Energy research Centre of the Netherlands

Tar formation in pyrolysis and gasification

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Acknowledgement/Preface

This report is an updated translation of an older ECN report written by John Neeft. The original confidential report was called: “Teren uit pyrolyse en vergassing van biomassa en reststromen; Kinetiek en mechanisme van ontledingsreacties” (ECN-CX--99-132). The following report deals with, as the names states, tar formation. It focuses on the kinetics for the largest part. For a more general overview of gas cleaning technologies, broader than just tar cleaning techniques, the reader is referred to a thorough overview of gas cleaning technologies by R.W.R. Zwart in the ECN report ECN-E--08-078.

Abstract

This report summarises knowledge from the open literature on the reactivity of tars during pyrolysis and gasification of biomass. Also other mechanism of the chemical reactions involved is considered. The goal of this summary is to make the knowledge accessible not only to ECN but for a broader community and help in the development of both producer gas cleaning technology and innovative gasification processes.

Gaseous biomass tars can react under inert conditions (thermal cracking) or with components in the producer gas such as H_2, H_2O or CO_2 (gasification). The reaction rate of thermal cracking is such that high temperatures of approximately 1200°C or higher (also depending on residence time) are needed to create a producer gas with low tar concentrations. The rate of thermal cracking of tars depends on the kind of tar. The rate decreases in the series:

biomass pyrolysis oils/tars
>
phenolic tar compounds
(phenol, cresol, naphthol)
>
Pyrolysis tars from coal
>
Polycyclic aromatic tar compounds
(anthracene, phenanthrene, naphthalene, benzene).

The rate of thermal cracking also depends on the atmosphere in which the tars are cracked because the gas phase components H_2, H_2O en CO_2 play a role in the cracking reactions. H_2O and/or CO_2 increase the decomposition rate of tars whereas H_2 decreases this rate. The aromatic rings of tars can also be hydrogenated which only occurs under hydrogasification conditions at high partial pressures of H_2. This leads to the production of CH_4.

Radical reactions are the main reactions in the mechanism of tar decomposition and the formation of methane. Radical formation is the rate-determining step in this mechanism. After radical formation, the composition of the gas phase determines what are the final products of the tar decomposition.

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Summary

This report summarises the information in the published literature on the reactivity of tars during the pyrolysis and gasification of biomass and discusses the mechanism of the reactions involved. The purpose of summarising this information is to make it accessible so that it can be used at ECN in the further development of fuel gas cleaning and innovative gasification processes such as OLGA and MILENA.

The report focuses on the rate at which reactions take place between gaseous tar compounds; for the most part it ignores reactions in liquid tars and between tars and solids, as these are less relevant to the development of biomass gasification technology and there is not so much data available on them.

Gaseous biomass tars can react under inert conditions (thermal cracking) or with fuel gas components such as H_2, H_2O and CO_2 (gasification). The rate of thermal cracking is such that high temperatures are required – in the order of 1200°C or higher (also depending on the residence time at high temperature) – in order to break down enough tars so that the remaining fuel gas can be used problem-free in a downstream device such as a gas engine, gas turbine or catalytic synthesis processes. This is evident from waste processing processes where thermal cracking is used (the Thermoselect and Noell dust cloud gasification) and from the small amount of data available on the large-scale thermal tar cracker downstream from a biomass gasifier, the Creusot-Loire gasifier, which was built and run in the mid-1980s.

The rate of thermal cracking depends on the type of tar being cracked and decreases in the following series:

biomass pyrolysis oils/tars
\>
phenolic tar compounds
(phenol, cresol, naphthol)
\>
coal-based pyrolysis tars
\>
polycyclic aromatic tar compounds
(anthracene, phenanthrene, naphthalene, benzene)

The rate of thermal cracking also depends on the atmosphere in which the tars are cracked, as the gas phase components H_2, H_2O and CO_2 play a role in cracking reactions in a biomass fuel gas (air, steam or oxygen gasification) or at elevated hydrogen pressures. H_2O and/or CO_2 increase the tar decomposition rate, whereas H_2 reduces it. In hydrogasification, because of the high hydrogen pressures at high temperatures, aromatic rings may also be hydrogenated, causing higher concentrations of CH_4 as well as tar decomposition.

The products of thermal tar cracking are solid as well as gaseous, as it converts a small to large portion of the tars into carbon (= carbon-rich dust or soot). This has two consequences for the use of thermal cracking to remove tar in a biomass gasification plant. The first is that, if the fuel gas is used in a gas engine or turbine or in synthesis processes, the carbon needs to be removed first by means of a (bag) filter. The second is that, as a result, thermal cracking makes only part of the energy content of the tars available to the lower heating value (LHV) of the fuel gas, as the carbon will not be used to generate energy if the gas is burned in the engine or turbine or converted in the synthesis.

Hydrogasification and steam gasification of biomass probably produce the same tar compounds as biomass gasification. Under hydro and steam gasification conditions high temperatures are needed to crack these tars; converting them into methane moreover requires high hydrogen and steam pressures.

The mechanism of tar decomposition and methane formation involves radical reactions, and radical formation is the step in the mechanism that determines the rate. The composition of the gas phase in the second reaction step determines what the products are.

1. Introduction

Research into the gasification of carbonaceous fuels has traditionally focused on the reactions between solid fuels (e.g. coal, char and biomass) and gaseous reactants (e.g. O_2, CO_2, H_2O and H_2). The follow-up reactions that occur after the initial gasification reaction take place between gaseous, or in some cases liquid, products. There is a significant amount of information available on these reactions, such as the water-gas-shift reaction ($H_2 + CO_2 \rightarrow H_2O + CO$) and the methane reforming reaction ($CH_4 + H_2O \rightarrow CO + 3\ H_2$). Some other reactions, however, have attracted less attention in the past, as they are relatively unimportant in coal and char gasification: for example the reaction (gasification or separation) of tar compounds, which is particularly important in biomass gasification. This has been an increasing area of research during the past decade because of the growing demand for a sustainable energy supply and more recently because of the desire to reduce greenhouse gas emissions.

Although plenty of studies have previously been carried out into decomposition reactions of biomass tars and the formation of tars in the hydropyrolysis and hydrogasification of biomass, this information is not readily accessible. This report therefore summarises the information in the published literature on the reactivity of tars during biomass gasification and discusses the mechanism of the reactions.

It should be noted that the information available focuses mainly on the reactivity of tars as a function of temperature and, to a lesser extent, pressure. Temperature is an important parameter, as it is particularly at higher temperatures that the radicals responsible for the decomposition and further reaction of biomass tars are generated. High temperature is not the only cause of radical reactions, there are other ways in which radicals can be generated, such as:

- The presence of a plasma
- The presence of radicals from other combustion reactions (e.g. partial oxidation or the admixture of combustion products)
- Raising the energy content of a molecule by means of electromagnetic radiation, e.g. microwaves or UV radiation

This report does not consider these other ways of initiating tar decomposition reactions, for the simple reason that hardly any data on them was found in the published literature. A concise summary on tar reduction using plasma can be found in [76].

Definitions

This report uses a number of terms and definitions that require some explanation or need to be defined first. Even the word ‘tars’ is far from unambiguous, as set out below.

- Definition of tars and measuring techniques

  For a discussion of the definition of tars and measuring techniques the reader is referred to an ECN report, No. C--04-014 [46]. In this report a conglomerate of Dutch research institutes and universities have developed a new classification system for tars and this is explained in detail. However this standard is not universally used and therefore other definitions are also applicable.

  In the case of the present report it is important to note that comparing data on tar concentrations and conversion from different studies is hampered by the fact that they use different definitions of tars and different methods of analysing them. Often the definition of tars used is a practical one, based on the method used to measure them, e.g.:
    - ‘condensable tars’ at temperature X
    - ‘tars that are soluble in solvent Y’[49]

  The present report sometimes compares data from different studies, e.g. on tar cracking under inert conditions, in CO_2/H_2O and in H_2. The author estimates that the data from the various studies are broadly comparable, without considering the definitions and measuring techniques in detail: for more details on these the reader is referred to the original articles. When, in the author’s estimation, the measuring technique or definition of tars rules out even a broad comparison of data from different studies, this will be mentioned.

- Primary, secondary and tertiary tars

  The terms ‘primary’, ‘secondary’, ‘tertiary’, ‘primary reactions’ and ‘secondary reactions’ are not used uniformly in the literature. The term ‘secondary tar’ is particularly confusing, referring in some studies to the products of secondary reactions (i.e. all tars other than primary tars) and in others to an intermediate category of tars (between primary and tertiary tars).

  This study uses definitions that can be regarded as a compromise between the commonly used terms ‘primary reactions’ and ‘secondary reactions’ and the definitions of ‘primary’, ‘secondary’ and ‘tertiary’ tars used in the studies by Evans and Milne, [26][51] as they relate their definitions to actual compounds. They do not give names for the follow-up reactions, however. Also, we have retained the term ‘secondary reactions’ as it is in common use.

  The compositions of the three types of tar given in [51] are:
  1. Primary products characterised by compounds derived from cellulose, hemicellulose or lignin, e.g. levoglucosan, hydroxyacetaldehyde, furfurals and methoxyphenols
  2. Secondary products characterised by phenols and olefins
  3. Tertiary products characterised by aromatic compounds without oxygen substituents, divided into:
     a. Alkalised tertiary products, including methyl derivatives of the aromatics, e.g. methylacenaphthylene, methylnaphthalene, toluene and indene
     b. ‘Condensed’ (simplified) tertiary products, i.e. the AHs/PAHs without substituents, e.g. benzene, naphthalene, acenaphthylene, anthracene, phenanthrene and pyrene

  The two reactions are not linked to these three types of tar:
    - Primary reactions are those where biomass decomposes, generating tar compounds (primary tar). Pyrolysis oil or bio-oil is largely made up of primary tars, with some secondary tars
    - Secondary reactions are the continued reactions of the primary tar and can take place both in the interior of the biomass particle and outside it, in the gas phase.

  Note that secondary reactions produce not only secondary but also tertiary tars!

