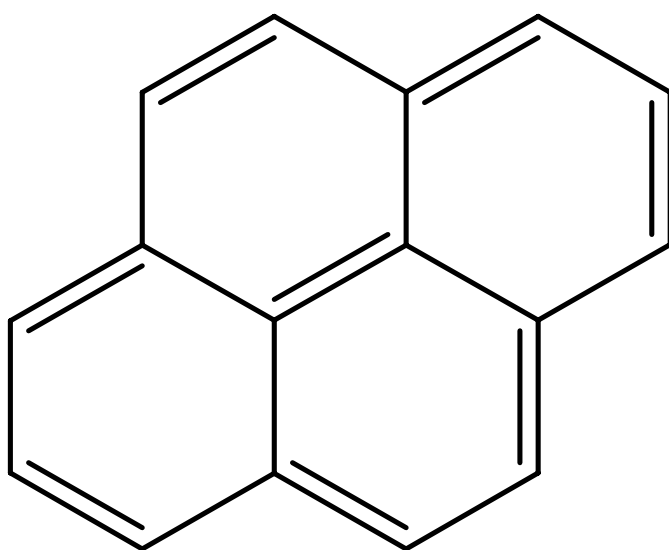


April 2005

# Formation, Decomposition and Cracking of Biomass Tars in Gasification



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## Introduction

In a biomass gasifier, the carbonaceous fuel is reacted with air/oxygen and/or steam resulting in a combustible gas. When a non-pyrolyzed fuel is used, hydrocarbons (tar) will be evolved which have a condensation temperature of 200-500°C when wood is gasified [Morris,2004]. This can lead to plugging or break down of the subsequent processes such as filters, engines, turbines or fuel cells. Therefore it can be necessary to remove or crack the tars. The allowable tar levels are about 50, 5 and 1 mg/Nm<sup>3</sup> for gas engines, gas turbines and fuel cells, respectively [Iversen,2004]. There is though a large uncertainty concerning these values.

In this report, the tar forming mechanism and reactions and biomass tars are described followed by a description of physical removal, thermal, partial oxidation, catalytic cracking and cracking using porous particles. The section with porous particles is divided into porous particles in fixed bed, fluid bed, activated carbon and char/activated carbon. At last the two-stage process, which uses partial oxidation and a char bed gasifier is described. The emphasis in this report is on the tar forming and cracking reactions taking place in a two-stage process. The section with physical removal of tar is an extract from the report by [Iversen,2004]. The mentioned tar components are listed in appendix with formula and structure.

## Tar formation—pyrolysis

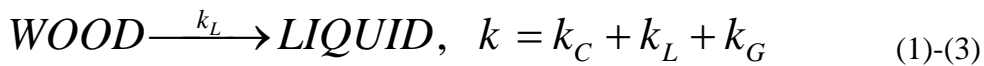
The biomass consists basically of three types of polymers: cellulose, hemicellulose and lignin. As a rule of thumb the biomass consist of 1/3 of each type, though wood have higher lignin content than straw [Pedersen,1999].

The first step in the gasification is a heating and drying of the biomass fuel. Subsequent heating results in a pyrolysis process which initiate at about 230°C, where the complex polymers in the biomass are broken down resulting in a gas consisting mainly of CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, CO, H<sub>2</sub>, tar and char. The tar consists of various heavy organics that can condense and break down subsequent processes [Milne,1998]. Various definitions of tar exist, according to the IEA Gasification Task meeting [Neeft,1999], it was stated, “all organics boiling at temperature above that of benzene should be considered as tar”.

[Di Blasi,2002] described the fast breakdown of wood particles using a mechanism with three parallel reactions for the formation of primary pyrolysis products, char, liquids and gas, as original proposed by [Shafizadeh and Chin,1977]:

### CHAR

↑  $k_C$



↓  $k_G$

$$k_j = A_j e^{-E_j/RT}$$

GAS

$$j = C, L, G$$

where  $k_G$ ,  $k_L$  and  $k_C$  are reaction rate constants for the formation of gas, liquids and char, respectively.  $k$  is the total reaction rate constant for the decomposition of wood.

The kinetic constants for wood is reported by [Di Blasi,2001]:

$E_G = 152.7 \text{ kJ/mol}$ ,  $A_G = 4.4 \times 10^9 \text{ s}^{-1}$ ,  $E_L = 148.0 \text{ kJ/mol}$ ,  $A_L = 1.1 \times 10^{10} \text{ s}^{-1}$ ,  
 $E_C = 111.7 \text{ kJ/mol}$  and  $A_C = 3.2 \times 10^9 \text{ s}^{-1}$ .

Reactions orders different from 1 are difficult to give a true physical meaning [Di Blasi,1998]. Therefore a first order reaction mechanism is used. The mechanism of three parallel reactions predict a continuous increase of both liquid and gas products at the expense of char as the reaction temperature is increased, which also is predicted by experiments [Di Blasi,2002]. [Branca,2003] has studied the liquids generated from low-temperature (600-900 K) pyrolysis of wood by feeding wood particles to a pre-heated reactor. The experiments were executed under conditions reproducing those of the pyrolysis section in counter current fixed-bed gasifiers. The tar liquid products were analyzed using GC/MS. The total amount of tar liquid varies from 40 to 55 % of the dry wood. The analysis shows that the thermal response of wood reflects the thermal response of cellulose, hemicellulose and lignin. As the temperature is increased, liquid and gases products is increased at the expense of char. Cellulose and hemicellulose are converted mainly into liquids while the other product classes, gases and char, are mainly due to lignin degradation [Branca,2003]. At low temperature there is a competition between liquid (cellulose and hemicellulose degradation) and char (lignin degradation) formation, with the former becoming successively more favored. At high temperature and heating rates, gas formation rates tend to increase due to the faster devolatilization rate of lignin.

[Ahrenfeldt, 2005] Has studied the “residual” tar content of char from slow pyrolysis of wood chips at heating rates of  $6^\circ\text{C}/\text{min}$ . Separate char samples were produced at identical heating rates for pyrolysis end-temperatures ranging from  $250\text{--}1000^\circ\text{C}$ . The residual tar content of the char was determined by analytical flash pyrolysis of the char combined with GC/MS analysis of the produced volatiles. The analyses showed that at a pyrolysis end-temperature of  $600^\circ\text{C}$  no residual volatile tar compounds were detectable. This implies that pyrolysis of wood char at temperatures above  $600^\circ\text{C}$  will not result in further release of tar compounds from the char.

### **Tars from biomass gasifiers**

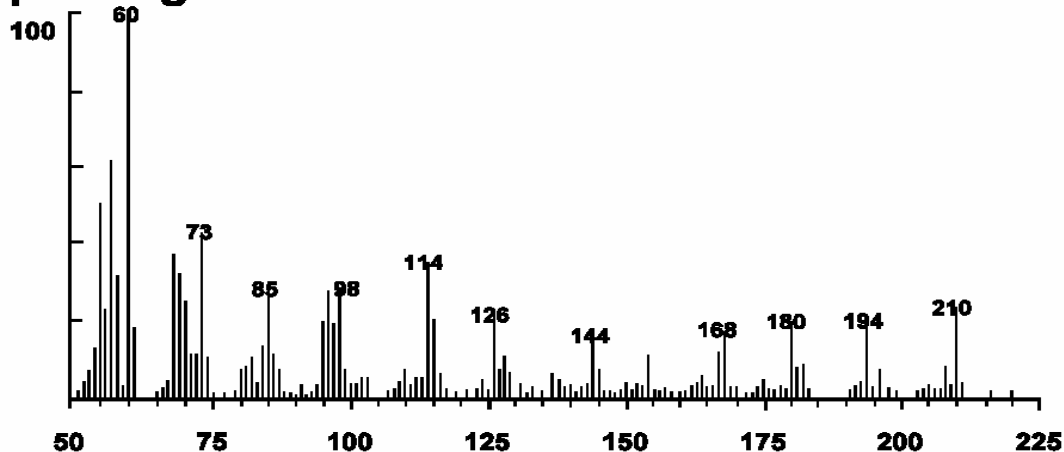
Biomass gasifiers are usually divided into updraft, downdraft and fluid bed gasifiers. There is general agreement that updraft gasifiers are the dirtiest, downdraft gasifiers the cleanest and fluid bed gasifiers intermediate. [Milne,1998] uses the crude generalization that places updraft at  $100 \text{ g/Nm}^3$ , fluid beds at  $10 \text{ g/Nm}^3$  and downdraft at  $1 \text{ g/Nm}^3$  in tar level. The two-stage downdraft gasifier is an especially clean gasifier, which will be mentioned later. Updraft gasifiers produces largely primary tar with oxygen content, with some degree of secondary character; downdraft gasifiers produces an almost tertiary tar and fluid beds produces a mixture of secondary and tertiary tar. The primary, secondary and tertiary tar will be defined in the section with thermal tar cracking.

