in this study, the term 'STR' is not restrictively used for conversion reactions that lead to secondary tar; it is used for all processes that convert the primary tar either into secondary *and/or* tertiary tar.

Table 1
Classification of quantitatively analysed tar compounds according to Ref. [2]

Tar compound class	Compound type	Compound name	
Primary tar compounds	Acids	Acetic acid	
		Propionic acid	
		Butyric acid	
	Ketones	Acetol (1-hydroxy-2-propanone)	
		Phenols	Phenol
	2,3-Dimethylphenol		
	2,4/2,5-Dimethylphenol ^a		
	2,6-Dimethylphenol		
	3,4-Dimethylphenol		
	3,5-Dimethylphenol		
	Guaiacols	Guaiacol	
		4-Methylguaiacol	
	Furans	Furfural	
Furfural alcohol			
5-Methylfurfural			
Secondary tar compounds	Phenols	Phenol	
		<i>o</i> -Cresol	
		<i>p</i> -Cresol	
		<i>m</i> -Cresol	
	Monoaromatic Hydrocarbons	<i>p/m</i> -Xylene ^a	
<i>o</i> -Xylene			
Secondary/tertiary tar ^b	Monoaromatic hydrocarbons	Benzene	
		Ethylbenzene	
		<i>a</i> -Methylstyrene	
		3&2-Methylstyrene	
		4-Methylstyrene	
		3-Ethyltoluene	
		4-Ethyltoluene	
		2-Ethyltoluene	
		Miscellaneous hydrocarbons	2,3-Benzofuran
			Dibenzofuran
	Biphenyl		
	Methyl derivatives of aromatics	Indene	
		2-Methylnaphthalene	
		1-Methylnaphthalene	
		Toluene	
	Tertiary tar compounds	PAH: 2-ring	Acenaphthylene
			Acenaphthene
Fluorene			
3-ring		Naphthalene	
		Phenanthrene	
		Anthracene	
		Fluoranthene	
		Pyrene	
4-ring		Benz[a]anthracene	
		Chrysene	
		Benz[e]acephenanthrylene	
		Benzo[k]fluoranthene	
		Benzo[a]pyrene	
5-ring		Perylene	
		Dibenzo[ah]anthracene	
		Indeno[1,2,3-cd]pyrene	
6-ring		Benzo[ghi]perylene	

^a Compounds lumped together for analysis.

^b There are several compounds that appear in the second and in one of the other two classes as well. This demonstrates the evolutionary development and the somewhat arbitrary boundaries for the three tar classes [2].

2. Experimental

2.1. Reactor system

A laboratory reactor system was constructed for the investigation of the conversion of tar produced under real fixed-bed conditions. The basic concept for the reactor design was the spatial separation of the primary pyrolysis and STR (Fig. 1). After the primary pyrolysis stage, the tar containing pyrolysis gas is swept to the tubular conversion reactors where homogeneous and/or heterogeneous tar reactions are investigated. A detailed description of the whole lab reactor system can be found in Ref. [15].

The most important features of the system are its continuous operation that allows the investigation of tar conversion at steady-state reactor conditions and the use of wood chips in technical size (mixture of fir and spruce, chips diameter 10–40 mm) as fuel. The implementation of these features led to the design of the wood pyrolysis unit (WPU) with a fixed-bed of fuel particles that is continuously conveyed through a heated tubular reactor.

The choice of the reactor type was based on the following considerations: it is impossible to produce and isolate tar experimentally without the occurrence of STR. Therefore, the term ‘primary’ tar is operationally defined. In various reactors, different reaction conditions, such as heating rates of the solids, cause STR to various extents, which influence the compositions of the primary tar. For reasons of comparability of the experimental results with findings from applied systems, the fixed bed reactor was chosen. The pyrolysis conditions in the WPU, especially the parameters *heating rate* and *final temperature*, should be comparable to those previously measured in an applied open-top gasifier [17]. In the following, the term primary tar refers to tar from the outlet of the WPU, being aware that this tar may have already undergone secondary reactions to a certain extent.

The operating procedure for the homogeneous tar conversion experiments is as follows: a pyrolysis gas with a high content of primary tar (approx. 300 g nm⁻³) is produced in the WPU by continuously pyrolysing fir/spruce wood chips (feed rate: 1.6 kg h⁻¹) at a mean temperature of 380 °C. The evolving gases are swept to the adjacent reactor for homogeneous tar conversion by means of an N₂-carrier gas flow (0.4 nl s⁻¹). The relatively high N₂-volume flow ensured space times in the homogeneous tar conversion below 0.2 s (i.e. *isothermal space times*, calculated with the equivalent isothermal reactor volume according to the method described in Ref. [16]) and minimised changes of the gas volume due to STR that change the total number of moles. At the end of the WPU, the produced char is separated from the gas flow and stored in a container. The homogeneous tar conversion is operated at several temperature levels from 500 to 1100 °C. Up and downstream of the homogeneous tar conversion, tar samples are taken and the concentrations of non-condensable gases (CO,

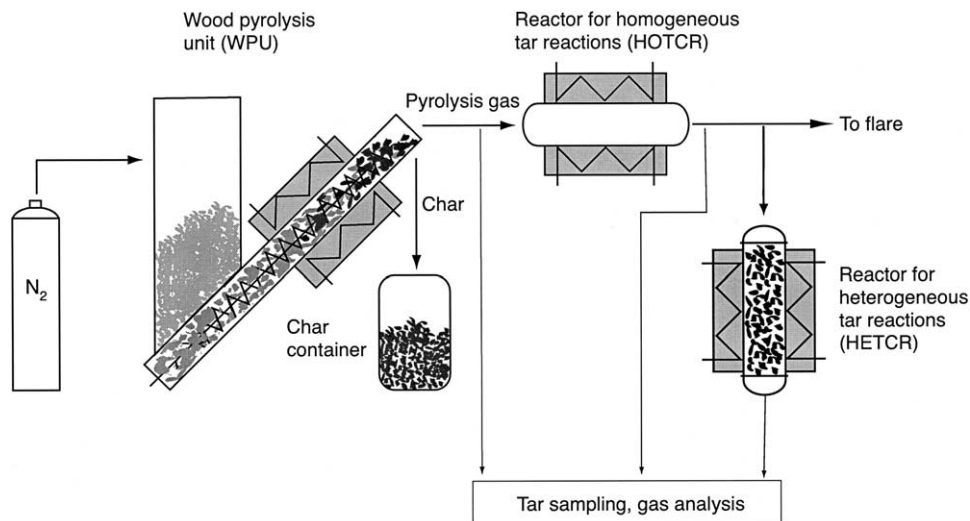


Fig. 1. Schematic of laboratory reactor system for the investigation of biomass tar conversion. The present work reports the experiments with the homogeneous tar conversion.