- Thermal cracking, heterogeneous thermal cracking and catalytic cracking
  In this study, cracking in the absence of a solid (i.e. in an empty, inert reactor) is referred to as ‘thermal’. In the presence of an inert solid it is referred to as ‘heterogeneous thermal’, and in the presence of an active solid as ‘catalytic’. Coal or char (such as activated carbon, anthracite, pyrolysis char, char in gasification ash) is regarded in this study as a catalyst (at high temperatures above 600°C) and also as a possible adsorbent (especially at low temperatures below 600°C). The 600°C dividing line is fairly arbitrary but probably lies in a region where the coal or char is not very active as a catalyst and does not adsorb tars to any significant extent.

- Decomposition reactions, thermal cracking, gasification, hydrogasification
  This report refers as consistently as possible to reactions of tars at high temperatures in general as ‘tar decomposition reactions’. The terms ‘thermal cracking’ and ‘gasification’ are used for decomposition reactions in an inert atmosphere and in the presence of O_2 (in a limited amount), CO_2, H_2O and H_2 respectively. Tar combustion reactions (with excess O_2) are not considered in this report. For the specific reaction of tars with H_2 the term ‘hydrogasification’ is used. The difference between hydropyrolysis and hydrogasification is explained in 3.5.1.

- Carbon/char/coke/dust/soot
  In this report the solid carbonaceous product of the thermal cracking of tars is referred to as ‘carbon’. This is only one of the many possible nomenclatures: others used in the literature are char, [19] coke, [47] ‘carbone’ (French), [20] dust, soot [42] and ‘pyrocarbon’[71] .

2. Reactivity of biomass tars

2.1 Introduction

The reactivity of biomass tars is very important to the further development of biomass gasification systems, as tars are difficult to remove from biomass producer gas (fuel gas or syngas, depending on the use to which it is put), so removal methods based on condensation, filtration or collecting tar droplets are at the very least in need of further development. The equipment ultimately required is likely to be more complicated and more expensive than standard gas cleaning devices. Decomposition off the tars could therefore be an attractive alternative that merits further study. Tars could decompose using plasma or in catalytic or thermal tar cracking process: this would involve a separate tar cracking reactor downstream or using the fluid bed or the freeboard of the gasification reactor itself.

Biomass tars undergo reactions when held at somewhat elevated temperatures at increased residence times. Reactions can even take place at room temperature if the tars are exposed to air. Various reactions can occur:

(1) Reactions between liquid/gaseous tar compounds and carbonaceous ash/char
(2) Reactions between liquid tar compounds
(3) Decomposition reactions in the gas phase in an inert atmosphere
(4) Reactions between gaseous tar compounds and gaseous reactants, which usually also result in the decomposition of the tar compounds

In the literature, reactions of types (1) and (2) are referred to as ‘tar polymerisation’ and decomposition reactions of types (3) and (4) as ‘tar cracking’.

Type (1) and (2) reactions are described in 3.2. They are discussed only briefly, for two reasons. First, the information on tars on which this report is based relates mainly to the gas cleaning of tars in biomass gasification systems. Here the reactions of tars in the gas phase are the most important, as they determine the temperature at which, and gas phase in which, the tars can be broken down. The reactions of tars in the liquid or adsorbed phase are less important, as liquid tars only form in cold parts of the plant, which can usually be prevented from occurring, and because an adsorbent such as carbon can be removed using standard filtration techniques, so when these reactions occur is less important. The second reason is that there is not much information in the published scientific literature on type (1) and (2) reactions.

Type (3) and (4) reactions are described in 3.3 and 3.4/3.5 respectively. In general terms, the reactivity of biomass tars in type (3) and (4) reactions can be said to be dependent on two sets of parameters. The first set comprises the standard parameters that affect the chemical reaction rate, i.e.:

- The reaction temperature
- The residence time of the tars at the reaction temperature
- The partial pressure of the tar and the partial pressure of the gaseous reactants (in this case CO_2, H_2O, H_2 and in some cases O_2).

The second set of parameters can generally be referred to as the ‘type of biomass tar’. They relate to the fact that the word ‘tar’ is an inaccurate defined collective term for a vast group of chemical compounds. A few parameters in this set that define the ‘type of tar’ are:

- The chemical composition of the tar (CHNO analysis or H/C, O/C and N/C ratios)
- The concentration of primary, secondary and tertiary tars in the tar
- The concentrations of characteristic tar compounds such as phenol, naphthalene, anthracene, phenanthrene and pyrene

Because of the second set of parameters it is impossible to give a general kinetic equation for the rate of thermal cracking of biomass tars or cracking in the presence of CO_2, H_2O or H_2. Kinetic equations can only be given for a precisely defined 'type of tar'. At the biomass conference in Seville a model was presented that used kinetic equations for six 'lumps' of tars [16]. The tars used were obtained from a fluidized bed gasifier and sampled before and after a catalytic tar cracker. The model did not discern between thermal and catalytic tar cracking mechanisms nor did it take reversible pathways into account. Besides a publication in 2003 [17] no follow up of this work could be found.

Chapter 3 considers the reactivity of tars under inert conditions (thermal tar cracking), gasification conditions (a CO_2 or H_2O atmosphere) and hydropyrolysis/hydrogasification conditions (an H_2 atmosphere). The author not only looked at the data in the literature on biomass tars but also at the reactivity of (brown) coal when thermally cracked or gasified, since there is a very limited amount of information available on the decomposition of biomass tars, and information from the literature on (brown) coal fills some of the gaps. Data based on these different input materials can be compared, provided a certain amount of caution is exercised, as the tars essentially comprise the same categories of compounds. The age of the input material (coal is older than brown coal, which is older than biomass) affects the quantity and type of tar formed in pyrolysis or gasification: coal tar, for example, is generally much more aromatic (i.e. has lower H/C and O/C ratios) than biomass tar. There are also substantial differences between the tar composition of different types of coal, e.g. bituminous coal and brown coal [49].

2.2 Reactivity of tars in heterogeneous reactions (liquid tars and/or with carbon)

Biomass tars can condense or adsorb on carbon at low temperatures. Sometimes this is what is wanted, for example in a steam trap or adsorption column, to sample tars or remove them from the gas stream. Sometimes it is not what is wanted, for example when tars condense on cold surfaces in a gasification system or inadequately heated sampling pipes, or when they adsorb on carbon collected in the system, e.g. on a cloth filter, which can result in sticky carbon, hence operational problems.

Gasification experts are aware that these condensed or adsorbed tars can undergo polymerisation reactions in which the tar compounds react to form larger tar compounds or 'fuse' with the carbon on which they have been adsorbed. There is hardly any description of this in the published literature, however, and the small amount of published information relates only indirectly to biomass tars. A literature survey of studies into the pyrolysis of model compounds (in the field of coal processing [61]), for instance, reports as follows:

- Compounds that also occur in biomass tars (e.g. naphthalene, anthracene, phenanthrene and larger compounds comprising up to five rings) undergo polymerisation reactions when heated to 400-500°C in the liquid phase (reference [61], pp. 36-37). Phenolic compounds (phenol, cresols and naphthols) are relatively inert at temperatures below 600°C (reference [61], pp. 166-86).
- Differences have been found between reactivity in the liquid and gas phases: there is hardly any conversion of naphthalene at 500°C in the gas phase, for example, whereas 70% of liquid naphthalene is converted at 500°C and 90 minutes residence time (reference [61], p. 37).

The author's own experience and that of others with biomass tars shows the following regarding polymerisation reactions:

- In heated pipes, e.g. sampling pipes of biomass pyrolysis or gasification plants at 200-400°C, tars tend to condense and then gradually carbonise or polymerise. These reactions first produce a sticky dark brown or black syrup, then after a longer reaction time a brittle, shiny carbon. Many scientists working in the field of biomass pyrolysis or gasification have experience of this sticky or solid condensed deposit, which can block sampling pipes and even pyrolysis or fuel gas pipes.

- Pyrolysis oil, which consists of the primary and secondary tar compounds mentioned in Chapter 2, polymerises when stored at room temperature under exposure to air, or when heated to temperatures of 100°C or higher [10]. This is also the case with tars from updraft gasifiers [19].
- Tars from biomass gasification, separated in a scrubber and subsequently exposed to the air, gradually polymerise (over a number of days) to form a solid [50]. If these tars are stored as a solution in water or an organic solvent they can be kept over long periods without ageing as a result of reactions. This would also seem to be the case with tars adsorbed in a solvent such as the amino phase adsorbent [7] used in the SPA method (see report [1]).
- Tars typically produced at lower temperatures and condense tend to polymerize in particular when maintained at temperature levels of 200-300°C. The reactions first produce a thermoplast, being converted in time to a thermalhard. This is quite similar to the reactions of Bakelite formation.

Tar compounds adsorbed in porous carbon (activated carbon, char or soot) can react and form part of the carbon by chemical bonding, making desorption of the tar compound impossible. No information on these reactions was found in the published literature.

2.3 Reactivity of tars under inert conditions (thermal cracking)

The reactivity of tars under inert conditions can be regarded as the basic reactivity of biomass tars. Reactivity in a different atmosphere (in the presence of O_2, CO_2, H_2O and H_2) will be compared with this. Inhibition (the reduction of reactivity by non-inert gas phase components) can occur: hydrogen and nitrogen (radicals) are known to slow down tar cracking reactions. Reactions under inert conditions are often referred to as the 'thermal cracking' of tars.

2.3.1 Practical experience of tar cracking

In large-scale thermal plants that process varied, generally high-calorific waste streams, pyrolysis gas is gasified at high temperature and at the same time brought to chemical equilibrium. As the tars and even almost all the methane (the most stable hydrocarbon) are broken down, these conditions provide a guide to the conditions for a thermal tar cracker. It should be noted, however, that oxygen is added in these plants, (a) to achieve the required temperature and (b) to add enough oxygen atoms to the gas so that CO and H_2 are the main products (without the extra oxygen very large quantities of soot would be formed). High temperatures combined with fairly long residence times are needed:

- The Thermoselect[1] process uses temperatures of 1200°C and up, with gas residence times of about 5 seconds.
- The Noell Conversion Process (dust cloud gasification) uses a temperature of 1400-1700°C.
- The Gibros PEC uses temperatures of 1200-1300°C to crack tars.