A representative tar composition from an updraft and downdraft gasifier is shown in figure 1 [Milne,1998]. The numbers (m/z) indicate molecular weight of the sample and the peak height represents concentration. According to [Milne,1998] the updraft tars (m/z 168, 180, 194, 219) are primary products from lignin and some hydrocarbons (m/z 60, 73, 85, 98, 114, 126, 144). The downdraft gasifier nearly eliminates these compounds except for a trace of compound with m/z 60. The tertiary aromatics are now

predominant: benzene (78), naphthalene (128), phenanthrene (178) and pyrene (202). Tertiary alkyl aromatics are also present: toluene (92), indene (116); and further some phenol (94).

The fluid bed tars can be identified as follows (figure 2): cyclopentadiene (66), benzene (78), toluene (92), phenol (94), cresols (108), naphthalene (128), methyl naphthalene (142), acenaphthalene (152), phenanthrene (178), pyrene/fluorenthrene /benzacenaphthalene (202) and chrysene (228).

### Updraft gasifier



### Downdraft gasifier

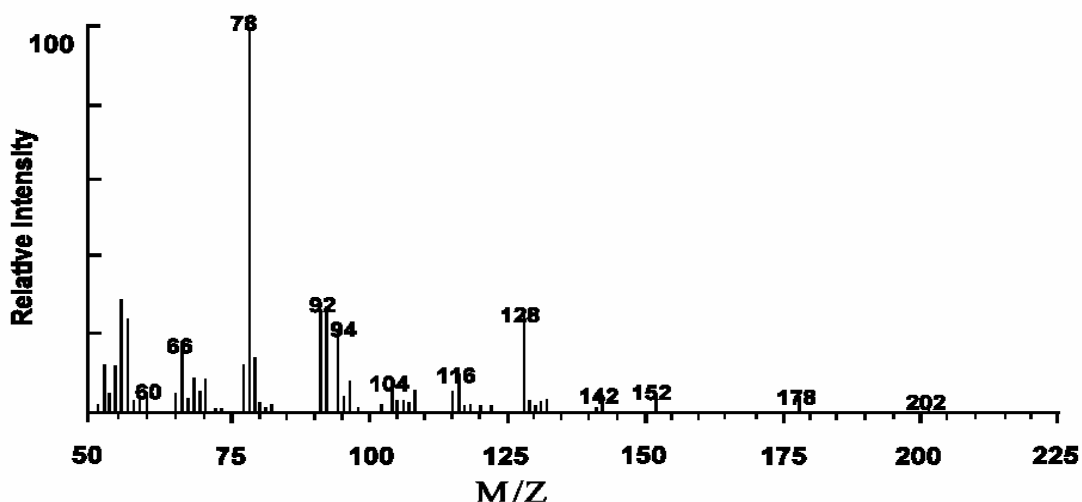


Figure 1. MBMS analysis of tars from updraft and downdraft gasifier [Milne,1998].

### Fluid Bed gasifier

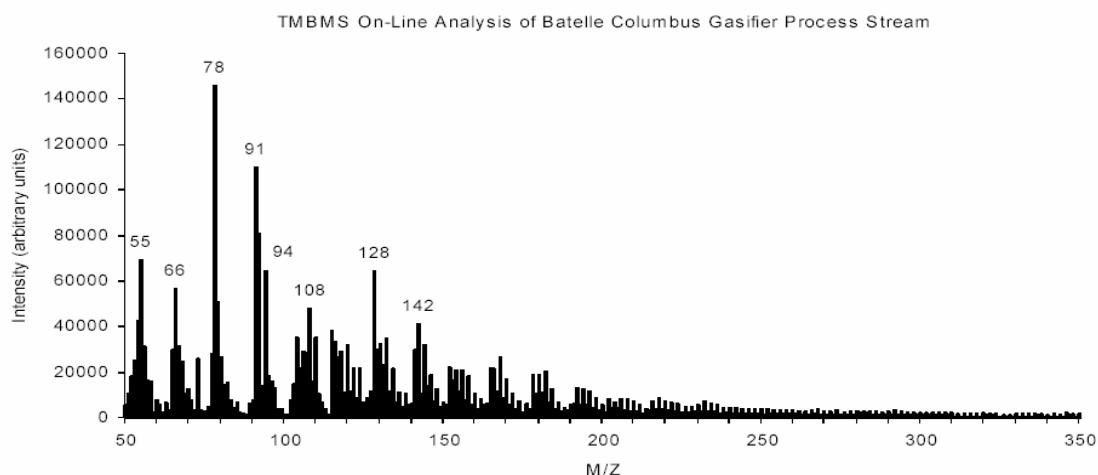


Figure 2. TMBMS on-line analysis of Batelle Columbus Fluid Bed atmospheric gasifier tar [Milne,1998].

The amount of tar and the composition of the tar from a given gasifier depends also on the temperature/time history of the particles and gas; the point of introduction of feed in fluid beds; the thoroughness of circulation in (fluid beds); the properties of bed materials (in fluid beds); the degree of channeling in fixed beds; the feed particle size distribution; the gaseous atmosphere ( $O_2$ , steam); the geometry of the bed; the tar analysis [Milne,1998]. One of the solutions to the tar problem is to use physical removal of the tars.

## PHYSICAL REMOVAL OF TARS

### Wet scrubbers

Using a wet scrubber to remove tar in the product gas requires a gas temperature of 35-60 °C if the scrubber liquid is water. Most biomass tars are hydrophobic such that only aerosols are removed. Using more organic liquids that also act as solvents such that gas phase tar is also removed can enhance separation. At the Güssing gasification plant in Austria, a wet scrubber is used with biooil (RME, Rape Methyl Ester) as scrubber liquid. Spent scrubber liquid saturated with tar and condensate is vaporized and recycled to the gasifier in the combustor. In addition, another scrubbing technology developed by ECN named OLGA will be described later. This technology also uses 'oil' as scrubber liquid. For more detail on wet scrubbers using water as scrubbing liquid see [Milne,1998] sections 3.3.3.1.

### Wet ESP's for tar removal

Wet Electro Static Precipitators (ESP) is also used for tar removal. It uses the same principle as for particle removal with ESP's. Using wet ESPs is a very efficient method to remove tars in the aerosol form with a removal efficiency of up to 99 % of materials under 0.1  $\mu m$  in diameter. This removal technology has successfully been applied at an updraft gasifier in Harboore, a downdraft gasifier at Wiener Neustadt and a circulating fluidised bed gasifier at ECN. For more information about wet ESP at ECN see [van Paasen,2004].

### Barrier filters for tar removal

Generally, barrier filters are not suitable for tar removal. The filter cake cannot easily be cleaned from the filter surfaces. In addition, there are problems with tar accumula-

tion on the filter surface that leads to eventual plugging. Despite this, a precoated fabric filter is used to remove particles and some tar at the Güssing Plant, Austria. The precoat is removed with the dust cake and then added to the system as make-up. This has been tested for more than 2500 h without any problems [Hofbauer,2002].

Packed bed filters have been used for tar removal in small-scale gasifiers where labour is inexpensive. For larger-scale commercial gasifiers, other methods are used.

### **Cyclones for tar removal**

Cyclones are generally not used for tar removal. This is due to the combination of the sticky tars and particles. Even if particles are removed after the cyclone, the tar removal efficiency is still low, because cyclones cannot remove particles of small diameter, including tar-droplets smaller than 1  $\mu\text{m}$  [Milne,1998].

Tar removal using a so-called RPS (rotating particle separator) has been tested at ECN. It was a wet RPS, using water and the results show that it was an unreliable process unit. The RPS simply clogged during the test [Boerrichter,2002].

### **Use and disposal of collected tars**

The most effective way to physically remove tars is to use wet scrubbers and electrostatic precipitators. But the waste usually consists of water mixed with tar components. Technologies are available to separate tars and water, but not complete as some organic components dissolve. The heavy tars can be burned to generate steam. The steam can be used as gasification agent. In a new process developed by Babcock & Wilcox Volund, the water mixed with tar is cleaned using a new-patented technology named TARWATC, used by the Haboore gasifier.

In two of the mentioned technologies in this update the tar is re-injected directly in the gasifier. This is done in the gasification plant at Güssing and in the OLGA technology.

At the gasification plant at Güssing, 'oil' is used as scrubber liquid. When saturated with tar and condensate it vaporizes and is led to the combustion zone of the gasifier.

The OLGA technology is mentioned later. This technology also uses 'oil' as scrubber liquid. In this case, the tar is released from the scrubber liquid and transferred to the air that is blown into the gasifier.

In addition, it should be taken into consideration that tars formed during the gasification process at temperatures less than 800°C can be handled using standard safety practices, while tars formed at temperatures above 800°C are much more hazardous to human health [Milne,1998].

OLGA – Advanced scrubbing technology. ECN has developed and patented the OLGA technology. OLGA is an advanced scrubbing technology where:

- The tar is removed prior to water condensation.
- Tar aerosols are removed
- The tars are recycled to the gasifier to be destroyed

The OLGA technology is a combination of the two basic approaches for tar removal, namely the physical removal and afterwards the destruction of the tars in the gasifier.

Figure 3 illustrates the OLGA technology. The removal of tar is done by contacting the tar-loaded product gas with a special developed scrubbing liquid ('oil') in an absorption column. All tar aerosols, heavy and light tars are removed from the product gas in the absorption column. The current design of the OLGA technology requires a dust free gas so a hot gas filter is used to ensure this.