CO_2 , CH_4 , H_2) are measured on-line. The measuring principles of the gas analysers used are non-dispersive infrared (NDIR) photometry (CO , CO_2 , CH_4) and heat conductivity (H_2).

2.2. Reactor temperatures

Due to heat transfer effects, isothermal operation of reactors for homogeneous gas-phase reactions is not possible. Therefore, the axial temperature profiles in the tubular homogeneous tar conversion were measured using moveable thermocouples (type K) coated with ceramics at the sensor tip. The recorded temperature profiles (see Fig. 2) are used for the kinetic modelling of STR based on the experimental data. The temperature measured in the axial

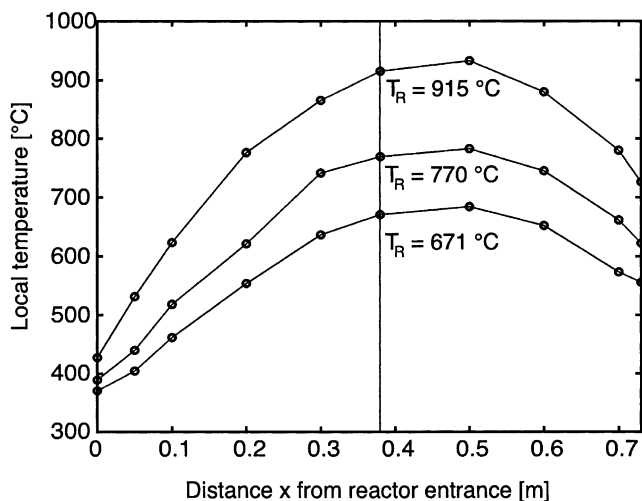


Fig. 2. Temperature profiles measured in the reactor for homogeneous tar conversion with the corresponding reference temperatures T_R , measured at the position indicated.

and radial centre of the homogeneous tar conversion was defined as the *reference temperature* T_R at a steady-state investigated. In the following sections, the experimental data are depicted as a function of T_R .

2.3. Tar sampling and analysis

The tar was sampled discontinuously by using impingers with an organic solvent maintained at -25°C . The first stage of the sampling train consisted of a liquid-quench system based on the work of Amand et al. [18]. The sampling train used is in accordance with the method proposed by Neeft et al. [21]. After several experiments with different organic solvents, 1-methoxy-2-propanol was found to be the best solvent for sampling both the primary and the converted tar. Its solubility with water simplifies the sampling procedure for tar, since only one organic phase is produced. Approximately 100 l_n of process gas was sampled from every interesting operation state of the reactor system during an experiment.

The tar samples were analysed using different methods. Gel-permeation chromatography with multiwavelength-UV-detection (GPC-UV) was used for qualitative characterisation of the tar; the method and results are reported elsewhere [19]. For the quantitative determination of the sample concentrations of the species listed in Table 1, gas chromatography–mass spectrometry (GC–MS) analysis was applied. The GC–MS method used was originally developed for the analysis of tar samples from fluidised-bed gasifiers [20].

The solvent from the wet chemical tar sample was evaporated in order to determine the gravimetric tar. The water content of the samples was determined using the Karl–Fischer titration method.

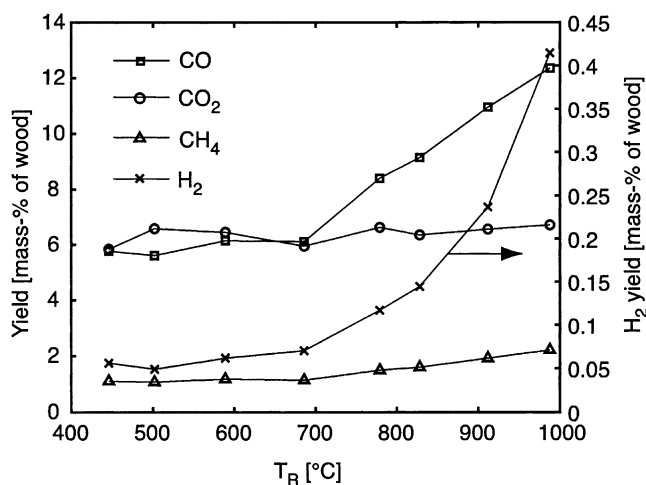


Fig. 3. Yields of CO, CO₂, CH₄, and H₂ during homogeneous tar conversion. The yields are based on the input wood feed in the WPU (1.6 kg wood h⁻¹, wood moisture: 13 m% of dry fuel).

3. Experimental results and discussion

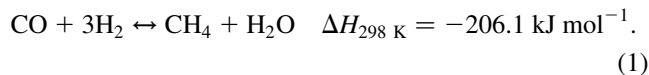
3.1. Gases

The yields of the non-condensable gas species carbon monoxide, carbon dioxide, methane and hydrogen during the homogeneous tar conversion experiments at different reactor temperatures (i.e. at the reference temperatures T_R) is shown in Fig. 3. The yields of CO, CH₄ and H₂ remain relatively stable in the temperature range from 450 to 680 °C. Then, the yields of CO and CH₄ increase almost linearly with increasing conversion temperature, whereas the hydrogen exhibits an exponential increase in its yield. On the other hand, the yield of carbon dioxide does not show significant changes during the whole temperature range investigated. The scattering of the values for CO₂ is attributed to insufficient resolution of the gas analyser used.