An ECN report on these pyrolysis processes [54] gives details of these processes and references.

2.3.2 Information from empirical studies

Various authors have done empirical research into the thermal, non-catalytic cracking of pyrolysis tars from biomass [6][8][41][43][45][70][72] and coal [11][34][35][39][69][74] in the 500-1000°C temperature range. There are also descriptions in the published literature of the results of studies into the pyrolysis of model compounds for tars such as benzene, phenol, toluene, cresol, naphthalene, phenanthrene and anthracene in the 600-1400°C temperature range [20][42][13][14][2][3][21][44][9][23]. Studies into catalytic cracking are not considered here, and reactions on carbon are also not mentioned, since carbon acts as a catalyst (see reference [40]for a review).

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[1] The process is owned by the ThermoSelect company (www.thermoselect.com) with licensees provided to JFE and Daewoo[76]

Studying this literature, one is struck by the fact that virtually all the empirical studies were carried out with model compounds or pyrolysis tars from coal or biomass; in other words, no studies have been done into the thermal cracking of tars from biomass gasification plants. This is acknowledged by other experts in the field such as Reed et al [64].

Biomass pyrolysis tars in particular, which can also be referred to as ‘pyrolysis oil’ and ‘bio-oil’, consist of relatively reactive compounds (compared with tars formed in the gasification process), because they contain a lot of pendant groups and oxygen and hydrogen atoms: to use the terminology of Milne and Evans, [26][51] they are ‘primary’ and ‘secondary’ tars. This is explained in more detail in a previously published literature review [56]. Pyrolysis tars from coal are made up to a larger extent than biomass pyrolysis tars of polycyclic aromatic hydrocarbons, which can be classified as tertiary tars.

The result of carrying out the studies with pyrolysis tars, therefore, is that the temperatures at which the tars are found to be thermally cracked are relatively low. This should come as no surprise if we consider that in biomass gasification these pyrolysis tars are formed as the first step in the gasification process but then, at gasification temperatures in the 750-1000°C range, converted into a much smaller quantity of tertiary tars

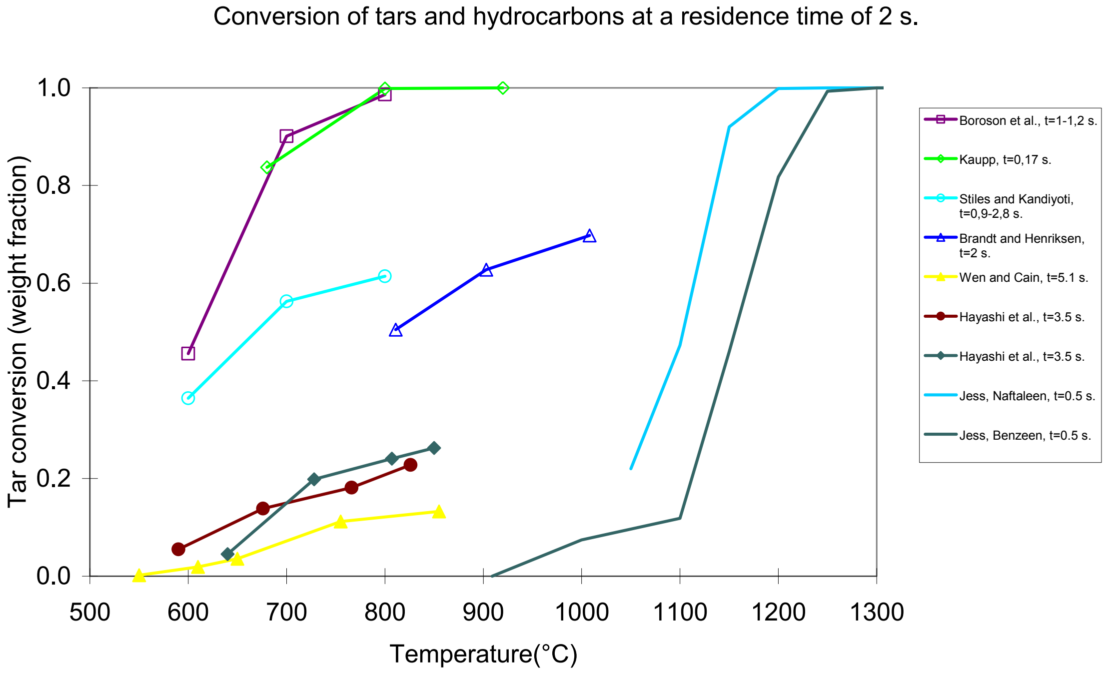


Figure 1*:* *Thermal cracking of biomass tars and coal tars. The times in the key are the residence times used in the studies. The data in the chart have been converted to a residence time of 2 seconds (see Appendix A for the method of computation used).The open symbols are data for biomass tars: pyrolysis tars from hardwood (Boroson et al. [6]), tar from an updraft gasifier (Kaupp [45]), pyrolysis tars from birchwood (Stiles and Kandiyoti [70]) and pyrolysis tars from straw (Brandt and Henriksen [8]). The closed symbols are data for coal tars (produced by pyrolysis of the tars at temperatures in the 500-640°C range) and based on data from Wen and Chain [74] and Hayashi et al. [34]. The two lines without symbols are included to enable this figure to be compared with Fig. 2 and are taken from Jess [42].*

All the reaction rates for the cracking of biomass tars and tars from coal found in the literature so far are shown in Figure 1.

In addition to data on the cracking of tars from biomass and coal, the literature also contains data on the cracking of the AHs/PAHs that occur in tars: these are shown in Fig. 2. This figure includes data on the cracking of biomass tars from Boroson et al.[6] and Kaupp [45] so as to facilitate comparison with the data in Figure 1.

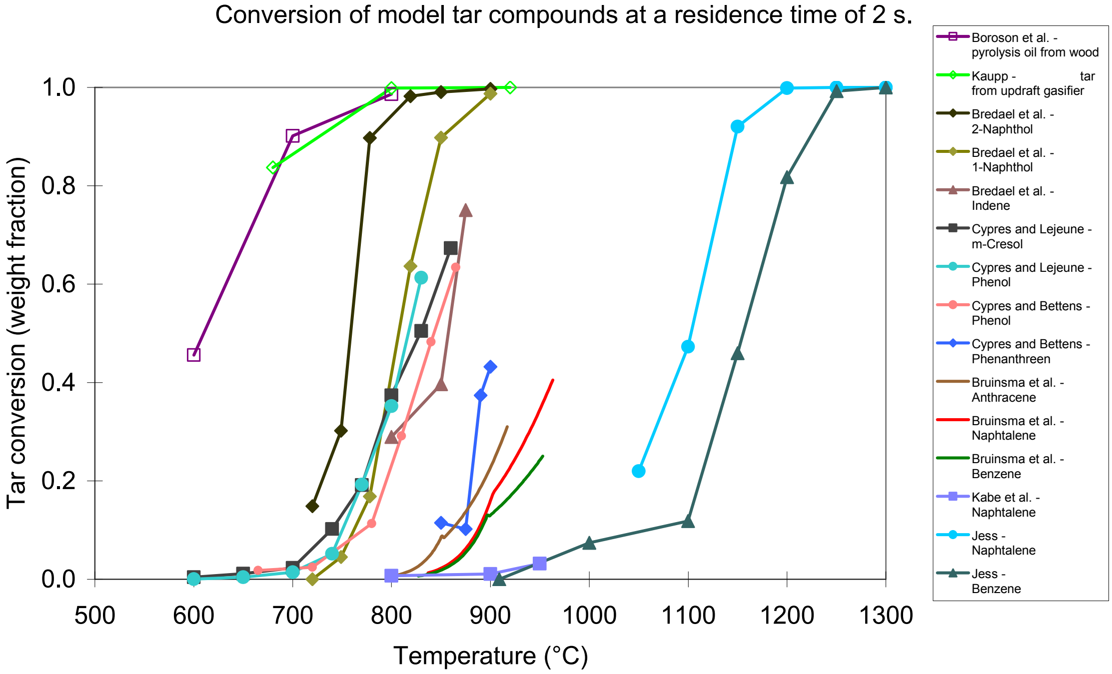


Figure 2: *Thermal cracking of individual tar compounds. The residence times used in the studies are not shown: the data in the chart have been converted to a residence time of 2 seconds (see Appendix A for the method of computation used). The data are from Bredael et al.,[9] Cypres and Lejeune,[20] Cypres and Bettens,[21][23] Bruinsma et al.,[75] Kabe et al.[44] and Jess [42]. The two lines with symbols are included to enable this figure to be compared with Fig. 1 and are taken from Boroson et al.[6] and Kaupp [45].*

Two comments are called for on these two figures:

- The empirical data were obtained at different residence times, ranging from 0.2 to 50 seconds, the majority at residence times between 0.5 and 5 seconds. As conversion of tars increases with residence time, it was decided to convert all the data to a residence time of 2 seconds, assuming that the cracking reaction is a first-order reaction (i.e. the tar cracking reaction rate is proportional to the concentration of tar or model compound). The method of computation is shown in Appendix A.
- The results of a number of studies are not included because:
  - The studies did not indicate the residence times [72][2][3].
  - The residence times were either very long, thus ruling out first-order kinetics, [35][11] or very short, resulting in recomputed conversion rates virtually equal to 1 [41].
  - Only the concentrations of tars after cracking are indicated, not those of 'light oils', resulting in a too high estimated conversion of approximately 80% (converted to a residence time of 2 seconds) at a temperature of 900°C [69].
- The conversion rates for the model compounds in Figure 2 are based on the component under consideration. Pyrolysis of these model compounds, however, results in the formation of other tar compounds (see e.g. [12]), so the conversion rate of 'tars' is lower than that of the model compound in question.