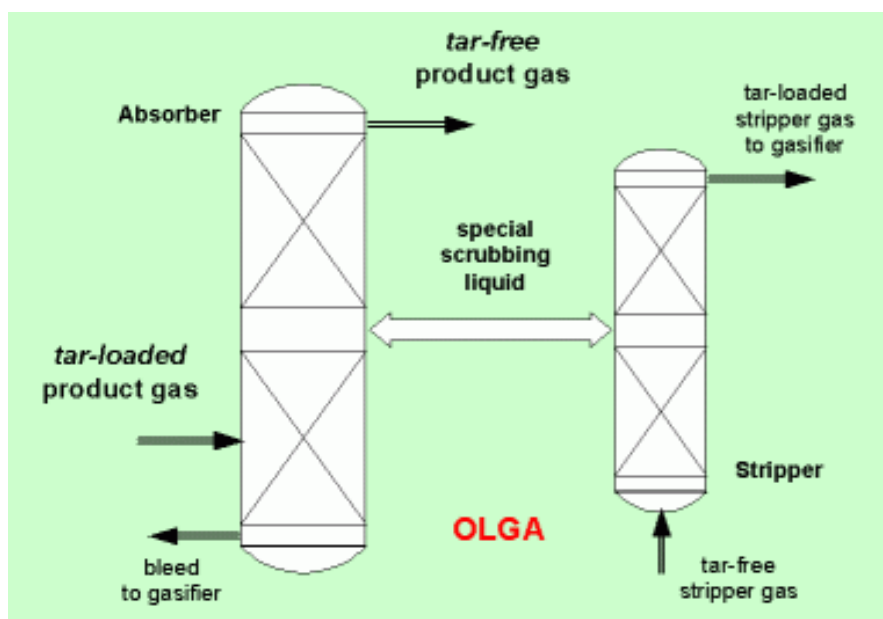


Figure 3. ECN's OLGA technology [ECN,2004]

The special scrubbing liquid, containing all the tars, is then drained to the so-called stripper column (fig.3). In the stripper column, the scrubbing liquid is regenerated by removing the tar. The tar is released to the stripper gas (air), which is then used as fluidisation gas in the gasifier where the recycled tars in the air are destroyed. The outlet temperature of the gas is kept above the water dew point at all times. This ensures that mixing of condensed water and scrubbing liquid is avoided.

According to ECN, the OLGA operated such that 99 % of phenol was removed. At those operating conditions essentially all heavy ( $\geq 4$  aromatic rings) and light tars (2-3 aromatic rings) are removed from the product gas. BTX (Benzene, Toluene and Xylenes) removal efficiencies range from ~50% for benzene to 90% for the xylenes. This has been tested in a small downstream bubbling fluidised bed gasifier called WOB (lab-scale). Figure 4 below shows removal efficiencies for different technologies including ECN's OLGA technology.

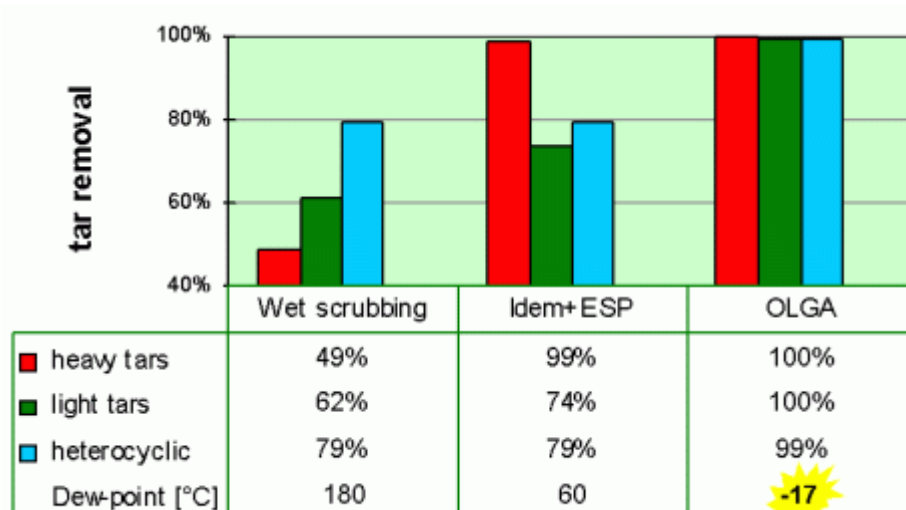


Figure 4: Removal efficiencies for different technologies. Heterocyclic components are components such as phenol, cresol, quinoline and pyridine [ECN,2004].

According to ECN, the OLGA technology has the following advantages:

- No condensation of tars: the tar dew point is well below -15°C.
- No pollution of the process water.
- No fouling of the system: increased reliability and availability.
- The clean gases are suitable for advanced applications like fuel cells and chemical synthesis (e.g. Fischer-Tropsch) [ECN,2004]

In September-October 2004, a 1000 hours test of the OLGA system was going to be carried out.

### Thermal tar cracking

In the thermal cracking, the raw gas (gasification) is heated and the tar molecules are cracked to lighter gases, refractory tars (condensable tar and char) and steam.

[Di Blasi,2002] proposed the following tar reactions:

*GAS*

$\uparrow k_{S1}$

*LIQUIDS*

(4–5)

$\downarrow k_{S2}$

*REFRACTORY–TARS + H<sub>2</sub>O*

$$k_S = k_{S1} + k_{S2}, k_j = A_j e^{-E_j/RT}, j = S1, S2$$

The model involves the gas-phase cracking of volatiles to gases (reaction rate  $k_{S1}$ ) and the gas-phase polymerization of volatiles to a refractory condensable (tar) and some water (reaction rate  $k_{S2}$ ). The reaction rate constants are described using an Arrhenius expression.

The reactions (4-5) are the sum of a sequence of tar reactions as a function of temperature from primary products to phenolic compounds to light and heavy aromatic hydrocarbons.

[Milne,1998] has classified the gasifier tar as a function of reactor temperature (500-1000°C). Small samples of biomass are injected in a preheated gas stream [Evans, 1987], the particles are then pyrolyzed in section 1 and the evolved gas then pass into reactor 2 where secondary gasphase reactions take place. The residual char does not enter reactor 2. The temperature in reactor 1 and 2 is the same. [Milne,1998] has studied gas phase reactions using the following four tar characterization classes.

Class 1 consists of cellulose-derived products such as levoglucosan, hydroxyacetaldehyde and furfurals; analogous hemicellulose's derived products and lignin-derived methoxyphenols. These class 1 components are the primary pyrolysis products at 500°C, they are reduced with temperature and they are virtually absent above 800°C. Secondary products are phenolics and olefins (components with double bounds), they are present in the temperature range 500-1000°C, with a maximum peak at 750°C. Alkyl tertiary products includes methyl derivatives of aromatics such as methyl acenaphthylene, methylnaphthalene, toluene and indene. The alkyl tertiary products are formed in the temperature range of 650°C to more than 1000°C with a maximum at about 900°C. The fourth class is the aromatics without substituents (tertiary-PNA) such as benzene, naphthalene, acenaphthylene, anthracene/phenanthrene and pyrene. This class is formed above 750°C. For processes above 1000°C usually naphthalene is the primary component.

The mentioned tar components are listed in appendix with formula and structure.

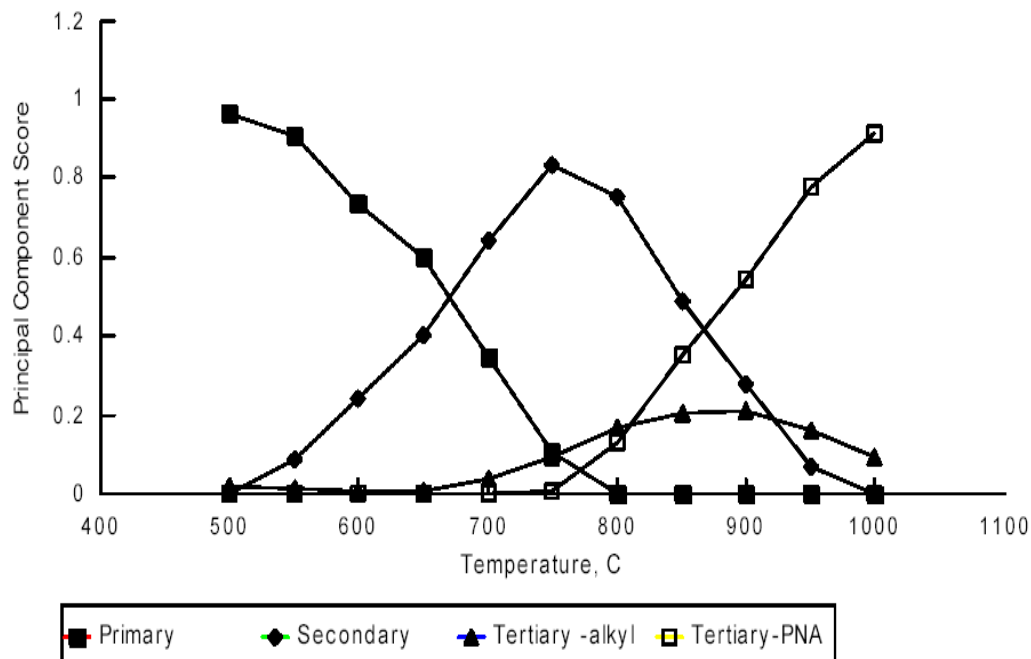


Figure 5. The relative distribution of the four tar component classes as a function of temperature (°C) at 300 ms (0.3 s) gas-phase residence time [Evans,1997].