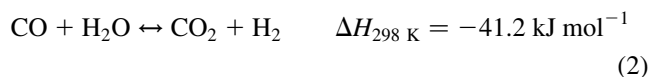
Carbon monoxide is the most important gaseous product from homogeneous tar conversion. Its yield doubles in the temperature range from 680 to 1000 °C. The quantitative importance of CO as a major secondary product from homogeneous tar conversion is confirmed by the work by Boroson [11]. The author, therefore, suggests that the CO yield can be used as an indication of the extent of cracking reactions during secondary tar conversion. However, the present results suggest that the hydrogen is even a better indicator for STR. H₂ is present in minor concentrations only in the pyrolysis gas at temperatures up to 700 °C. At higher temperatures, its evolution curve shows the steepest rise of all gases measured. At $T_R = 990$ °C, the hydrogen yield is 7.4 times higher than in the primary pyrolysis gas. Moreover, the hydrogen plays an important role in the formation and conversion of tertiary tar components, as will be elucidated in Section 3.3.3.

Interpreting the experimental data of the non-condensable

gases, it should be kept in mind that the measured gas concentrations may not exclusively be the result of tar cracking. Pure gaseous products from tar cracking may undergo gas-phase reactions among themselves. Thus, the methane content may be affected by the methanation reaction:



The yield of water in the primary pyrolysis gas (not shown) is slightly higher than the moisture content of the wood (13 mass percent (m%) of the initial, dry fuel chips). Water appears to be formed during the experiments on homogeneous STR up to a reference temperature of 600 °C, which can be explained by separation of corresponding functional groups from tar compounds. The subsequent decrease of the water yield with increasing conversion temperature may be attributed to gasification reactions, such as the homogeneous water-gas shift reaction:



3.2. Gravimetric tar

There are internationally driven efforts to create a commonly accepted guideline for the sampling and analysis of tar from biomass producer gases [21]. As a measure to compare the tar contents of producer gases from different gasifiers systems, the guideline will provide a definition for the *gravimetric tar*. Because of the practical importance of this measure, the gravimetric tar values determined in the homogeneous tar conversion experiments are discussed in the following.

The gravimetric tar represents a lump, which includes an enormous number of individual tar compounds. However, it is not equal to the total ‘tar mass’, i.e. there are compounds that are present in the liquid tar sample but that will disappear during the evaporation procedure for the determination of the gravimetric tar. This loss of tar mass was estimated based on results from comparing analysis of single tar compounds in the liquid tar sample and in the evaporation residue. Fig. 4 shows the yields of the gravimetric tar and of the estimated ‘total’ tar determined at the homogeneous tar conversion outlet. The data point for the gravimetric tar at 590 °C seems to be an outlier, possibly caused during the analytical procedure for the determination of the gravimetric tar. This assumption is confirmed by a comparable experimental series on homogeneous tar conversion, where the gravimetric tar exhibits a monotonously declining trend curve with increasing conversion temperatures T_R . Moreover, an increase in the gravimetric tar with increasing conversion temperature is unlikely, unless there is a dramatic change in composition of the tar, which causes a different behaviour of the tar sample during the determination of the gravimetric tar. However,

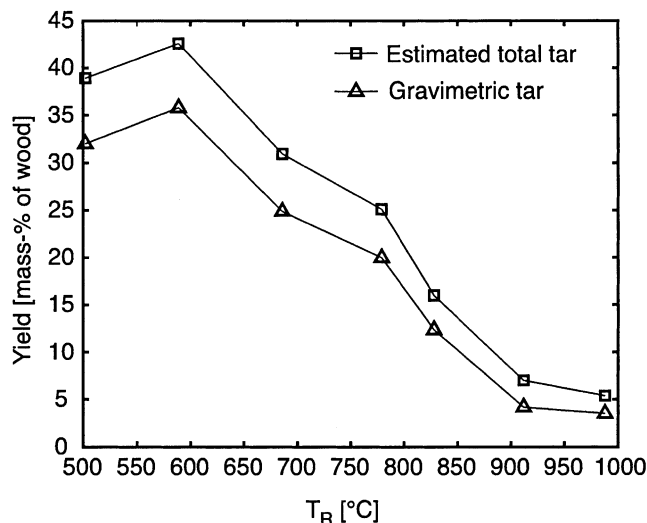


Fig. 4. Yields of gravimetric and estimated total tar during homogeneous tar conversion. The yields are based on the input wood feed in the WPU (1.6 kg wood h^{-1} , wood moisture: 13 m% of dry fuel).

this change in composition is not probable at these relatively low temperatures.

Based on a primary gravimetric tar yield of 29 m% (mean value of 2 measurements downstream of the WPU), the highest experimental conversion reached by homogeneous reactions at $T_R = 990$ °C and at an isothermal space time of approx. 0.12 s was 88%.

3.3. Selected tar compounds

Typical representatives of each primary, secondary and tertiary tar compounds (Table 1) were quantitatively analysed by GC–MS. From this data material on total 53 single compounds, the thermal behaviours of important representatives of each tar class are presented in the following. The experimental results are also discussed with regard to proposed mechanisms on tar compound interactions reported in the literature.

3.3.1. Primary tar compounds

The class of the primary tar is characterised by oxygenated compounds that give the primary tar its high reactivity. The thermal behaviour of selected compounds in this class during homogeneous STR is shown in Fig. 5. The quantitatively most important of *all* of the analysed compounds is the primary tar constituent acetol (1-hydroxy-2-propanone). Its share in the estimated total tar yield is approx. 16 m% in the primary tar (or approx. 5 m% of the fuel input into the WPU, see Fig. 5) and keeps relatively stable between 12 and 18 m% in the temperature range from 500 to 830 °C. In the homogeneous tar conversion experiments, acetol reaches a maximum conversion of approx. 97% at the highest reference temperature (990 °C).