The data in Figure 1 and Figure 2 give rise to the following observations and conclusions:

- Tars produced in the pyrolysis of biomass (straw and wood) and coal crack at lower temperatures than the polycyclic aromatic hydrocarbon (PAH) model tar compounds (naphthalene, phenanthrene, etcetera), owing to heteroatoms (N and O) and pendant groups in the form of -OH and -CH_3. Bruinsma et al.[13] show that model compounds with heteroatoms (N and O) and/or pendant groups are much more reactive than similar compounds without heteroatoms and pendant groups, and therefore decompose at lower temperatures.
- Pyrolysis tars from coal crack thermally less readily than pyrolysis tars from biomass. This can be explained by a difference in the composition of the tars: coal tar is more aromatic, with fewer compounds that react (with heteroatoms and/or pendant groups) than biomass tars.
- The curves for biomass and coal tars are much flatter than those for model compounds such as benzene, phenol, cresol, naphthalene and anthracene. This can be explained by the fact that biomass and coal tars are made up of a wide variety of compounds. The most reactive compounds (with heteroatoms (N and O) and/or pendant groups) react first, with the result that the remaining tars end up with a different composition. This has indeed been found in practice: the remaining tars have a lower H/C ratio and are more aromatic than the original tars [34]. Ultimately, to convert the last tars – the polycyclic aromatic hydrocarbons (PAHs) always present in biomass and coal tars – cracking needs to take place at the temperatures required to crack anthracene, phenanthrene and naphthalene.
- Oxygen-containing phenolic model compounds such as phenol, cresol and naphthols are converted in the 700-850°C temperature range. Non-oxygen-containing aromatic or polyaromatic model compounds only crack at higher temperatures, between 850 and 1200°C.
- The data shown for the decomposition of benzene and naphthalene are inconsistent: those in Bruinsma et al. [13][14] are some 100-200°C below those in Jess [42]. The data in Diener et al. (Fig. 2 in [24]) for the cracking of benzene and naphthalene, which are not included in Fig. 2 because they were obtained at 2 (and 30) bar, are close to the data in Jess. A report by CRE Group [19] gives data for the temperatures required to crack benzene somewhere between those in Bruinsma and Jess. These CRE Group data are not included here as they do not include residence times.

  Two possible reasons for the discrepancies between the Bruinsma et al. and Jess data are:

  1. The carbon layer that Bruinsma et al. used in their reactor may have had a catalytic effect, thus reducing the decomposition temperatures (Jess and many other researchers use quartz or silica reactors). Bruinsma et al. claim, however, that their carbon layer *reduced* the reactivity.
  2. The different gas phase that Jess used (40-48% by vol. H_2 and 20% by vol. steam, as against the inert conditions under which Bruinsma operated) affected the reaction rate of the model tars. Jess shows in his study ([42], Fig. 2) that hydrogen sharply reduces the cracking rate of naphthalene.

  The higher concentrations of hydrocarbons at which Jess obtained his data may have increased the reactivity. This could have a major effect in the case of benzene, as we know from other studies that the kinetics of benzene cracking are complicated, taking place via biphenyl and varying between first and second order in the concentration of benzene [37]. This, however, does not explain the discrepancies, as higher reactivity would result in lower temperatures, not the higher temperatures reported by Jess compared with Bruinsma's data.

An important conclusion that can be drawn from these data is that much higher temperatures and/or longer residence times are required for the thermal cracking of tertiary tars than those required for the cracking of pyrolysis oils reported in a number of empirical biomass studies.

2.3.3 Kinetic equations

In addition to data from empirical studies, extrapolations from kinetics data can provide information on the decomposition of biomass tars or individual tar compounds occurring in these tars.

2.3.3.1 Form of kinetic equations

Kinetic equations for chemical reactions are often based on the following two equations:

$$r = \frac{\delta C_{tar\ compound}}{\delta t} = k(T) \cdot \left(C_{tar\ compound}\right)^m \cdot \left(C_{CO2}\right)^n \cdot \left(C_{H2O}\right)^o \cdot \left(C_{H2}\right)^p$$

where r is the reaction rate, C the concentration, t the time, k(T) the reaction rate constant and m, n, o and p the orders in the reaction rate for the concentrations of the tar compound, CO_2, H_2O and H_2 respectively. The temperature dependency of the reaction rate constant k(T) is usually described using the Arrhenius equation:

$$k(T) = k_0 \cdot \exp\left(\frac{-E_a}{R \cdot T}\right)$$

where k_0 is the pre-exponential factor, E_a the activation energy, R the gas constant and T the temperature.

2.3.3.2 Kinetics of tar cracking reactions

It is generally assumed in the literature that the radical-forming reaction is the step that determines the rate of cracking reactions of (hydrocarbon) compounds [61][13]. Radical formation is the reaction in which two radicals are generated by breaking a covalent chemical bond (in hydrocarbons usually C-C, C-O or C-H). This is described in more detail in Chapter 4 of this report. The rate of cracking reactions depends on a number of parameters (for the sake of simplicity, we consider the cracking reactions of an individual model compound), the first three being as follows (for the others see [13]): (1) the strength of the weakest bond in the model compound; (2) the number of weak bonds; and (3) the size of the compound. Parameter (1) is generally assumed to be very important. The activation energy of this reaction can be approximated by the bond energy D_0 of the bond broken in the radical-forming reaction [61][13]. Benzene cracking thus has an activation energy equal to the bond strength between the H- and the -C_6H_5 group, which is 464 kJ mol^{-1} [18]. If the other parameters play only a minor role (for a more detailed description see [13]), the frequency factor k_0 in the Arrhenius equation (see Appendix A) is more or less the same for all radical-forming reactions. Both Poutsma [61] and Bruinsma et al. [13] state that k_0 needs to be in the order of magnitude of 10^{16}. In that case, the cracking rate of model compounds can be easily computed using the Arrhenius equation. This is shown for benzene and toluene in Fig. 3, assuming a first-order reaction in 'tar' (m=1). This figure includes the data from Jess, [42] which, although obtained in an atmosphere of 40-48% by vol. H_2 and 20% by vol. H_2O, are the best data for comparison. The data in Bruinsma et al. [13] are not included for comparison for the reasons stated in 3.3.2.

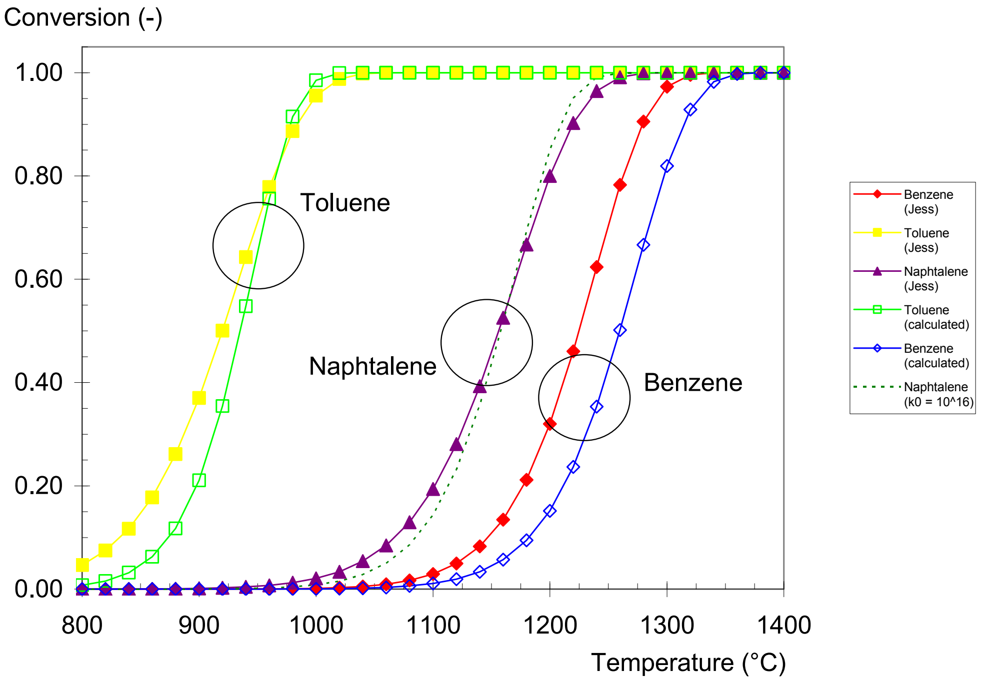


Figure 3: *Comparison of computed tar cracking rates (using the Arrhenius equation with 10^{16} for k_0, bond energy as E_a and a residence time of 0.5 seconds) with the tar cracking rates obtained by Jess [42]. The naphthalene curve has also been recomputed with a k_0 of 10^{16} and a fitted E_a (see text).*

It can be concluded from this figure that this very simple method of computing the reactivity of tar compounds in cracking reactions yields reasonable results. It should come as no surprise that the results are not more accurate, as the method is very robust and, apart from many other factors, does not take into account the fact that:

1. The bond energies used under standard conditions (T = 25°C) should be corrected for temperature, which is difficult as the heat capacities of radicals are not readily available.
2. The other parameters mentioned above play a role: the number of weak bonds (6 in benzene and 1 in toluene) and possible parallel reactions (toluene can react to form not only $C_6H_5\bullet$ and $CH_3\bullet$ but also $C_5H_6CH_2\bullet$ and $H\bullet$, which is even faster at low temperatures but slower at higher temperatures because of the different heat capacities [13]).

2.3.3.3 Kinetics of naphthalene cracking

Using the method of computation given in the previous section, we can easily estimate the temperature and residence time required to break down biomass tars in a thermal tar cracker. For this purpose we assume that:

1. Naphthalene is a typical tar compound that is less reactive than, or at most as reactive as, larger tar compounds such as anthracene, phenanthrene and pyrene.
2. The composition of the gas phase can be approximated with that of Jess [42]. These are the only data on the cracking of model tars in a gas containing H_2 and H_2O.

The naphthalene curve has been recomputed with a k_0 of 10^{16}, the associated E_a has been determined by varying this and fitting the curve to the data from Jess [42] to find the best fit (least squares method). This yielded an E_a of 434 kJ/mol. The resulting curve is also shown in Figure 3. Taking this k_0 and E_a, the temperatures required for a given residence time were computed to arrive at a particular conversion rate. These are shown in Table 1 and plotted in Fig. 4.