It may be necessary to use high temperature to achieve a sufficiently high tar cracking. [Brandt,2000] reports that it is necessary to use a thermal cracking temperature of 1250°C to achieve a sufficiently high tar cracking of gas from an updraft gasifier using a residence time of 0.5 s. At 1290°C a tar content of 12 mg/Nm<sup>3</sup>, and 15 mg/Nm<sup>3</sup> including heavy tar, was obtained from a thermal tar cracking unit. However using such high temperature, the thermal tar cracking produced agglomerated soot particles with a size of 0.1 µm. The amount of soot was measured to 3.6 g/kg dry feedstock from the updraft gasifier.

The effect of thermal cracking can be increased using a longer residence time. [Houben,2004] performed thermal tar cracking experiment using temperatures of 900-1150°C and residence time between 1 and 12 s (fig.6). A small nitrogen flow is saturated with naphthalene in a saturator using a temperature of 200°C. The nitrogen-naphthalene gas stream is mixed with other gases in a saturator and led to the cracking chamber. The inlet concentration of naphthalene is about 8 g/Nm<sup>3</sup> to the cracker. The residence time is adjusted by changing the flow through the cracker. The naphthalene content is analysed using the Solid Phase Absorption (SPA) method [Houben,2004]. Figure 6 shows that increased residence time and temperature cracks the naphthalene. For a temperature of 1150°C a residence time of 4 s is necessary to diminish the Naphthalene concentration to 0.2 g/Nm<sup>3</sup>. This tar level may be too high for some engines.

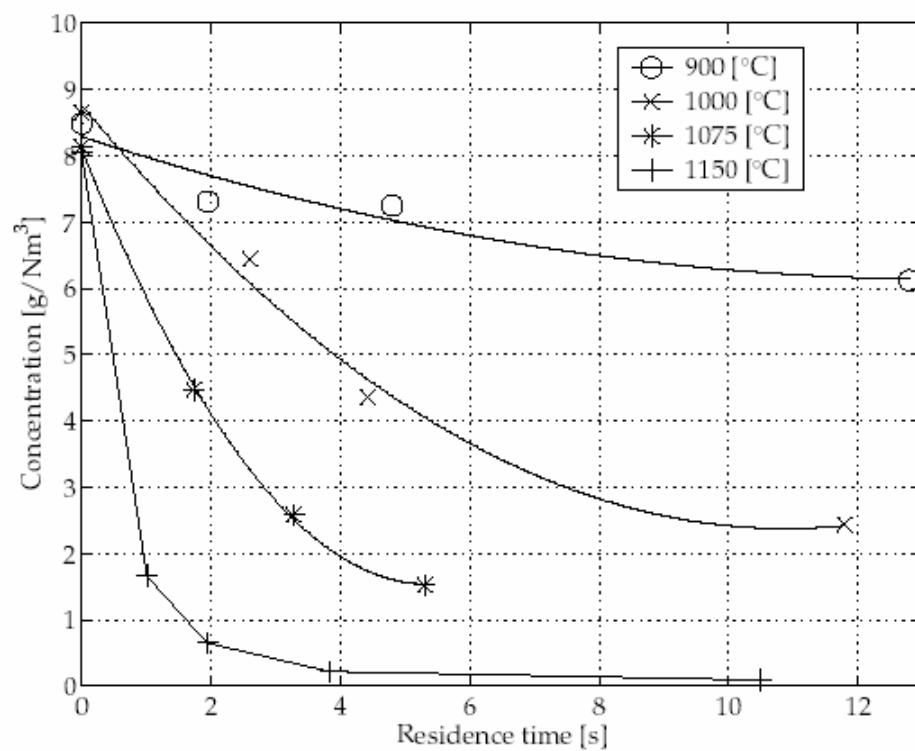


Figure 6. Naphthalene concentration as a function of residence time for temperatures 900, 1000, 1075 and 1150°C.

## Partial oxidation

Tar cracking using partial oxidation of pyrolysis gas has been performed by [Brandt,1998].

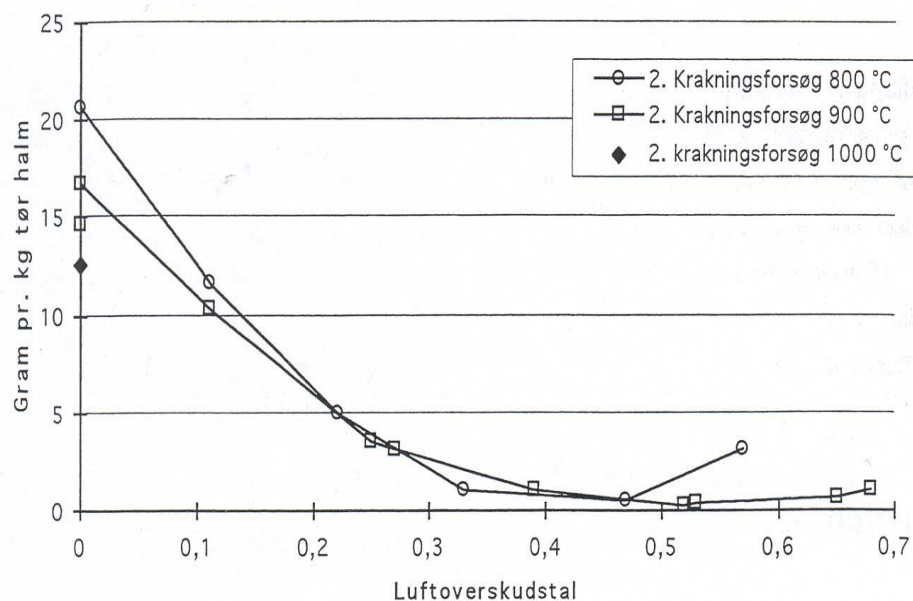


Figure 7. Partial oxidation experiments. Tar collected in condenser and aerosol filter in gram per kg dry straw as a function of excess air ratio, temperatures 800, 900 and 1000°C.

Cracking using air is performed by partially oxidization of pyrolysis gas; the air ( $O_2$ ) reacts with the tar molecules [Brandt,1998]. The minimum tar content measured was 0.5 g pr. kg dry straw giving a 98-99 % tar reduction at 900°C with an excess air ratio of 0.5. Figure 7 shows that when the air ratio is above 0.2 the results using 800 and 900°C are close to each other. The temperature has only a small influence in this interval. The partial oxidation has a certain selectivity on the tar components, which will be mentioned in next section.

### Selectivity in partial oxidation

Thermal cracking and partial oxidation of primary tars from pyrolysis of bituminous coal has been investigated by [Ledesma,2000] (figure 8). Pyrolysis was performed at 600°C in a fluidised-bed reactor in an Ar atmosphere, and the volatile products—including tar—were transferred into a tubular-flow reactor operating at 1000°C where the tar reacts either under pyrolytic or partial oxidizing conditions. In this way the partial oxidation in the tubular reactor can be studied in the absence of residual char. The residence time in the tubular-flow reactor was maintained at approximately 1 s.

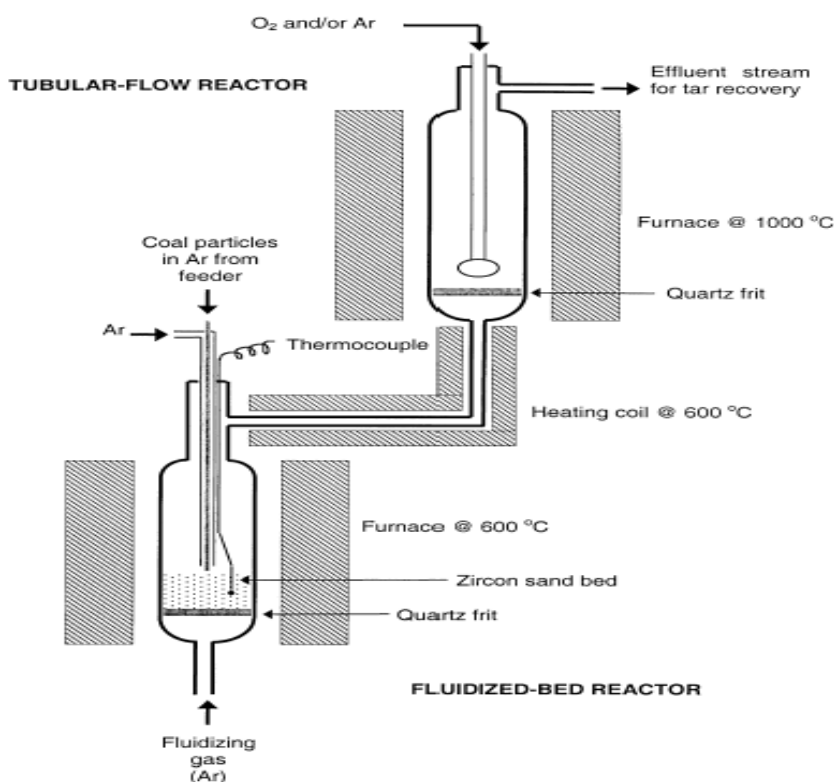


Figure 8. Tubular flow reactor used in partial oxidation

The primary tar compounds identified from the fluid-bed pyrolysis (600°C) was detected using GC/MS and FTIR. Phenols, alkyl substituted benzenes and naphthalene's were among the major compounds detected. The PAH's from the tubular-flow reactor (1000°C) after thermal cracking were detected by HPLC. 2 and 3 rings aromatic compounds dominate at thermal cracking conditions.