Acetic acid is another primary tar component that is present in rather large quantities. Its yield shows a slower decrease with increasing temperature than in the case of

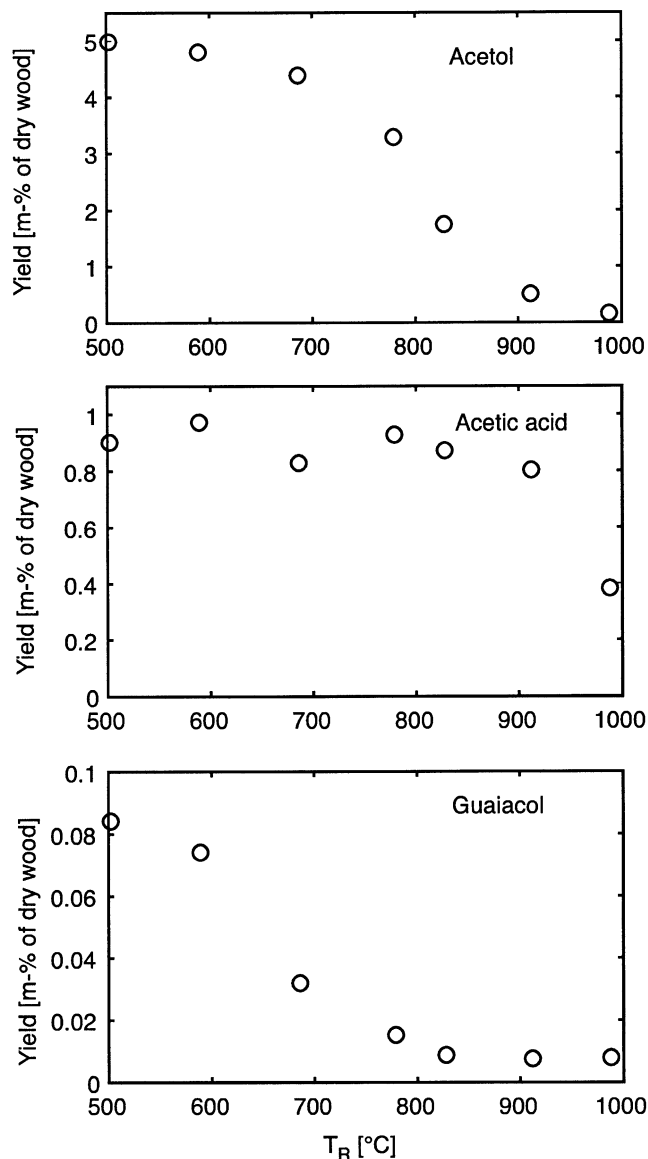


Fig. 5. Yields of the primary tar compounds acetol, acetic acid and guaiacol during homogeneous STR. The yields are based on the input wood feed in (1.6 kg wood h^{-1} , wood moisture: 13 m% of dry fuel).

acetol; only 58% of its initial amount is converted at the highest temperature investigated.

The yield of guaiacol in function of the conversion temperature T_R exhibits a steep decrease with increasing temperature. According to Egsgaard and Larsen [22], guaiacol is the important precursor in the formation of aromatic aldehydes. The authors suppose that these formed oxo-compounds are important for the formation of the higher-molecular tar fractions, i.e. for the PAH formation.

3.3.2. Secondary tar compounds

Phenolic compounds and other monoaromatic hydrocarbons are typical representatives for the secondary tar component class.

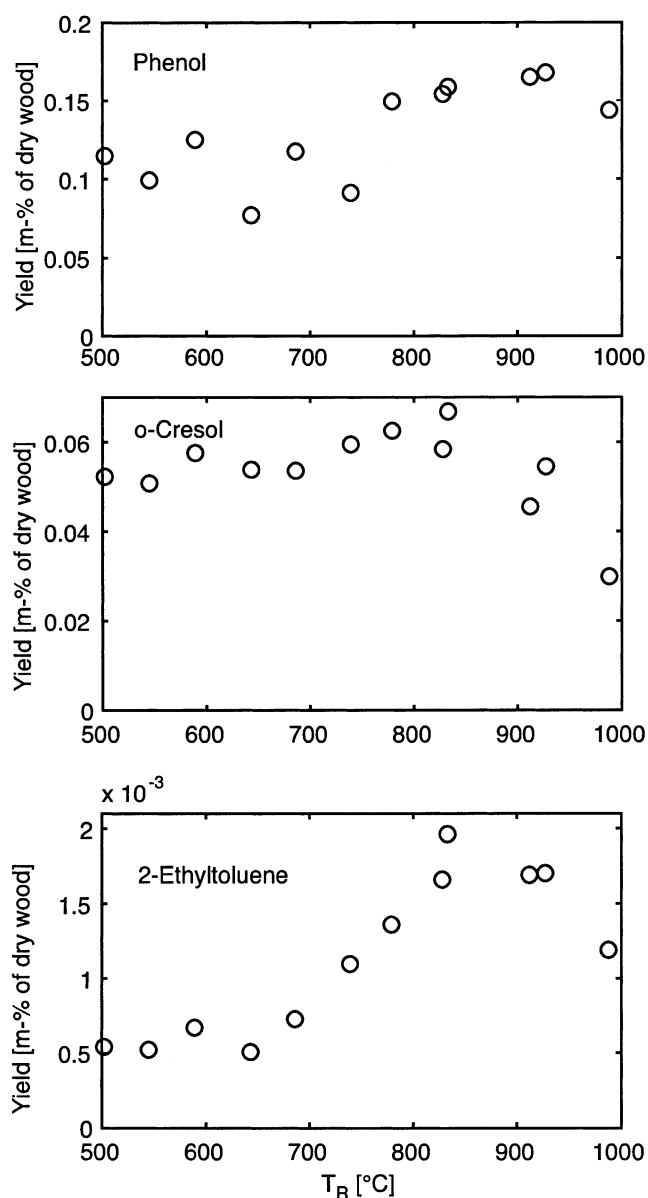


Fig. 6. Yields of the secondary tar compounds phenol, *o*-cresol and 2-ethyltoluene during homogeneous STR. The yields are based on the input wood feed in ($1.6 \text{ kg wood h}^{-1}$, wood moisture: 13 m% of dry fuel).