Table 1: *Computed temperatures (all in °C) depending on residence time and conversion rate of naphthalene as a representative tar compound. These numbers are based on the kinetic parameters fitted using the data from Jess [42]. They are indicative because of the fitted kinetics and the assumption that (a) naphthalene is a representative compound and (b) the gas phase does not affect the kinetics.*

Residence time t (s)	T/°C (60% conversion of naphthalene)	T/°C (80% conversion of naphthalene)	T/°C (90% conversion of naphthalene)	T/°C (95% conversion of naphthalene)	T/°C (99% conversion of naphthalene)	T/°C (99.9% conversion of naphthalene)
0.1	1239	1264	1281	1294	1315	1336
0.2	1208	1233	1249	1261	1281	1301
0.5	1169	1193	1208	1220	1239	1257
1	1141	1164	1179	1190	1208	1226
2	1115	1136	1151	1161	1179	1196
5	1081	1101	1115	1125	1142	1158
10	1056	1076	1089	1099	1115	1131
20	1033	1052	1064	1074	1089	1104
50	1003	1021	1033	1042	1057	1071

The conclusion from this exercise is that, based on the limited data and the assumptions, at residence times in the order of magnitude of 0.5-1 second, cracking temperatures of 1200°C or higher are required to thermally crack 95-99.5% of biomass tars. While longer residence times permit lower temperatures, they also require very large reactors.

The temperature actually required to thermally crack tars (to the extent that the gas could be used in a gas engine) may be lower, for two reasons: naphthalene is a very stable tar compound (more stable than larger compounds: see Figure 2), and it can exist at a concentration of roughly 0.5 g/m^3_n (see Table 3.2 in report [55]) without naphthalene or tar condensing. On the other hand, it can be generated as a decomposition product of larger tars (see the next section, 3.3.4).

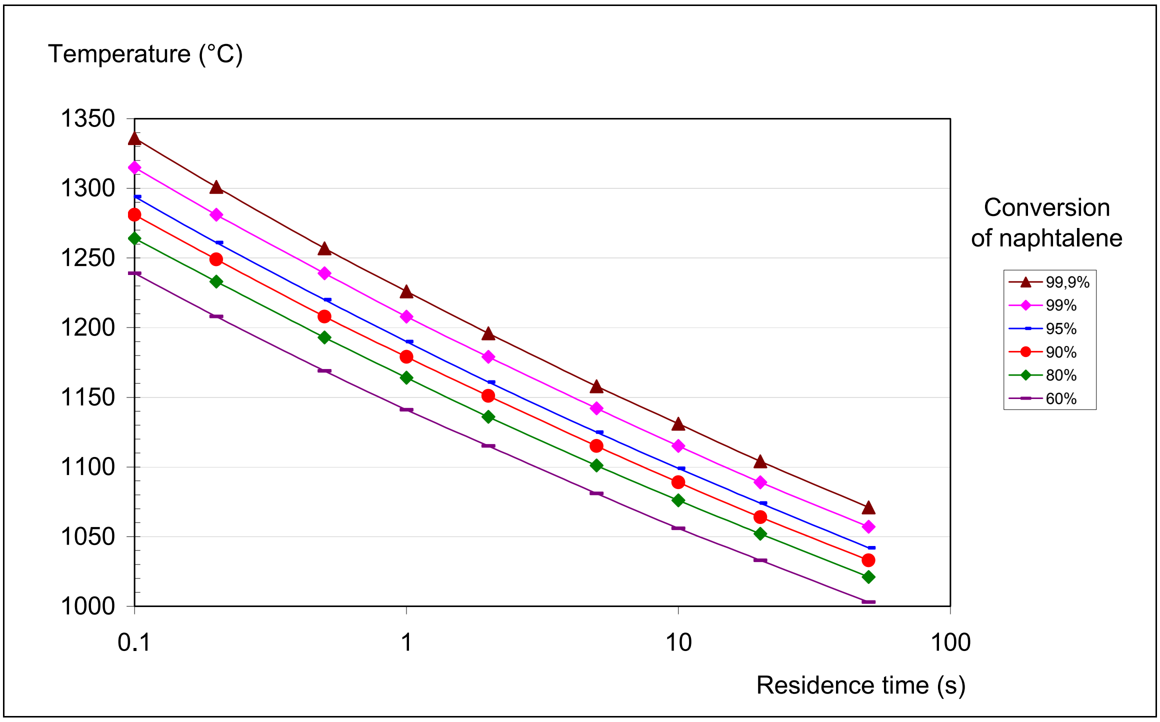


Figure 4: *Graph of the conversion of naphthalene as a function of residence time and temperature (°C). These figures are based on the kinetic parameters fitted using the data from Jess* [42]*. They are indicative because of the fitted kinetics and the assumption that (a) naphthalene is a representative compound and (b) the gas phase does not affect the kinetics.*

2.3.4 Products of the thermal cracking of tar compounds

To estimate how useful thermal tar cracking could be for converting biomass tars in gasification plants, we need to consider not only the reactivity but also the product distribution of the tars, as the reaction rates given in the preceding sections are based on converting the input product, the tar or model tar. If 90% of a biomass tar is thermally cracked, this does not mean that the tar problem has been largely solved, as (a) the remaining tar may have a different (possibly worse) composition from the input product and (b) unwelcome by-products such as carbon may be formed. This section looks at product distribution. The data on model tars are even more dangerous if they are not interpreted with caution, since not only carbon but also other tar compounds may be formed: '90% conversion' of a model compound only means that 90% of the compound has been converted; it does not indicate to what extent other tar compounds have been formed.

In general, the following about the formation of carbon in thermal tar cracking can be said:

- H_2 suppresses carbon formation and the naphthalene cracking reaction rate (Fig. 3 in [42]; see also 4.2).
- Larger (3-ring and higher) polycyclic aromatic hydrocarbons such as acenaphthylene, anthracene and chrysene have a much greater tendency to form carbon than smaller 1 and 2-ring compounds [47]. Jess [42] even notes that soot-forming tar compounds do not break down directly but by way of carbon as an intermediary.
- The reactivity of this carbon in a gasification atmosphere is low, compared with that of tars (high temperatures and/or long residence times are needed to gasify carbon), and it depends to a large extent on the conditions (pyrolysis or gasification) under which it was generated [31][25][67][5].

The table below shows what products are formed when hydrocarbons are pyrolysed at high temperatures.

Table 2: *Product distribution (carbon=char/tar/gas) in high-temperature pyrolysis of model tar compounds*

Input material	Conditions		Product composition (from converted input material)			Reference
	Temperature (°C)	Residence time (s)	Carbon (%)	Tar (%)	Gas (%)	
Phenols						
Phenol	830	10	12	56	32	[20]
Cresols	800	1.5 - 4.5	1 - 5	26 - 55	22 - 40	[59]
	900	1.5 - 4.5	7 - 34	12 - 37	38 - 46	[59]
m-Cresol	860	10	6	60	34	[20]
Xylenols	750	1.5 - 4.5	1 - 5	28 - 84	16 - 39	[60]
	850	1.5 - 4.5	5 - 17	14 - 30	27 - 48	[60]
Aromatics						
Benzene	1200-1400	0.5	15-50			[42]
Naphthalene	1100-1400	0.5	35-70			[42]
	1200	0.5	65			[42]
	1300	0.5	55			[42]
	1400	0.5	35			[42]
Anthracene	700	not known	21			[3]
	900	not known	59			[3]
Phenanthrene	700	not known	14			[2]
	850	not known	21			[2]
	850	2.5	6	94	1	[23]
	900	2	39	60	2	[23]

The following conclusions are drawn from this table:

- The amount of carbon as a cracking product appears to decrease with increasing temperature in the case of naphthalene and to increase in the case of cresols, xylenols, anthracene and phenanthrene.
- The amounts of carbon are substantial, up to 70% of the model tar compound reacted away. The amounts of tar can also be large at very low gas yields.
- There are not many figures available for the amounts of tar and gas produced, and it is unclear whether the output of gaseous products increases as a function of temperature.

An important conclusion from these figures is that, when cracking tars, a large proportion of them may be converted into carbon, so if this carbon is not used in the subsequent process, its energy content is lost.

2.4 Reactivity of tars in CO_2 or H_2O (gasification)

Not many studies have been carried out into the reactivity of tars under gasification conditions. Virtually all the studies that have been done into tar cracking in biomass gasification systems took place under inert (pyrolysis) conditions, with the result that one of the products is carbon. CO_2 and H_2O may speed up the decomposition of tars.

There is interesting information in a VTT article [48], where the temperature of the freeboard was varied so that the tars were cracked there. It follows from the results that, under gasification conditions, benzene and naphthalene are stable aromatic compounds that survive at temperatures higher than 1000°C. Other important tar compounds are broken down at that temperature, e.g. toluene and pyridine (occurring only in very low concentrations above 1000°C), phenol (no longer occurring above 850°C) and phenanthrene (no longer present above 950°C).

Two other studies have shown that steam speeds up tar cracking. Results from Jönsson [43] show that increasing the steam concentration (steam added after the pyrolysis reactor and before the thermal tar cracker) markedly reduces the amount of tar after the tar cracker. Adding a small quantity of oxygen reduces the amount even further. This pattern is confirmed by a study by Garcia and Hüttinger [28] into pyrolysis in the presence and absence of steam. In the presence of steam, the outputs of hydrogen and methane are almost five times higher than under pyrolysis conditions. Even in the presence of steam (at a steam/naphthalene ratio of 20), however, larger tar compounds and carbon are generated from naphthalene under all the experimental conditions tried (residence times of 5-60 seconds, temperatures of 750-900°C). At 750°C the composition of the tars is still relatively simple, but those formed in steam gasification at 950°C are complex, containing 4 and 5-ring aromatics. Hydrogen slows down the naphthalene-steam reaction, at the same time suppressing the formation of carbon [28].

It may be possible to obtain more information on tar decomposition rates under gasification conditions from data on char gasification, as the structure of char has a lot in common with that of large polycyclic aromatic hydrocarbons. In the case of biomass and coal the gasification reactivity is higher in H_2O than in CO_2 [33]; Graboski [31] reports a higher reaction rate for coal, with a factor of 3 to 5 for reactivity in pure steam compared with pure CO_2. The combustion rate is many times higher (240 times higher than with gasification) [31]. There is reason to assume, then, that biomass tars will display a higher reactivity in H_2O than in CO_2.