Addition of small amounts of oxygen  $\lambda < 0.3$  resulted in a significant reduction in the yield of naphthalene (fig. 9), the yield of phenanthrene and anthracene remained stable (fig.9). The yield of indene, fluorene and benzofluorene increased with  $\lambda$  until  $\lambda = 0.3$  (fig. 10), thereafter the yield decreased with  $\lambda$ . The yield of other PAH's increased, especially 9-fluorenone and cyclopentaphenanthrene. At  $0.3 < \lambda < 0.9$  the yield of all examined PAH's decreased significantly except for 9-fluorenone and cyclopentaphenanthrene which yields continued a significant increase until  $\lambda = 0.6$ . At  $\lambda > 0.6$  the yield of 9-fluorenone and cyclopentaphenanthrene started to decrease.

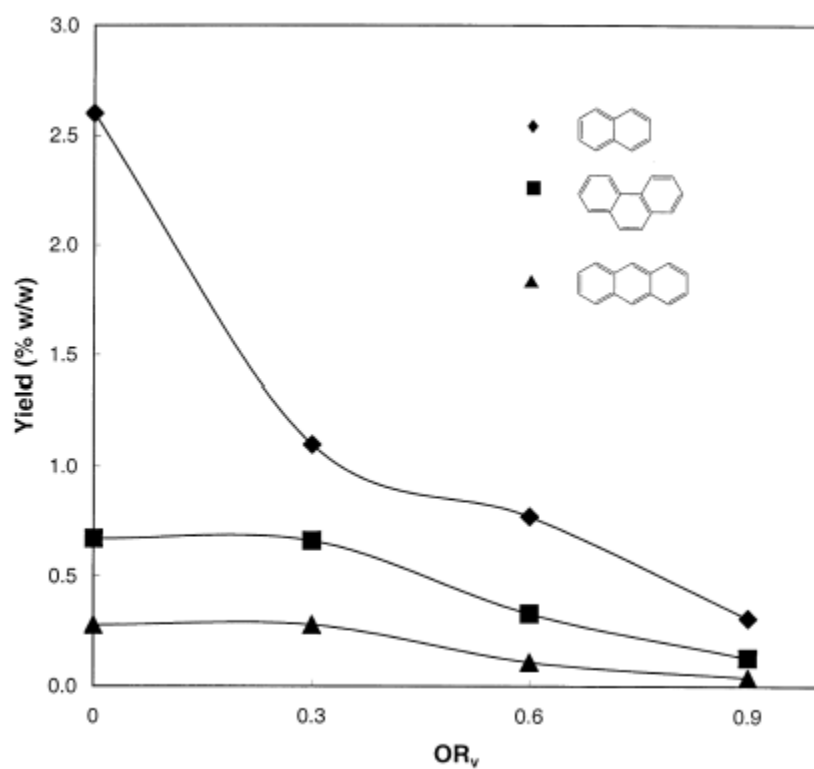


Figure 9. Yields of naphthalene, phenanthrene and anthracene as a function of lambda during the pyrolysis and partial oxidation of bituminous coal tar at 1000°C.

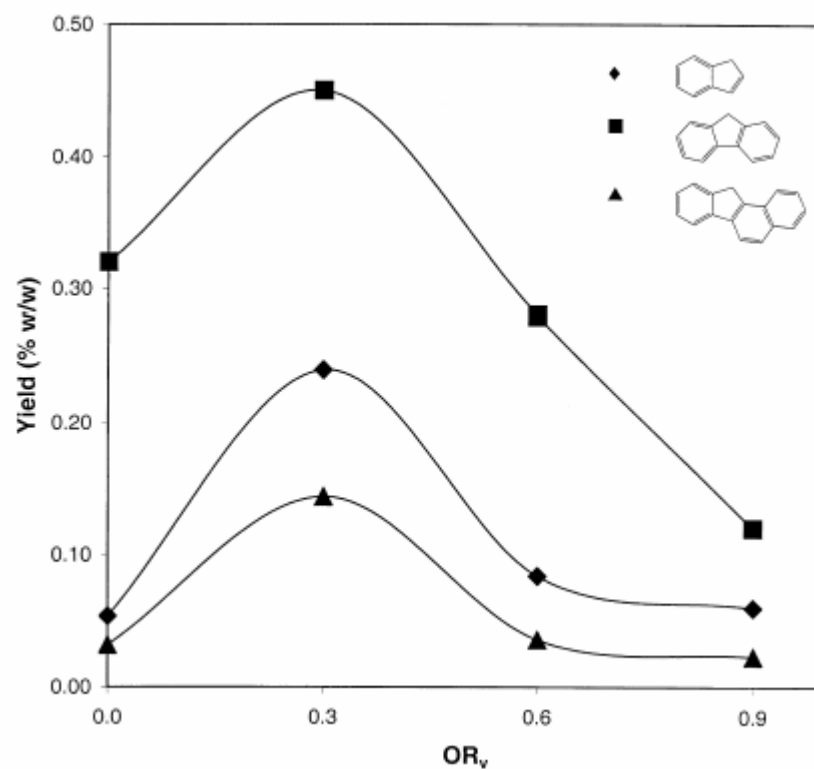


Figure 10. Yields of indene, fluorene and benzofluorene as a function of lambda during the pyrolysis and partial oxidation of bituminous coal tar at 1000°C.

## Effect of primary and secondary air on the tar cracking in biomass gasification

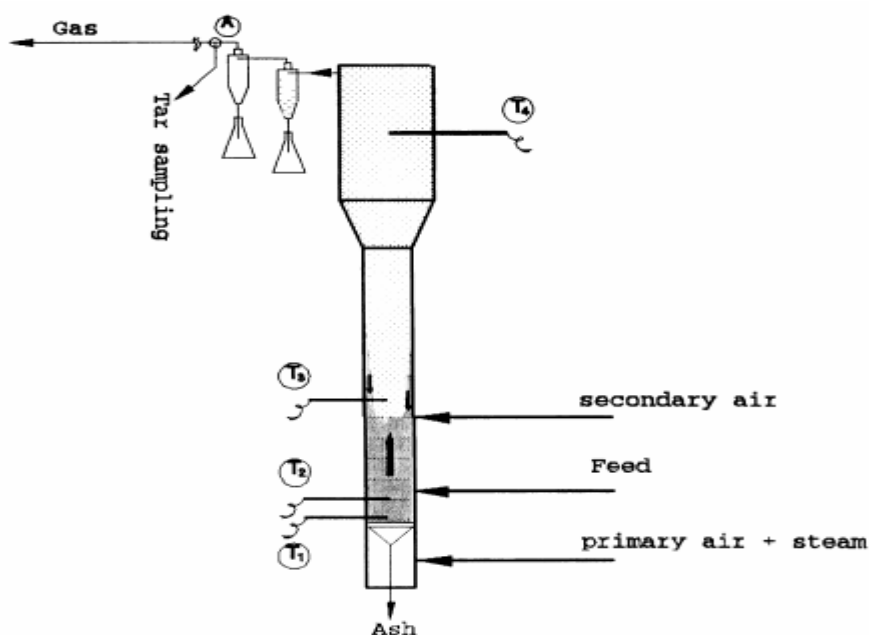


Figure 11. Fluidised bed gasification unit with secondary air feed.

[Pan,1999] tested the effect of secondary air injection in a laboratory scale fluidised bed gasifier using forest waste and lignite. The bubbling fluidised bed gasifier can be seen in figure 11. Before the secondary air is injected, it was necessary to wait until the gasification bed temperature reached 830-850°C. The secondary air is heated up to 180-230°C before injection. Tar content was obtained by the weighing method using the same collection condition for all runs. The product gas is first filtered and then sent to a series of four ice-cooled impinger trains, where tar is absorbed in dichloromethane. After the absorption, the solvent containing the absorbed tar was evaporated and the remaining tar was weighed. The study of secondary air injection was carried out in a range of up to 50 vol % of secondary air to primary air ratio. As can be seen in figure 12, using the two fuels forest waste and lignite, the tar content quickly decreases with the air ratio until a tar minimum is reached, the minimum is 0.42 g/Nm<sup>3</sup> for forest waste and 0.80 g/Nm<sup>3</sup> for lignite.

For the former, the corresponding optimum is about 20% (ratio of secondary to primary air) and the tar removal efficiency 88.7 wt.% for a gasification temperature of 840 to 880°C. For lignite the corresponding optimum is about 10% at 900-920°C and tar removal efficiency reaches 77.5 wt.%. Pan adds that it is senseless to use a ratio of more than 20 or 10 % for the two fuels, respectively, because the tar content increases and the gas quality decreases (figure 13). As can be seen the concentration of hydrogen and CO decreases with the ratio due to dilution of the product gas.