The experimental data on the yield of phenol exhibits no clear trend (Fig. 6). The scattering of these values is attributed to analytical problems (i.e. in the gas chromatograms, phenol peaks cannot be completely separated from other substances' peaks).

The corresponding experimental values for the cresols more clearly show the behaviour of secondary tar components: a slight increase with temperatures up to around $830 \text{ }^\circ\text{C}$ followed by steep decrease with further increasing temperatures.

Phenolics are important tar constituents for several reasons. It was demonstrated in previous studies that they are important precursors for the formation of PAH compounds [22]. In particular, the parent phenol was identified

as a unique precursor for the formation of naphthalene. For the practical application of biomass gasification, phenolics belong to the problematic producer gas impurities. First, they are suspected to cause corrosion in IC engines [23]; and secondly, they appear in large quantities in the waste water from biomass gasifier systems, and therefore, make a costly waste water treatment indispensable [24].

Among the analysed secondary tar constituents, the compounds 2-ethyltoluene (Fig. 6), 3-ethyltoluene, the xylenes, and the methylstyrenes exhibited the typical behaviour for this class, e.g. the behaviour of an intermediate product from STR.

3.3.3. Tertiary tar compounds

The dominant compound types in the tertiary tar class are aromatics, which include the PAH. In the present study, 17 PAH up to six-ring PAH compounds were quantitatively determined. All these compounds show a very similar qualitative behaviour during the homogeneous tar conversion experiments. The PAH are present in negligible amounts in the tar up to reference temperatures of approx. $750\text{--}800 \text{ }^\circ\text{C}$. Then, a dramatic increase in their yields with increasing reactor temperatures is observed. Naphthalene is the quantitatively most important analysed PAH tar compound (Fig. 7).

The qualitative behaviour of the PAH compounds during the homogeneous tar conversion experiments was also found to be similar to that ascertained for the hydrogen. These experimental findings are self-evident since the formation and growth of PAH is accompanied by hydrogen abstraction. However, the water-gas steam and the heterogeneous carbon-steam reaction (e.g. gasification of soot) should also be considered as hydrogen sources.

Various theories on the formation of PAH are found in the literature. For example, Frenklach and Wang [25] presented a model for PAH growth and subsequent soot formation. The growth of aromatics to higher molecular compounds is explained by a mechanism consisting of two reaction pathways:

- Direct combination* of intact aromatic rings, e.g. the combination of two benzene rings leads to biphenyl, which reacts further towards PAH compounds.
- H₂-abstraction–C₂H₂-addition (HACA) sequence.* Aromatic rings grow by H-abstraction, which activates the aromatic molecules, and acetylene addition, which propagates molecular growth by cyclisation.

Pathway (a) is important for the initial stages of pyrolysis of aromatic fuels, such as gasoline. According to the authors [25], the precursor for PAH formation, benzene, is decomposed forming acetylene, as the reaction progresses. As the acetylene concentration approaches that of benzene, the PAH growth switches to path (b).

As mentioned earlier, Egsgaard and Larsen [22]

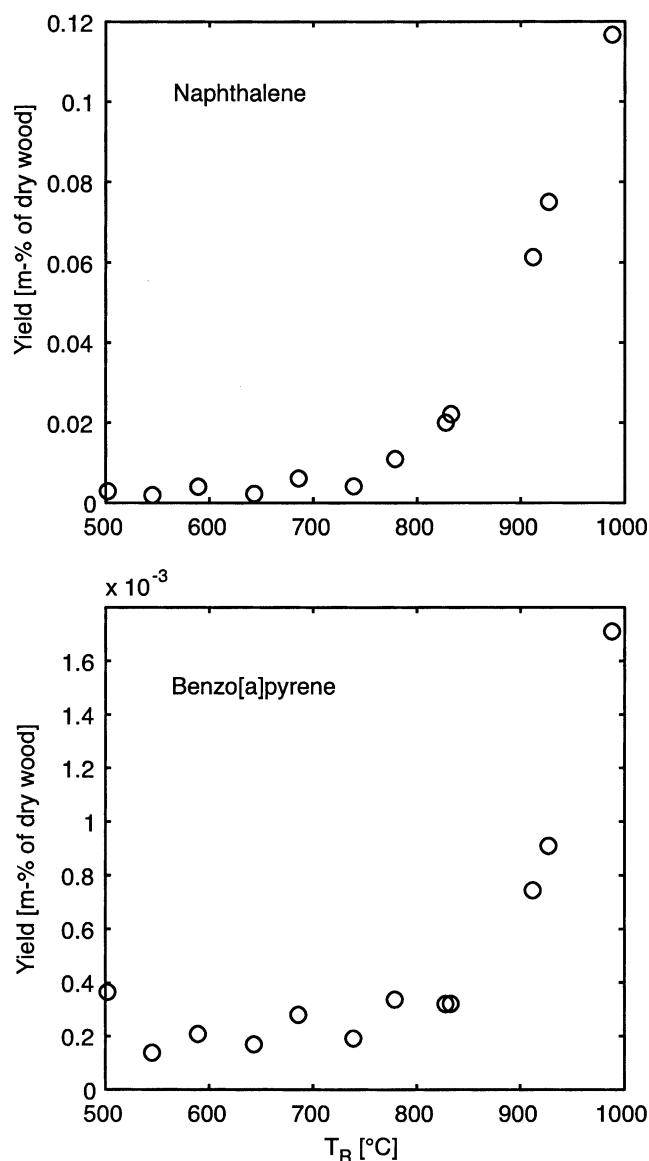


Fig. 7. Yields of the tertiary tar compounds naphthalene and benzo[a]pyrene during homogeneous STR. The yields are based on the input wood feed in (1.6 kg wood h⁻¹, wood moisture: 13 m% of dry fuel).

suggested an alternative mechanism of PAH formation. This starts from phenol as precursor and proceeds via a Diels–Alder reaction and separation of hydrogen to low molecular mass PAH such as naphthalene and indenes.