2.5 Reactivity of tars in H_2 (hydrogasification)

Reactions between hydrocarbons (such as tars and PAHs) and hydrogen are referred to in the petrochemical industry as ‘hydrogenation’, ‘hydrotreating’ or ‘hydrocracking’ reactions. They are used there on a large scale to convert heavy petroleum fractions into lighter ones, and to remove heteroatoms (oxygen, sulphur and nitrogen) from hydrocarbons. A good deal of research has also been done into the remediation of coal tars (removal of PAHs). Hydrogenation reactions in the petrochemical and coal chemical industry take place at hydrogen pressures of 20-200 bar and temperatures of 350-550°C. Catalysts are sometimes used: for an overview of coal tar reactions see reference [1].

Biomass is hydropyrolysed or hydrogasified for two reasons. The first is to produce an oil with much better properties (less oxygen and a slightly higher calorific value) than pyrolysis oil, so as to enable it to be used more easily as a transport fuel. A comparison between pyrolysis oil and hydropyrolysis oil can be found in reference [1]. The second reason for hydropyrolysing and/or hydrogasifying biomass is to produce methane (synthetic natural gas).

2.5.1 Difference between hydropyrolysis and hydrogasification

For the purpose of this report, the difference between hydropyrolysis and hydrogasification is presumed to be as follows:

Hydropyrolysis refers to pyrolysis reactions in the presence of hydrogen under relatively mild conditions (temperatures of up to 600°C). In the case of biomass these are the decomposition reactions that produce char, tar and gas; in the case of coal these are the reactions or physical processes that release the volatile fraction (including tar) from the coal. In the case of coal the tars are to a large extent present in the input material, so they are formed to a lesser extent during heating than in the pyrolysis/hydropyrolysis of biomass. The hydropyrolysis of coal produces a residual char (coke) that is less reactive than the original coal.
Also, the decomposition reactions of the primary tar products fall under the heading of hydropyrolysis: these are the primary reactions (for definitions see Chapter 2) that produce secondary tars. Hydrogen influences the composition of the products of these reactions, as the secondary tars contain less oxygen under hydropyrolysis conditions than under pyrolysis conditions.

Hydrogasification refers to reactions of hydrogen with biomass char, coal and the resulting char, and tars. Compared with hydropyrolysis, then, it includes gas phase reactions. Hydrogasification reactions occur at temperatures of 600°C and higher, the main product being methane.

It follows from the foregoing that hydropyrolysis reactions always take place when biomass or coal is hydrogasified. Conversely, hydropyrolysis can be done in such a way (at relatively low temperatures and short residence times) that hydrogasification reactions hardly occur (see reference [38], 12.5.1).

In this report we shall refer as far as possible to 'hydrogasification', unless it is clear that no high-temperature reactions occur, in which case we shall use the term 'hydropyrolysis'. Thus in the ensuing text 'hydrogasification' will be used regularly to refer to hydropyrolysis plus hydrogasification. Confusingly, in the literature the terms 'hydropyrolysis' and 'hydrogasification' are sometimes used without distinction for both reactions: in other words, 'hydropyrolysis' includes reactions of hydrogen with char and tars. In effect, then, those studies use different definitions for the terms 'hydropyrolysis' and 'hydrogasification' from the ones used in this report.

At first sight the idea of being low in or free from tar seems strange, as many of the studies into biomass hydrogasification (e.g. [66][63][65]) were carried out with the aim of producing bio-oil that is low in oxygen. Analysis of the research findings, however, shows that tar formation may be low in the case of high-temperature (850°C and above) hydrogasification. Therefore the hypothesis is formulated that 'hydrogasification does not yield much tar' [52].

2.5.2 Effect of pressure, temperature and residence time

It is difficult to gain a good impression of the product distribution resulting from hydrogasification for three reasons:

1. It is affected by a large number of parameters, e.g. the type of biomass or coal, temperature, hydrogen pressure, residence time, whether a catalyst is used, and the particle size of the biomass or coal.
2. The way the products are measured and/or the definition of the liquid products in particular: these are referred to variously as 'oil', [63][68][22] 'tar' [65][32][58] and 'heavy hydrocarbons [31] and are measured in many different ways, making it extremely difficult to compare data.
3. In effect, there are two successive reactions: (a) the formation of tars during hydropyrolysis and (b) the subsequent reaction and/or decomposition of tars under hydrogasification conditions.

In this section two types of studies are discussed separately as regards the effect of pressure and temperature. The first type concerns studies into the hydropyrolysis or hydrogasification of biomass and coal. In these studies, tars are both formed (hydropyrolysis of the biomass or coal), and broken down under the influence of high temperature and/or pressure, so it is not so easy to establish the effect of pressure and temperature on the individual processes (formation and decomposition). Studies of the second type look at the effect of pressure and/or temperature on the decomposition of tar compounds or model compounds that have already formed, so simultaneous formation is avoided.

Effect of pressure on tar formation

A number of studies have ascertained the effect of pressure on product distribution in hydropyrolysis. Rocha et al. [65] studied the product distribution of cellulose at 520°C using an FeS catalyst. This did not vary much as a function of pressure (5-100 bar); only the quantity of gas increased, from 1% to 5.5%, and the amount of oxygen in the tars decreased with increasing pressure (30% at 25 bar and 20% at 100 bar). Between 28% and 45% oil was obtained as a product [65].

A figure in Graboski [31] referring to studies by Punwani et al. and Weil et al. also shows that the amount of tar (here in the form of 'heavy hydrocarbons') decreased slightly as a function of pressure (0-20 bar), then remaining stable at higher pressures up to 70 bar at approximately 15% (of the feed on a carbon basis) heavy hydrocarbons. This was found at a higher temperature than in the study by Rocha et al., namely 760°C, with a residence time of 4-7 seconds and using peat as feed [31]. Pindoria et al. [58] found the same trend in the hydropyrolysis of sugar cane bagasse at 600°C, i.e. a slight decrease at 0-10 bar and a virtually constant amount of tar at higher pressures up to 70 bar; they also give a possible explanation for this observation, that at elevated pressures the primary tars are not released from the biomass until later and they thus subsequently react more to form gas and secondary char [58].

Pütün et al. [63] also found a fairly constant amount of oil (40-50%) as a function of pressure (50-150 bar) in the hydropyrolysis of pressed sunflower bagasse.

A study by Güell et al. [32] into the hydropyrolysis/gasification of pine wood at 400 and 700°C found that the amount of tar at low pressures of 1-10 bar went down from approximately 50% to 40%; at higher pressures up to 70 bar the amount of tar remained virtually constant, between 35% and 40%.

Effect of pressure on tar decomposition

Studies by Gräber, Hüttinger and Nelson [29][30][57] involving model tar compounds such as naphthalene at temperatures of 700-1000°C show that, at atmospheric pressure, hydrogasification produces higher yields (up to 70%+) of other tars [29][30]. In the hydrogasification of toluene, naphthalene, 1-methylnaphthalene, naphthol and quinoline at temperatures in the 700-1000°C range and residence times of 10-70s, with increasing pressure (5-20 atm.) a larger fraction of methane (0.05-0.8) is formed and a larger fraction of the carbon is converted into methane (0.02-0.7) [57].

Evidently, pressure does affect the decomposition of tar compounds (less tar at higher pressure) but not the formation of tars from biomass during hydropyrolysis.

Effect of temperature on tar formation

When studying the effect of temperature on product distribution in hydrogasification, two temperature regimes can be identified.

At relatively low temperatures the amount of tar or oil decreases as a function of temperature, as can be seen in Fig. 7 in Pütün et al. [63], Figs. 1-6 in Pütün et al.[62], Fig. 1 in Rocha et al. [65], and Fig. 2a in Güell et al. [32]. These results were obtained at maximum temperatures of up to 600°C (Pütün), 520°C (Rocha) and 700°C (Güell) and pressures of 150 bar (Pütün), 5 bar (Rocha) and 1.5 bar (Güell).

At higher temperatures the amount of tar decreases, as shown in two of the six figures in Pütün et al. [62], where measurements were also obtained at 700°C. A study into the hydrogasification of coal also indicates an increase in the amount of gas and a decrease in the amount of char and especially tar at increasing reaction temperatures above 600°C [22],

The rate of heating does not seem to have much of an effect on the product distribution in hydrogasification at a relatively low temperature (520°C) [66].

Effect of temperature on tar decomposition

At higher temperatures in particular tar compounds may be broken down. It follows from data in Gräber, Hüttinger and Nelson [29][57] that, once formed, stable tar compounds with naphthalene as a major component are broken down at high temperatures in the 850-1000°C range, pressures of 5-20 bar and residence times of tens of seconds; the decomposition is not complete, however.

Information on the behaviour of tars at high temperatures can also be obtained from studies into the hydrogasification of coal. We must assume here that the tars that are formed at high temperatures in biomass hydrogasification will be the same as the high-temperature coal tars: this is probably not a bad hypothesis, as in both cases the same AHs/PAHs are involved, the most common compounds being BTX, naphthalene, anthracene and phenanthrene. From Table 12.24 in Howard [38], which is part of a well thought-out overview, we may conclude that the tar concentrations continue to go down with increasing temperature, and that at high temperatures (950 and even 1200°C) tars are found in the product gases from hydrogasification.

Effect of residence time

The effect of residence time on the product distribution in hydrogasification is straightforward: the longer the residence time, the more methane and the less oil/tar and char are produced [57]. The composition of the tar may also change as a function of residence time, as Furfari and Cyprès show in a study into secondary reactions of the volatile components from coal hydropyrolysis [27]. At longer residence times the tar contains a larger fraction of tertiary tars.