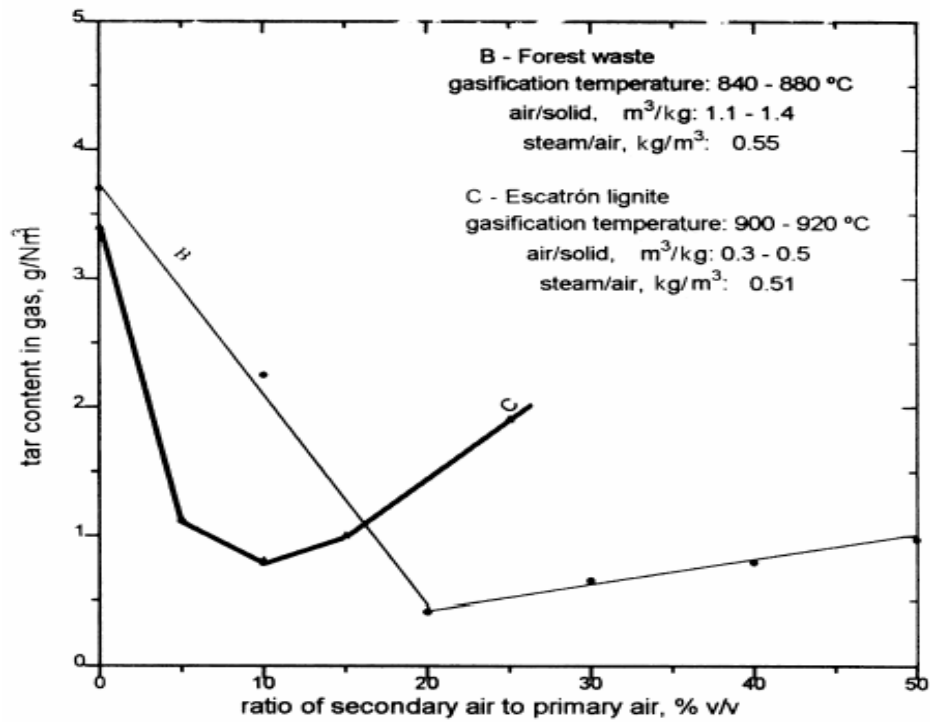


Figure 12. Effect of secondary air to primary air on the product gas tar content from the fluidised-bed gasification of forest waste and lignite.

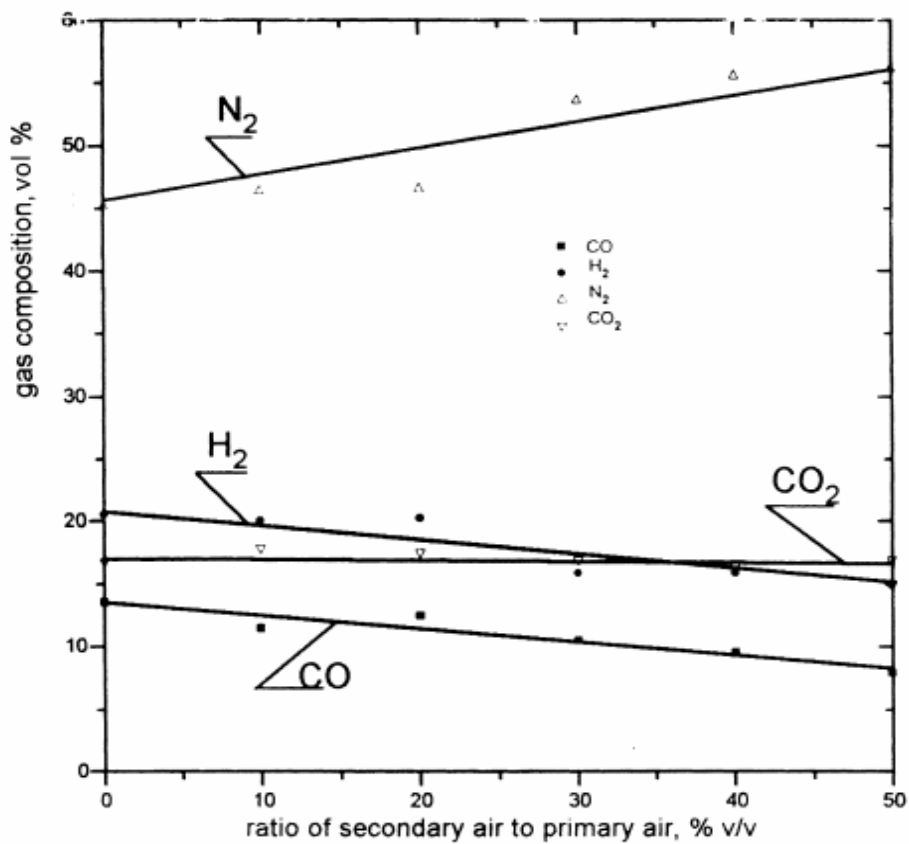


Figure 13. Effect of the ratio of secondary air to primary air on the gas composition for the fluidised-bed gasification of forest waste.

### Modelling the partial oxidation zone

[Houben,2004] describes partial oxidation of a gas saturated with naphthalene. It was possible to crack 95% of the naphthalene. [Hoeven,2004] describes that during partial oxidation the tar is cracked by free radicals formed during the oxidation of a part of the product gas. Hoeven performed simulations of the partial oxidation using the Perfectly Stirred Reactors code of the Chemkin 2.0 package together with the GRI 3.0 Reaction Mechanism. This code assumes a small thermally insulated chamber with a feed stream and a product stream. The code assumes that reactants are mixed instantaneously in the reaction chamber, and that there is a definite residence time  $\tau$ . The partial oxidation is modelled as a two-step process with two Perfectly Stirred Reactors (PSR's) (figure 14). In the first PSR's a fuel gas is added together with a stoichiometric amount of air. At a certain residence time the reactions in the first PSR are stopped, and the reaction products are mixed in the second PSR with some extra products gas. The second PSR represents the chemistry that happen when the reaction products from the product gas oxidation are mixed with the unreacted products gas. Hoeven assumes that the free radicals are the main causers of the tar cracking. The residence time of the first reactor is chosen such that at that residence time, the amount of radicals is highest (figure 15).

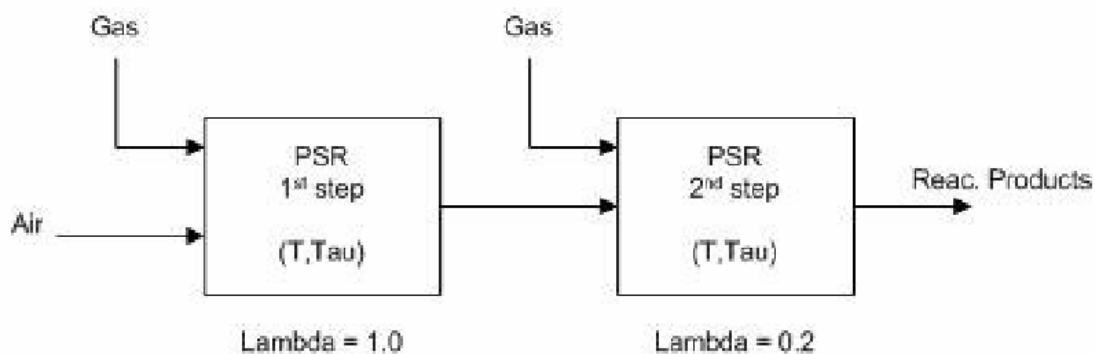


Figure 14. Model used for Chemkin chemical kinetics calculation of partial oxidation.

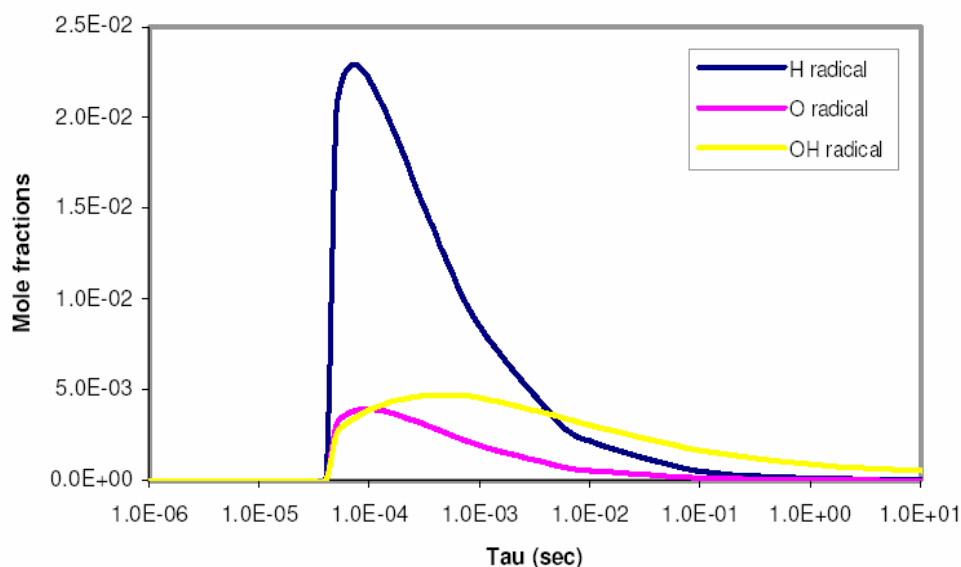


Figure 15. Mole fraction of the main radicals H, O and OH as a function of residence time ( $\tau$ ) for the first PSR.