With increasing PAH content, the toxic potential of the tar increases considerably [8]. PAH compounds like benzo[a]pyrene are known as a highly cancerogeneous substances. The thermal behaviour of benzo[a]pyrene is shown in Fig. 7.

3.4. Estimation of soot formation

During the experiments on homogeneous tar conversion, the formation of considerable amounts of soot was observed; either as very fine particle deposits at fixtures in

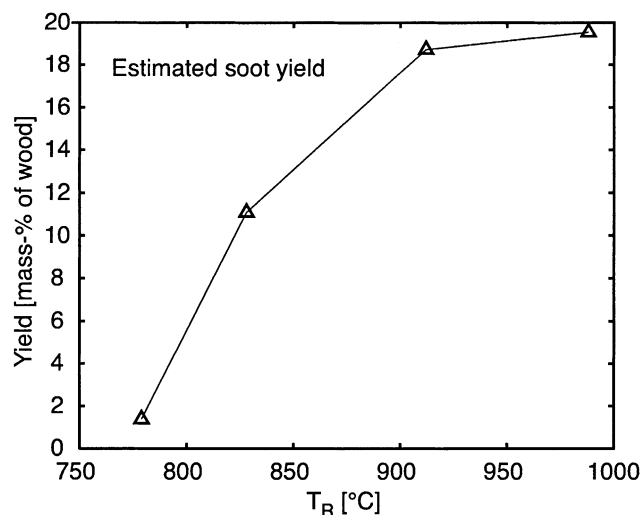


Fig. 8. Estimated yield of soot during homogeneous STR. The yield is based on the input wood feed in (1.6 kg wood h⁻¹, wood moisture: 13 m% of dry fuel).

the reactor system tubes or as sparks in the gas flare flame when the reactor system was flushed with nitrogen for cleaning.

Since the experimental set-up was not intended to direct quantification of soot formation, its mass flow rate was estimated. For this purpose, mass balances over the conversion reactor at various temperatures were determined; the differences between the sums of in- and out-flowing reactive pyrolysis gas compounds were attributed to 'soot'. The possible formation of gaseous C₂ compounds (acetylene, ethene, ethane) at higher temperatures is neglected. Based on data material from other studies on homogeneous tar conversion [11], the maximum sum of the yields of these C₂ species is estimated to be approx. 6 m% at the highest reactor severity used in the present experiments.

Fig. 8 shows the soot yield determined by calculation. The formation of soot begins in the same temperature range as the PAH formation and increases with increasing conversion temperature. The largest soot yield is approx. 20 m% of the dry wood. Hence, in the absence of an oxidising atmosphere, between half to two-thirds of the 'total primary' tar mass are assumed to be converted into soot.

However, it should be noted that the estimated values for soot are *net* yields. Since the pyrolysis gas contains water, gasification of the soot by means of steam should be considered. Therefore, the extent of soot depletion by steam gasification at 1000 °C was calculated using the gasification rate determined by Jess [16]. The results indicated that the gasification of soot under the experimental conditions is negligible.

4. Kinetic modelling of homogeneous tar conversion

In order to improve biomass gasifiers design with regard

to the producer gas quality, the kinetics of tar conversion during thermal processes in the reactor are requisite. A model describing tar conversion should provide information about the change in quantity and composition of tar during the thermal processes. This can be accomplished by describing the tar by means of compound classes of similar thermal behaviour ('lumps'), which allows the definition of a strongly simplified model reaction network. An alternative modelling strategy is the description of the thermal behaviour of single tar compounds that are characteristic for a specific tar compound class. In the present study, the procedure for modelling of homogenous tar conversion combines these two strategies.

The formal kinetics of the gravimetric tar conversion and of the naphthalene formation due to homogeneous STR without external supply of oxidants were studied. As discussed earlier, the gravimetric tar provides a measure for the estimation of the overall tar mass. Naphthalene was chosen as the quantitatively most important representative for PAH in biomass tar. All other PAH compounds investigated exhibit thermal behaviours very similar to naphthalene.

The secondary tar constituents did not show a uniform thermal behaviour. The complicated interactions of these compounds need further experimental investigation in order to provide a basis for their kinetic modelling.

4.1. Modelling approaches

Homogeneous conversion of the gravimetric tar was modelled as a single reaction:



Assuming a first-order reaction, the formal reaction rate becomes

$$r_h = k_h c_{gT}, \quad (4)$$

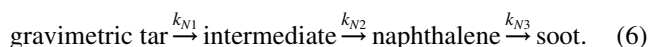
where k_h is the Arrhenius rate constant and c_{gT} is the concentration of gravimetric tar, expressed as mass per volume. In the tubular homogeneous tar conversion, plug flow behaviour was assumed. Due to the large excess of nitrogen in the pyrolysis gas, the change of moles during the homogeneous STR is assumed to be negligible. This leads to the ordinary differential equation describing the conversion of gravimetric tar in the plug-flow reactor:

$$v(T) \frac{dc_{gT}}{dx} = -A e^{-E_A/RT} c_{gT}, \quad (5)$$

where v , x , A , E_A are the (temperature dependent) gas velocity, the reactor length coordinate, the frequency factor and the activation energy, respectively. The equation was integrated numerically, using the measured temperature profiles (Fig. 2). The kinetic parameters A and E_A were determined by a non-linear least-square regression routine based on the Marquardt method.

The formation of naphthalene was modelled as a series

of three consecutive reactions:



The pseudo-specie 'intermediate' could stand for substances like phenols, resulting from STR of the primary tar that subsequently lead to PAH like naphthalene, according to the mechanism proposed by Egsgaard and Larsen [22]. Hydrogen-inhibited soot formation from naphthalene was considered in the last reaction step using the rate of soot formation determined by Jess [16]. The first two reactions in series were assumed to be first-order. This leads to a system of four coupled ordinary differential equations. The parameter for the Arrhenius reaction rate constants k_{N1} and k_{N2} were determined by non-linear least-squares regression analysis using the second-order Runge–Kutta method for the solution of the system of differential equations.