Table 3: *Table 12.24 in Howard [38], entitled 'Rapid hydrogasification and hydropyrolysis product distributions*

			Yield (wt % of original coal, except as noted)						
Investigators and Residence Time Information	Temp (°C)	H_2 Pressure (atm)	CH_4	C_2H_6 + C_3H_8	CO	CO_2	H_2O	Oil + Tar	Char
Birch et al.[123] (includes slow gasification)	754	42	22.3	-	[15.7]		22.3	4.8	43.1
	850	42	45.0	-	[11.9]		29.3	0.9	29.8
	855	20	25.8	-	[18.6]		28.9	0.9	41.8
	951	42	61.1	-	[14.2]		28.4	0.4	16.4
Hiteshue et al.[94] (120 s)	800	35	8.2	1.8	-	-	-	10.0	59.6
	800	69	10.9	2.6	-	-	-	15.2	54.5
	1200	35	46.7	2.5	-	-	-	1.7	43.0
Moseley and Paterson[142] (several seconds)	900	106	35.7	-	6.8	-	-	-	50.0
Feldmann et al.[212] (several seconds)	850	69	14.5	0.9	1.5	1.0	4.1	3.0	64.6
	900	35	22.8	0.0	3.7	0.0	3.6	1.7	61.8
	900	76	27.2	0.3	3.5	0.4	3.2	0.5	66.3
Graff et al.[116,a]									
Vapor Solids									
0.6 s 30 s	817	100	27.7	7.3[b]	-	-	-	11.7	57
23 s 30 s	814	100	44.7	0.5[b]	-	-	-	2.3	55
Fallon and Steinberg[138] (12-20 s)[c]	700-800	103-137	12-32	6-15[b]	[7-16]		-	11-26	11-64
Suuberg[146] (10-20 s)[c]									
Lignite	850-1000	69	11.4	1.7[d]	8.5	10.2	11.0	9.6	46.3
Bituminous	870-930	69	26.6	2.6[d]	-	1.5	-	19.8	46.0

[a] Yields expressed as carbon in product, percentage of carbon in coal.

[b] Ethane only.

[c] Yields expressed as weight percent of maf coal.

[d] Ethane only. All other hydrocarbon gases, excluding methane, were 5.2% for the lignite and 3.6% for the bituminous coal.

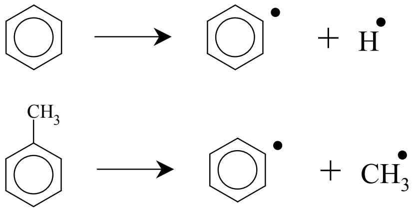
3. Mechanism of gas phase reactions of biomass tars

3.1 Thermal tar cracking

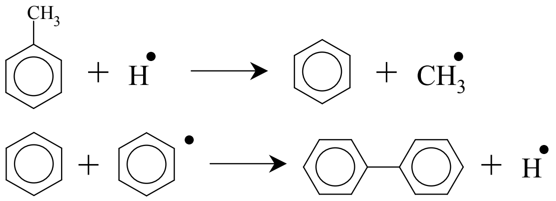
Many studies into the thermal cracking (or pyrolysis) of aromatic hydrocarbons have tried to unravel the mechanism of pyrolysis reactions in detail. These studies show that larger tar compounds – chrysene, benzopyrenes, etcetera – can be formed during the pyrolysis of smaller AHs/PAHs. Examples are studies into model compounds such as benzene and related monoaromatics [12], phenantrene [2], anthracene [3], and pyrene [53].
Overview articles contain more general discussions of the mechanism of the pyrolysis of hydrocarbons in general and monoaromatics and PAHs in particular. An overview of – somewhat outdated – literature can be found in Badger [4], and Poutsma [61] has a very detailed study into pyrolysis reactions of model compounds relevant to the processing of coal. The following mechanism for the thermal cracking of tars is collected from these two studies.

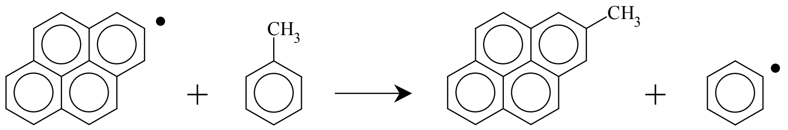
Radical reactions play a vital role in thermal cracking. The main reaction steps are: (1) radical-forming reactions caused by the breaking of chemical bonds, (2) propagation reactions through the formation of new chemical bonds, (3) hydrogen transfer, (4) isomerisation reactions, and (5) termination reactions in which two radicals react with each other (reference [61], pp. 10-15). Below we take as examples the cracking of benzene, toluene and pyrene, with biphenyl, methane and a series of bipyrenes [61][14][53] as possible products:

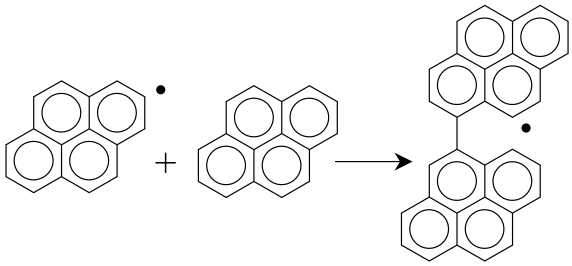
(1) The breaking of chemical bonds, or to be precise the breaking of a covalent bond generating two radicals, is referred to as 'homolysis'. This reaction is highly temperature-dependent, as the bond dissociation energy has to be overcome. Poutsma ([61], p.11) gives an estimate of the reaction temperature required depending on this dissociation energy at a given reaction time of 1 hour and a conversion rate of 50%.

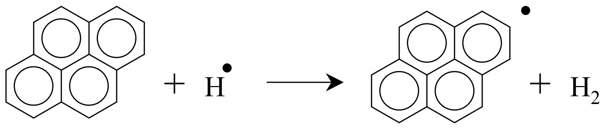


(2) The radicals generated can react with other tar compounds to form a new tar compound plus a radical, or a larger radical. The accretion of radicals of AHs/PAHs, via ring crosslinking reactions as shown at (4), results in the condensation of aromatics. This generally takes place at high temperatures and long residence times, generating two products: hydrogen (as in the last reaction shown below) and heavy tar fractions and ultimately soot or char [36].

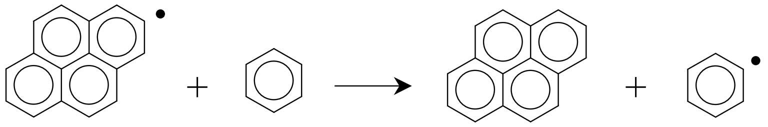




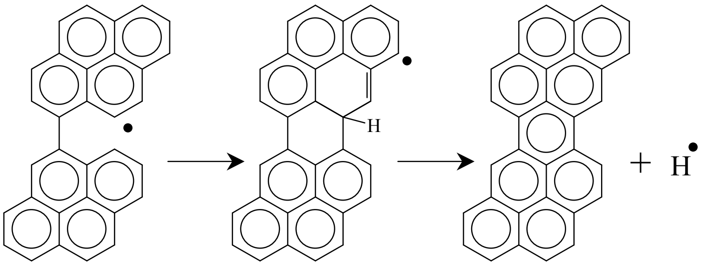




(3) Hydrogen transfer reactions, in which a hydrogen atom is transferred from one molecule to another with no hydrogen radical being released.

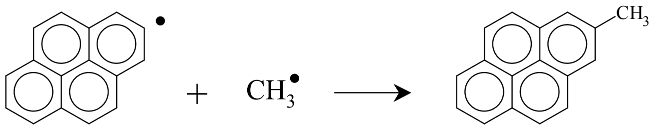


(4) Isomerisation reactions, in which new rings are formed or hydrogen atoms or $-CH_2-$ or $-CH_2-CH_2-$ groups in a compound are displaced, generating another radical.



(5) Termination reactions, in which two radicals react, thus eliminating them (two reactive unbonded electrons react to form a stable electron pair).

$CH_3^\bullet + H^\bullet \longrightarrow CH_4$



Many authors (e.g. [13] and [61]) claim that reaction (1) is the one that determines the reaction rate.

3.2 Gasification of tars in CO_2, H_2O or H_2

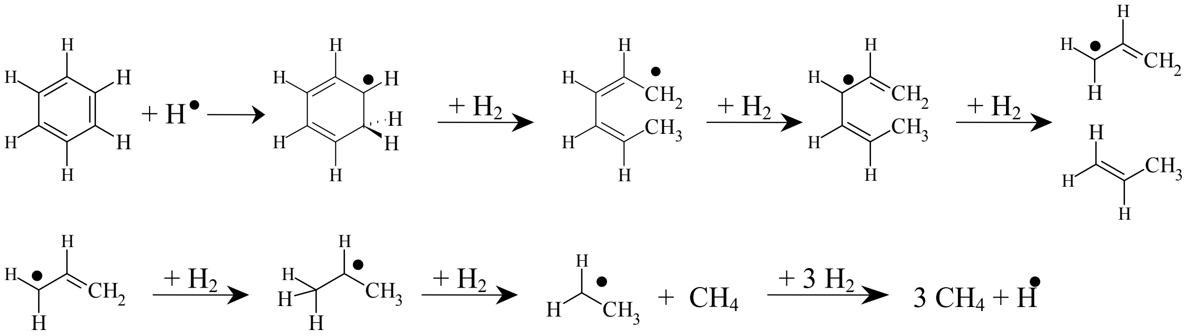
The mechanism of the steam gasification of naphthalene has been studied by Garcia and Hüttinger [28], who come to the following conclusions, based on comparing the pyrolysis rate and gasification rate in steam and steam/hydrogen:

1. The generation of radicals, in this case the formation of the naphthyl radical, is the step that determines the reaction rate in both pyrolysis and steam gasification.
2. Introducing hydrogen in the steam gasification of naphthalene reduces the gasification rate, as the steam does not react directly with the naphthalene but with naphthyl radicals, and hydrogen reacts more rapidly with these radicals than steam.
3. Under all conditions larger hydrocarbon compounds are also formed (tar and carbonaceous residue). The formation of these compounds is also explained by the radical formation: once a radical is generated it can react with other radicals to form larger compounds.

A mechanistic model is also proposed in the literature for the hydrogasification of tars. It comprises three steps: (1) destabilisation of the aromatic system; (2) fragmentation due to the breaking of C-C or C-H bonds; and (3) further reactions by the fragments (see Graber and Hüttinger [29]). As it is generally assumed that reaction step (1) determines the reaction rate and is not affected by hydrogen, the atmosphere (H_2 or inert) only influences the product distribution (e.g. the ratio between the methane and secondary carbon products), not the reaction rate.