Figure 15 shows that the maximum level of  $H\cdot$  is much higher than the maximum level of  $O\cdot$  and  $OH\cdot$ . Hoeven further adds that the  $H\cdot$  radicals have a high reactivity because they might be able to induce tar-cracking reactions, however a detailed tar reaction sequence is not described. The high level of  $H\cdot$  might be the reason why partial oxidation is able to crack the tar. The time scale of the chemical kinetics is about  $10^{-3}$ s compared to the gas residence time in the partial oxidation reactor, which is estimated to be  $10^{-2}$ s. [Hoeven,2004] concludes, that this means that the chemistry and the mixing process influence each other, and that there exist a complex path of free radical production inside the partial oxidation reactor. Equilibrium is reached after about 1s [Hoeven, 2004], this means that equilibrium is not reached during the estimated residence time of  $10^{-2}$ s and the partial oxidation can thus not be calculated using equilibrium models

## Catalytic tar cracking

### Catalytic materials

In catalytic tar cracking, the raw gas is passed over a catalyst and the tar molecules are broken down to lighter gases and soot. One advantage of catalytic cracking is that it does not reduce the heating value of the gas, as would be the case if the tars were thermally cracked at a high temperature [Morris,2004]. In catalytic cracking, the catalyst may be used either insitu in the gasification reactor or in a separate reactor downstream of the gasifier. Various catalyst have been used, among them limestone, dolomite ( $\text{CaCO}_3\cdot\text{MgCO}_3$ ), olivine, alumina ( $\text{Al}_2\text{O}_3$ ), alumina silicates and zeolite ( $\text{Al}_x\text{Si}_y\text{O}_z$ ), magnesites ( $\text{MgCO}_3$ ), Ni, Mo, Pt,  $\text{K}_2\text{CO}_3$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and char [Milne,1998].

One of the most popular and studied tar catalysts is dolomite, which is an effective catalyst when calcined ( $\text{CaO}\cdot\text{MgO}$ ) [Simell,1995]. Dolomite is not sensitive to deactivation by carbon. However calcined dolomite is quite soft and it might erode if it is used insitu in a fluid bed gasifier. This can result in a large production of fines [Devi, 2003]. To avoid this erosion, the dolomite can be placed in a separate fixed bed reactor downstream of the gasifier [Milne,1998]. Dolomite can also be used as a guard bed prior to a Ni catalyst bed, which has a high catalytic activity but is not very robust. The guard bed will lower the tar and dust concentration to a level acceptable for the Ni catalyst.

[Henriksen,1992] measured the tar concentration from a fixed bed calcined dolomite cracking of gases from a pyrolysis reactor pyrolyzing barley straw. The temperature in the pyrolysis reactor was increased up to  $800^\circ\text{C}$  and the temperature in the tar-cracking reactor was  $900^\circ\text{C}$ . The tar amount was reduced from 12 wt % of the fuel to about 0 % after the tar cracker.

The use of dolomite catalyst is less effective in high-pressure systems, because the dolomite may become decalcined at high pressure unless the temperature is high. At 25 bar the corresponding temperature for decalcination is in the range of  $950\text{--}1000^\circ\text{C}$  [Morris,2004].

An alternative to dolomite is olivine, which are a naturally occurring mineral containing magnesium, iron oxide and silica. Olivine is used in the Güssing gasification plant. Olivine has a favourable attrition resistance compared to dolomite [Devi,2003].

[Rapagna,2000] measured the catalytic activity of olivine and found that it has an activity comparable to dolomite. They reported more than 90 % reduction in average tar content from a fluidised bed gasifier. [Ptasinski,2004] reported that pre-treatment of olivine improves the catalytic activity. Pre-treatment is done using air at  $900^\circ\text{C}$  for several hours. It is also possible to pretreat the olivine with Ni, this will improve the catalytic activity of olivine.

[Hayashi,2002] and [Sathe,2003] reported that the inherent content of Na, Ca, Mg, and Fe in the char from brown coal and lignite, respectively, catalyses the tar cracking reactions.

## **Ni catalyst**

Ni-based steam reforming catalysts are commercially available because of their use in the petrochemical industry for reforming of naphtha and methane reforming to make syngas [Dayton,2002].

[Garcia,2000] described the catalytic tar reforming using Ni catalyst as follows. First the tars are dissociatively adsorbed on the ceramic support where Ni-catalysed dehydrogenation occurs. Water is also adsorbed onto the ceramic support where it hydroxylate at the surface. At a certain temperature the OH radicals migrates to the metal sites which leads to oxidation of intermediate hydrocarbon fragments and surface carbon to  $\text{CO} + \text{H}_2$ . In some of the studies using Ni catalyst, a dolomite guard bed was used to reduce the initial tar level from the gasifier. The Ni catalyst was operating at 750-850°C and tar conversion was greater than 99%. A first order rate expression was used to describe the kinetics [Dayton,2002].

The Ni catalyst can be poisoned by sulphur, chlorine and alkali metals from the product gas. Coke from the tar cracking can also poison the catalyst, especially when the tar level is high [Dayton,2002]. The coke can be removed by regenerating the catalyst using combustion, however repeated high temperature processing of Ni catalyst can lead to sintering, phase transformation and volatilisation of the Ni [Dayton,2002]. According to Dayton, the use of Ni catalyst in fluid bed gasifiers has not been successful. Coke formation and catalyst attrition led to rapid loss of tar catalyst activity. Instead the Ni catalysts are used in secondary fixed bed reactors.

In the following sections, newly developed external Ni-monolith tar reformers will be described in more detail.

## **Commercial Ni tar-catalyst**

### **Monolith tar reformer developed at Fraunhofer UMSICHT**

Fraunhofer UMSICHT, Germany has developed a CFB gasifier with a fixed bed monolith tar reformer [Ising]. The pilot-plant of 0.5 MW input is located at Oberhausen, Germany. It has been running successfully with non-contaminated wood chips. A downstream Ni monolith catalytic tar converter (figure 16) is used and subsequently a fabric filter to remove particles. This results in a high quality-fuel gas that can be burnt in an IC-engine.

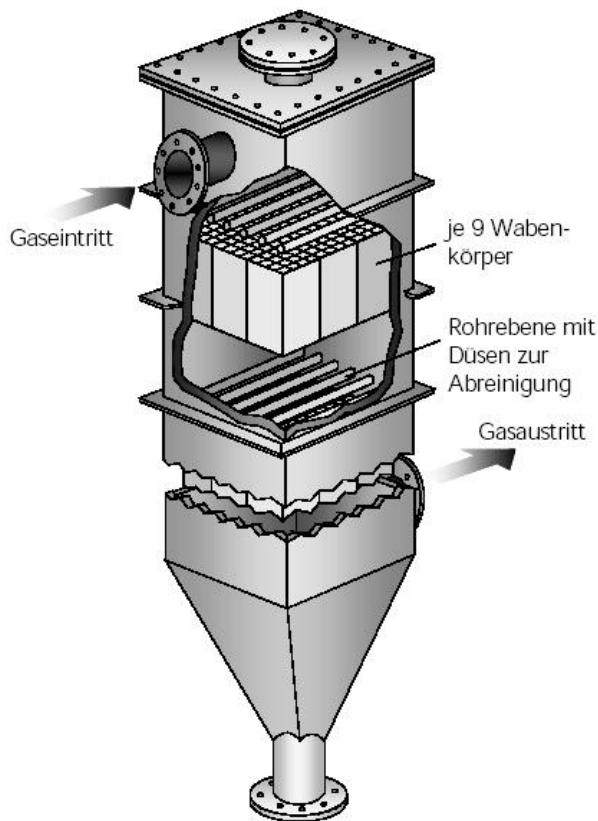


Figure 16. The catalytic tar converter developed by Fraunhofer UMSICHT (Ising).

The monolith Ni catalyst developed is a suitable method for tar reforming in combination with a CFB-gasifier because placing it in a high dust environment directly downstream from the CFB-gasifier is acceptable. But it requires several technical devices though to keep the activity (tar reforming) at a constant level. These are:

- A cleaning device e.g. a jet pulse for dedusting the monolith tar reformer
- A temperature control device to keep the temperature of the raw product gas at a constant level. This is done by controlled air injection for partial combustion.
- Well-distributed and controlled injection of regeneration gas for regenerating the catalytic surface.

Process development at the pilot scale plant has finished. [Ising] concludes that the developed monolithic catalyst is a suitable option for tar removal but the complexity of the system limits the practical application of this technology, especially regarding biomass feedstock. In addition, he concludes that further R&D is needed to develop the technology for a concrete application. For more info see [Ising et al.].