4.2. Modelling results and discussion

The resulting kinetic parameter from regression analysis for both models are given in Table 2. The frequency factors and activation energy are highly correlated in both models, therefore, all the frequency factors A were fixed at the values given and the activation energies were the only regression parameters. Since there were no repeated data for the same experimental conditions available, the indicated standard error of the estimate was the only measure for the evaluation of a model.

The experimental values for the gravimetric tar conversion and the results from the regression model are shown in Fig. 9. The model chosen satisfactorily fits the experimental data. The model indicates that, in the temperature range up to 600 °C, STR occur to a minor extent only, which is in agreement with the experimental findings concerning the evolution of non-condensable gases.

The kinetic parameters determined are very low for these kinds of reactions (see Table 2). The reason for these findings is the assumption of a single-reaction first-order kinetic model for a reaction network that is far more complex in reality. In a previous work [26], it was theoretically shown

Table 2
Kinetic parameters determined by regression analysis for the models for gravimetric tar conversion and naphthalene formation

Model	Frequency factor A (s^{-1}) ^a	Activation energy E_A (kJ mol ⁻¹)	Standard error of estimate ^b
Conversion of gravimetric tar			
k_h	4×10^4	76.6	7.8
Naphthalene formation			
k_{N1}	1.0×10^4	136	14.8
k_{N2}	1.0×10^7	100	

^a The frequency factors were fixed at the values given (see text).

^b Defined as $s = \sqrt{\sum_i^n (c_{gT,exp_i} - c_{gT,model_i})^2 / (n - k)}$, where the numerator in the square root is the sum of the squared residuals and the denominator stands for the degrees of freedom.

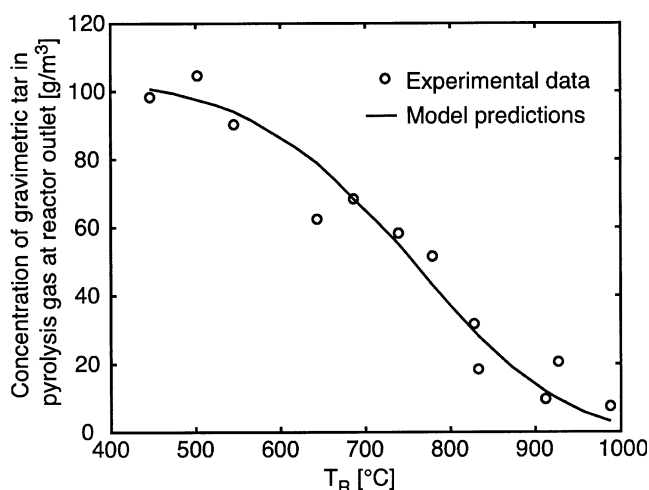


Fig. 9. Experimental gravimetric tar conversion data for homogeneous STR compared with predictions from the single reaction regression model. The concentrations refer to the gas volumes at the corresponding temperatures.

that a set of overlapping, independent, parallel first-order reactions can be approximated by a single first-order expression with both lower activation energy and pre-exponential factor than any of the reactions in the set. Therefore, a distributed activation energy model (DAEM), developed for secondary reactions of coal tar [27,28], was used to correlate experimental biomass conversion data in a previous work [11]. The use of this model provided more reasonable kinetic parameters. However, since tar conversion includes multiple, parallel and series reactions, the use of a reaction network based on lumps would provide an even more realistic model concerning tar conversion mechanisms.

A good correlation of the experimental data with the model defined was achieved for naphthalene formation

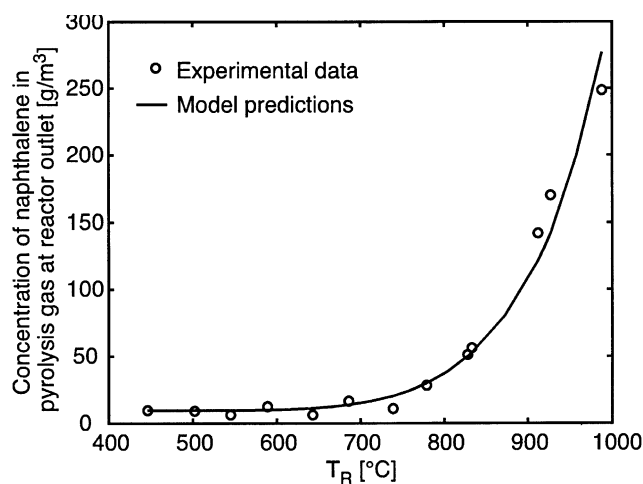


Fig. 10. Experimental data on naphthalene formation during homogeneous STR compared with the predictions from a multiple-reaction regression model. The concentrations refer to the gas volumes at the corresponding temperatures.

(Fig. 10). The findings and remarks concerning the determined kinetic parameters made in the case of gravimetric tar conversion are equally valid here.

Using the corresponding model approach by Jess [16], it was shown that the highest temperatures investigated were still too low for significant naphthalene conversion into soot. Hence, the last reaction step in the model proposed can be omitted for the description of the reaction conditions investigated. Since soot is already produced in considerable quantities at these temperatures during homogeneous STR, there are either other soot formation pathways which do not include naphthalene, or naphthalene conversion into soot actually occurs, but at a rate different from the one given in Ref. [16] under the present experimental reaction conditions.