A subsequent study by Nelson and Hüttinger [57] gives a general reaction model for the hydropyrolysis of aromatic compounds, which looks very similar to the mechanism described in 4.1 for thermal cracking. An important step that determines the reaction rate is destabilisation of the tar compound plus radical formation. As hydrogen plays no role in this step, it is unclear to what extent hydrogen affects the tar decomposition rate. No information on this has been found in the biomass literature, but studies into the hydropyrolysis/gasification of coal do provide information on the subject. When coal tars decompose and reactive volatiles (Howard) or radicals (Wanzl) are generated, H_2 can react with them, forming stable tar compounds that do not decompose any further [38][72]. This reaction with hydrogen prevents the reactive volatiles or radicals to react and to form carbon or high-molecular tar or pitch (see [38], pp. 763 and 772). Such subsequent reactions of radicals to form tar or pitch increasingly occur if the pressure is raised, taking place in the carbon particles, with the result that the volatile compounds (tars) can cannot escape [38]. Thus hydrogasification reactions result in a reduced char yield and an increased yield of methane and other gases, while the tar concentration remains about the same [38] or rises [72], compared with pyrolysis reactions under inert conditions. According to Wanzl [72], the BTX yield increases sharply at pressures above 50 bar.

The formation of methane cannot be described in terms of the reaction steps in 4.1, as there the aromatic rings are not broken. An additional reaction step (6), then, is the hydrogenation of a double bond, thus weakening the aromatic structure and enabling the C-C bond in the original aromatic ring to be finally broken. Here is the process for benzene:



The first reaction, in which an aromatic ring is broken, is one with a high activation energy, which only takes place at high temperatures or as a result of the bond being activated in some other way (radiation, plasma). The same is true of the hydrogenation of carbon (char or soot): this is a succession of reactions virtually identical to those described above.

The overall conclusion that the author of this report draws from all these data is that radical formation is the step that determines the reaction rate in both thermal cracking and tar gasification. The composition of the gas phase in the second reaction step then determines what the products are:

- In an inert environment (thermal cracking) the tar radicals may decompose, but they may also react with other tars to form larger tar molecules and ultimately soot. Thus radical formation does not directly result in tar decomposition but initially in even worse (larger) tar molecules.
- In H_2O or CO_2 there is a chance of the radical reacting with one of these two molecules, contributing to tar decomposition and increasing the rate at which it takes place.
- In H_2 the radical can react with H_2 fairly readily, causing a tar molecule to be reformed. In this way, then, H_2 depresses the tar decomposition rate.
- In an $H_2/H_2O/CO_2$ atmosphere the reaction rate of the tar radicals with H_2 is higher than the reaction rate with H_2O or CO_2. Tar decomposition as a result of the tar radicals reacting with H_2O and/or CO_2 is therefore suppressed by the presence of H_2.
- In hydrogasification, aromatic rings may be hydrogenated, causing higher concentrations of CH_4.

4. Conclusions

This study has collected information on the reactivity and decomposition mechanisms of biomass tars from the published literature.

As regards the rate at which biomass tars are thermally cracked, it can be concluded that it depends on temperature and residence time at high temperature. Another important parameter is the type of tar being cracked. The rate decreases in the following series:

biomass pyrolysis oils/tars (primary and secondary tar compounds)
>
phenolic (secondary) tar compounds (phenol, cresol, naphthol)
>
pyrolysis tars from coal (secondary and tertiary tar compounds)
>
tertiary tar compounds (anthracene, phenanthrene, naphthalene, benzene)

The specific conclusions on which this overall conclusion is based are:

- Much higher temperatures and/or longer residence times are required for the thermal cracking of tertiary tars than those required for the cracking of pyrolysis oils reported in a number of empirical biomass studies.
- Tars produced in the pyrolysis of biomass (straw and wood) and coal crack at lower temperatures than PAH model tar compounds (naphthalene, phenanthrene, etcetera)
- Pyrolysis tars from coal crack thermally less readily than pyrolysis tars from biomass. This can be explained by a difference in the composition of the tars: coal tar is more aromatic, with fewer compounds that react (with heteroatoms and/or pendant groups) than biomass tars.
- Oxygen-containing phenolic model compounds such as phenol, cresol and naphthols are converted in the 700-850°C temperature range. Non-oxygen-containing aromatic or polyaromatic model compounds only crack at higher temperatures, between 850 and 1200°C.

In the thermal cracking of tars, a large portion of the tars may be converted into carbon (= carbon-rich dust or soot).

The gas phase components H_2, H_2O and CO_2 play a role in cracking reactions in a biomass fuel gas (air, steam or oxygen gasification) or at elevated hydrogen pressures (hydrogasification). Based on the information found in the literature we can conclude that:

- The presence of H_2O and/or CO_2 increases the tar decomposition rate.
- The presence of H_2 (hydrogasification) depresses the tar decomposition rate. This is also true of an $H_2/H_2O/CO_2$ atmosphere, in which the reaction rate of tars with H_2O or CO_2 is depressed by the presence of H_2.
- In hydrogasification, aromatic rings may be hydrogenated, causing higher concentrations of CH_4.
- In high-temperature hydrogasification ($T > 800°C$), raising the temperature and/or pressure results in greater tar decomposition. In the hydrogasification of biomass and coal under mild conditions ($T < 800°C$ and residence times up to a few seconds), the amount of tars formed is virtually independent of pressure.

Carbon is an important product in the air, steam or oxygen gasification of biomass as well. This has two consequences for the use of thermal cracking to remove tar in a biomass gasification plant. The first is that, if the fuel gas is used in a gas engine or turbine, the carbon needs to be removed first by means of a (cloth) filter. The second is that, as a result, thermal cracking makes only part of the energy content of the tars available to the LHV of the fuel gas, as the carbon will not be used to generate energy.

There are indications that biomass hydrogasification produces the same tar compounds as those formed in the air, steam or oxygen gasification of biomass. Even under hydrogasification conditions, high temperatures are needed to break down these tars, and converting them into methane also requires high hydrogen pressures.

The mechanism of tar decomposition and methane production involves radical reactions, and radical formation is the step in the mechanism that determines the rate. The composition of the gas phase in the second reaction step then determines what the products are:

- During thermal cracking the tar radicals may decompose, but they may also react with other tars to form larger tar molecules and ultimately soot. Thus radical formation does not directly result in tar decomposition but initially in even worse (larger) tar compounds.
- During gasification (H_2O or CO_2) the tar decomposition rate is increased, probably as a result of the formation of smaller (gas phase) molecules.
- During hydrogasification H_2 depresses the tar decomposition rate, as it reacts with the radicals generated to form a stable tar molecule and a hydrogen radical, causing larger concentrations of small, stable AHs/PAHs such as naphthalene and benzene.

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APPENDIX A

Calculation of the tar conversion for one single residence time

The table below depicts the original conversions and residence times from the used studies. For more information the reader is referred to the original publication.

Authors	Reference	Temperature range (°C)	Residence time range (s)	Conversion range	Conversion range (recalculated, 2 s.)
Boroson et al.	[6]	600-800	1,0-1,2	0,31-0,88	0,46-0,99
Kaupp	[45]	580-920	0,17	0,14-0,84	0,84-1,00
Stiles and Kandiyoti	[70]	600-800	0,9-2,8	0,17-0,58	0,32-0,66
Brandt and Henriksen	[8]	811-1008	2,0	0,51-0,70	0,51-0,70
Wen and Cain	[74]	550-855	5,1	0,01-0,30	0,00-0,13
Hayashi et al.	[34]	590-850	3,5	0,08-0,41	0,05-0,26
Bredael et al.	[9]	720-900	0,5	0,00-0,77	0,00-1,00
Cypres and Bettens	[23]	850-900	2,0-2,5	0,14-0,43	0,12-0,43
Cypres and Bettens	[21]	665-865	2,5	0,02-0,72	0,02-0,63
Cypres and Bettens	[20]	600-860	10,0	0,00-1,00	0,00-0,67
Kabe et al.	[44]	800-950	50,0	0,16-0,55	0,01-0,03
Bruinsma et al.	[14]	700-1000	5,0	*	*
Jess	[42]	910-1400	0,39-0,61	0,00-1,00	0,00-1,00

*: converted into Arrhenius parameters, the measured values are not given in the article.

The conversions are recalculated to a residence time of 2 seconds according to the following procedure. A first order reaction is assumed (which means that the reaction rate r is proportional to the tar concentration to the power one). This results in the following reaction rate equation:

$$r = \frac{\partial C}{\partial t} = C \cdot k(T) \qquad (1)$$

in which r is de reaction rate (in mol/m_n^3 s), C the tar concentration (in mol/m_n^3), t the time and k(T) the temperature dependent rate constant (in s^{-1}), which can be written according to the Arrhenius equation as $k(T) = k_0 \exp(-E_a/RT)$ with k_0 the pre exponentional factor (s^{-1}), E_a the activation energy (J/mol), R the gas constant (J/mol K) and T the temperature (K). The term k(T) will be further used as k. After integration follows for the concentration C:

$$C = C_0 \,.\, e^{(-k\,t)} \qquad (2)$$

with C_0 the starting concentration at the beginning of the experiment.
The following equation follows for the conversion ξ:

$$\xi = \frac{C_0 - C}{C_0} = \frac{C_0 - C_0 \cdot e^{(-k\,t)}}{C_0} = 1 - e^{(-k\,t)} \qquad (3)$$

For the relation between the conversions ξ_1 and ξ_2, which are determined at the residence time $t_1$and t_2, it follows that:

$$\frac{\xi_2}{\xi_1} = \frac{1 - e^{(-k\,.\,t2)}}{1 - e^{(-k\,.\,t1)}} \qquad (4)$$

The conversion ξ_2 at t_2 can be calculated from the conversion ξ_1 at t_1 as follows:

$$\xi_2 = 1 - (1 - \xi_1) \wedge \left(\frac{t_2}{t_1}\right) \qquad (5)$$