5. Conclusions

Experimental investigation of homogeneous tar conversion without the external supply of oxidants was successfully conducted. The study provides quantitative data that are related to clearly defined process conditions. Based on the experimental data, gravimetric tar conversion and PAH formation are modelled by formal kinetic approaches assuming a simple single reaction and a system of reactions in series, respectively. The interpretation of the experimental and modelling results allows the following conclusions:

- Under the reaction conditions chosen for the experiments, homogeneous tar conversion reactions without the external supply of oxidising agents become important at temperatures higher than 650 °C, which is indicated by increasing concentrations of the gases CO, CH₄, and H₂ in the pyrolysis gas.
- During homogeneous tar conversion, the gravimetric tar yield decreases with increasing reaction temperatures. At the reaction conditions investigated ($T_R = 990$ °C, isothermal space time = 0.12 s), a maximum conversion of 88% was reached.
- Carbon monoxide is the quantitatively most important product from homogeneous tar conversion. Hydrogen is an indicator for the occurrence of STR. The qualitative behaviour of the hydrogen can be attributed to the mechanisms of PAH formation.
- The primary tar representative acetol was the quantitatively most important tar compound measured. Among the tertiary tar compounds, naphthalene was found to be the dominant compound. All PAH compounds measured exhibited a very similar thermal behaviour. Due to analytical uncertainties, the experimental results for the secondary tar components were the most difficult for interpretation. The secondary tar compound phenol appears in all tar classes.
- Soot seems to be the major product from homogeneous

tar conversion. Therefore, further investigations providing quantitative data on soot formation are recommended.

- Good fits of the experimental data describing the conversion of the gravimetric tar and the formation of naphthalene, respectively, were achieved by means of the model approaches selected.

Acknowledgements

Financing of this work by the Swiss Federal Office of Energy, Berne, is gratefully acknowledged. The authors also thank G. Heinzelmann and S. Biollaz from the Laboratory for Energy and Materials Cycles of the Paul Scherrer Institute (PSI), Switzerland, for undertaking a part of the GC–MS analysis of the tar samples.

References

- [1] Hasler P, Nussbaumer T. *Biomass Bioenergy* 1999;16:385–95.
- [2] Milne TA, Abatzoglou N, Evans RJ. *Biomass Gasifier Tars: their nature, formation and conversion*. US Department of Energy, 1998.
- [3] Piskorz J, Scott DS, Radlein D. *Pyrolysis oils from biomass: producing, analysing and upgrading*. In: Soltes J, Milne TA, editors. *Symposium Series*, vol. 376. Washington, DC: American Chemical Society, 1988.
- [4] Padkel H, Roy C. *Energy Fuels* 1991;5:427–36.
- [5] Horne PA, Williams PT. *Fuel* 1996;75(9):1051–9.
- [6] Evans RJ, Milne TA. *Energy Fuels* 1987;1(2):123–37.
- [7] Evans RJ, Milne TA. *Energy Fuels* 1987;1(4):311–9.
- [8] Elliott DC. *Pyrolysis oils from biomass: producing, analysing and upgrading*. In: Soltes J, Milne TA, editors. *Symposium Series*, vol. 376. Washington, DC: American Chemical Society, 1988.
- [9] Diebold JP. *The cracking kinetics of depolymerized biomass vapors in a continuous, tubular reactor*. MS Thesis, Colorado School of Mines, 1985.
- [10] Liden AG. *A kinetic and heat transfer modelling study of wood pyrolysis in a fluidized bed*. MASC Thesis, University of Waterloo, 1985.
- [11] Boroson ML. *Secondary reactions of tars from pyrolysis of sweet gum hardwood*. PhD Thesis, Massachusetts Institute of Technology, 1987.
- [12] Rath J, Staudinger G. *Fuel* 2001;80:1379–89.
- [13] Boroson ML, Howard JB, Longwell JP, Peters WA. *Energy Fuels* 1989;3:735–40.
- [14] Ekström C, Lindman N, Petterson R. In: Overend RP, Milne TA, Mudge LK, editors. *Fundamentals of thermochemical biomass conversion*. Amsterdam: Elsevier, 1985.
- [15] Morf Ph. *Secondary reactions of tar during thermochemical biomass conversion*. PhD Thesis, Swiss Federal Institute of Technology, Zurich, 2001.
- [16] Jess A. *Fuel* 1996;75(12):1441–8.
- [17] Morf Ph, Nussbaumer Th. *Grundlagen zur Teerbildung bei der Holzvergasung*. Report of the Swiss Federal Office for Energy, Bern, 1998.
- [18] Amand LE, Kassmann H, Karlsson M, Leckner B. *J Inst Energy* 1997;70:25–30.
- [19] Morf Ph, Hasler Ph, Hugener M, Nussbaumer Th. In: Bridgwater AV, editor. *Progress in thermochemical biomass conversion*. Oxford: Blackwell Science, 2001.
- [20] de Sousa L. *Gasification of wood, urban waste wood (Altholz) and other wastes in a fluidised bed reactor*. PhD Thesis, Swiss Federal Institute of Technology, Zurich, 2001.
- [21] Neeft JPA, Knoef HAM, Buffinga GJ, Zielke U, Sjöström K, Brage C, Hasler Ph, Simell PA, Suomalainen M, Dorrington MA, Greil C. In: Bridgwater AV, editor. *Progress in thermochemical biomass conversion*. Oxford: Blackwell Science, 2001.
- [22] Egsgaard H, Larsen E. *Proceedings of the First World Conference and Exhibition on Biomass for Energy and Industry*. Spain: Sevilla; June 2000. p. 1468–71 (published 2001).
- [23] Hasler Ph, Bühler R, Nussbaumer Th. *Evaluation of gas cleaning technologies for small scale biomass gasifiers*. Swiss Federal Office of Energy and Swiss Federal Office for Education and Science, 1997.
- [24] Morf Ph, Hasler Ph, Nussbaumer Th. *Biomass for energy and industry*. In: Kopetz H, Weber T, Palz W, Chartier P, Ferrero GB, editors. *Tenth European Conference and Technology Exhibition*. Germany: Würzburg, 1998.
- [25] Frenklach M, Wang H. In: Bockhorn H, editor. *Soot formation in combustion—mechanisms and models*. Berlin: Springer, 1994.
- [26] Jüntgen H, Van Heek KH. *Fortschritte in der chemischen Forschung* 1970;13:601–99.
- [27] Pitt GJ. *Fuel* 1962;41:267.
- [28] Anthony DB, Howard JB, Hottel HC, Meissner HP. *Fifteenth Symposium (International) on Combustion*. Pittsburgh: The Combustion Institute, 1975.