### **Monolith tar reformer developed by VTT and Condens Oy, Finland**

At Skive Fjernvarme, Denmark a new CHP plant is planned to be in operation before the end of 2005 (5.5 MW electricity and 11.5 MW district heat). A developed tar reformer by VTT and Condens Oy, Finland is going to be a part of the gas-cleaning system together with a filter and a wet scrubber using water as scrubber liquid. The catalytic tar reformer is based on nickel monolith catalysts. Details about the technology of the tar reformer have not been published yet but the basic technology of the nickel monolith catalysts are described in [Simell,1997]. A long-term test on the catalyst has

been made and also a lot of process development since the paper was published in 1996 (see figure 17)

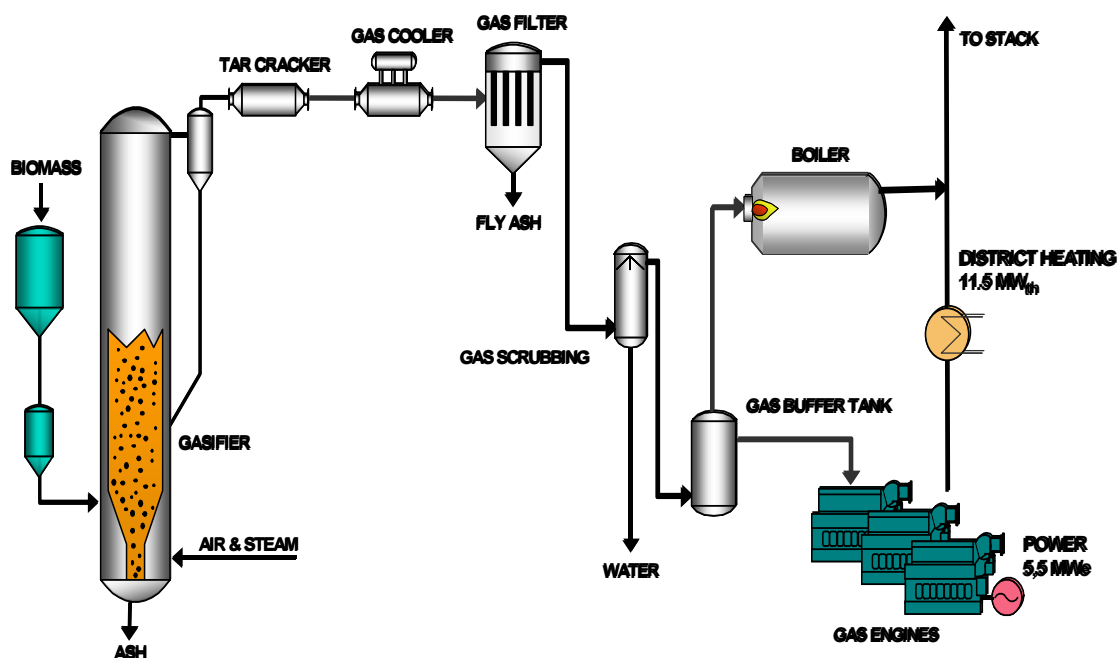


Figure 17. The process flow sheet of the Skive BGGE-Plant

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## Reverse Flow Tar Converter (RFTC) developed by BTG, the Netherlands

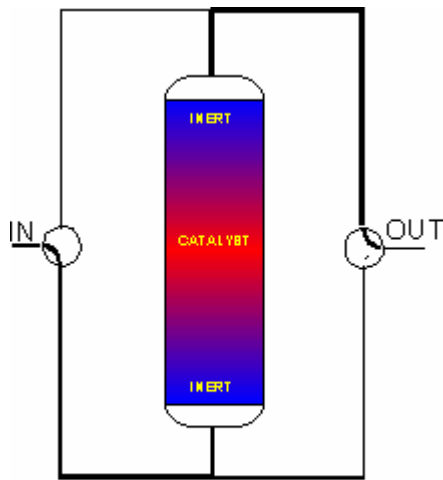


Figure 18. Reverse Flow Tar Converter.

Component	Conversion (%)
Benzene	82
Naphthalene	99
Phenol	96
Total aromatic	94
Total phenol	98
Total tar	96
Total ammonia	99

Table 1. Tar conversion from the RFTC reactor.

The Reverse-Flow, Catalytic Tar Converter (RFTC) has been developed by BTG to remove tars from gasifiers in an energy efficient way using a Ni-catalyst (figure 18). Raw producer gas from a biomass gasifier is fed to the RFTC at a temperature between 350 and 650°C. In the entrance section of the RFTC the producer gas is heated up to the desired reaction temperature of 900 - 950°C. Steam reforming takes place in the central section where also the Ni-catalyst is placed. This results in the conversion of tar components and light hydrocarbons including methane into CO and H<sub>2</sub> (table 1). In addition, almost all of the ammonia in the product gas is converted into N<sub>2</sub> and H<sub>2</sub>. Additionally, nearly all NH<sub>3</sub> is removed (forming N<sub>2</sub> and H<sub>2</sub>, reverse ammonia synthesis). To counterbalance these endothermic reactions a small amount of air is added to the reactor (about 5 % of the producer gas flow). Effectively, the heating value of the gas is reduced slightly, but fully compensated by the increased amount of gas. Experimental test have been performed with the catalytic reactor, but the reactor principle can also be applied to thermal tar cracking. The stability of the catalyst is an important aspect in these systems. The RFTC has been tested for over 6000 h showing no detectable change in catalyst activity.



**Reverse-flow system**

Figure 19. Reverse flow operation mode of RFTC reactor [www.btgworld.com]

The reverse flow operation is characterized by the periodic reversal of the feed flow direction. Operating a packed bed reactor under such transient is beneficial because

- A high degree of heat integration is realized, as the chemical reactor and heat exchanger are both included in a single apparatus, resulting in high energy efficiencies
- The construction is simple compared to conventional reactor/heat exchanger systems, which results in reduced investment costs.

For more information about the catalytic, reverse-flow tar converter see <http://www.btgworld.com/technologies/tar-removal.html#process>

The RFTC has been integrated in the DUIS demonstration plant. That unit will treat about 200 Nm<sup>3</sup>/hr producer gas.

## Tar cracking using porous particles

### Tar cracking using porous particles in a fixed bed

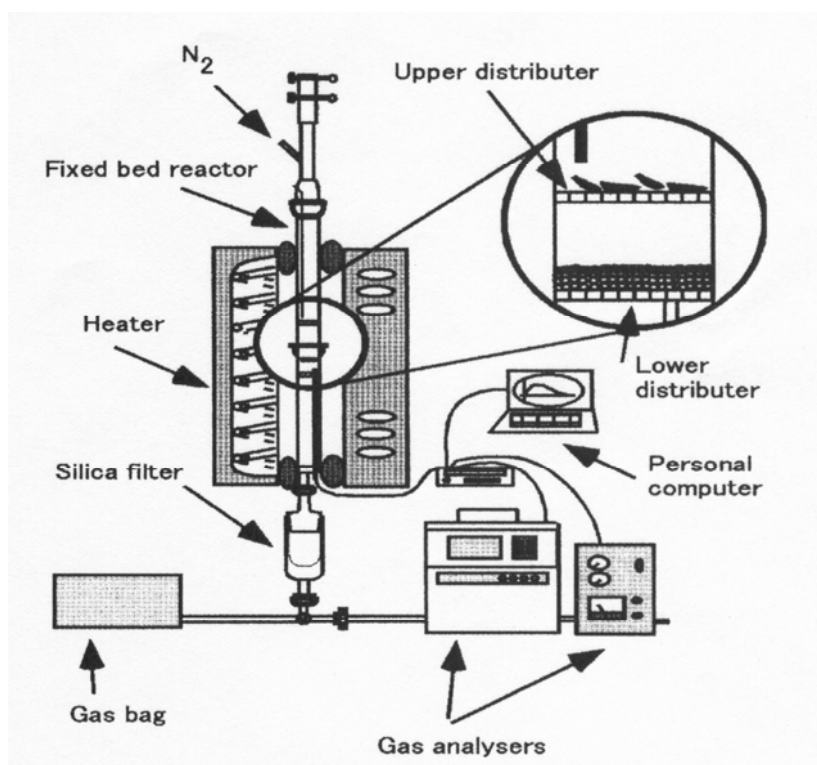


Figure 20. Two stage gasifier used by Namioka

[Namioka,2003] has studied tar reduction when gasifying sawdust in a co current fixed bed reactor, see figure 20. The reactor is divided into two parts, the upper part contains the char fixed bed and lower part contains a bed with porous particles. There is a quartz filter between the upper and lower part of the reactor, which keeps the char in the upper part. However the gasification gas passes from the upper part to the lower part, which is filled with bed materials (table 2). In this way the tar cracking in the lower part can be separated from the effect of the char. A silica filter is connected to the outlet of the reactor in order to capture tar that was not held by bed materials. As can be seen from table 2 the porous materials have a high surface area.

Table 2. Properties of the bed materials in the lower reactor

	Physical characteristics			Chemical composition		
	BET surface area [m <sup>2</sup> /g]	Pore volume [cm <sup>3</sup> /g]	Size [mesh]	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O
Activated alumina	299	0.39	14-28	99.64	0.02	0.31
Zeolite	351	0.47	14-28	24.3	60.7	15
Silica sand	----	----	14-28	---	99	---

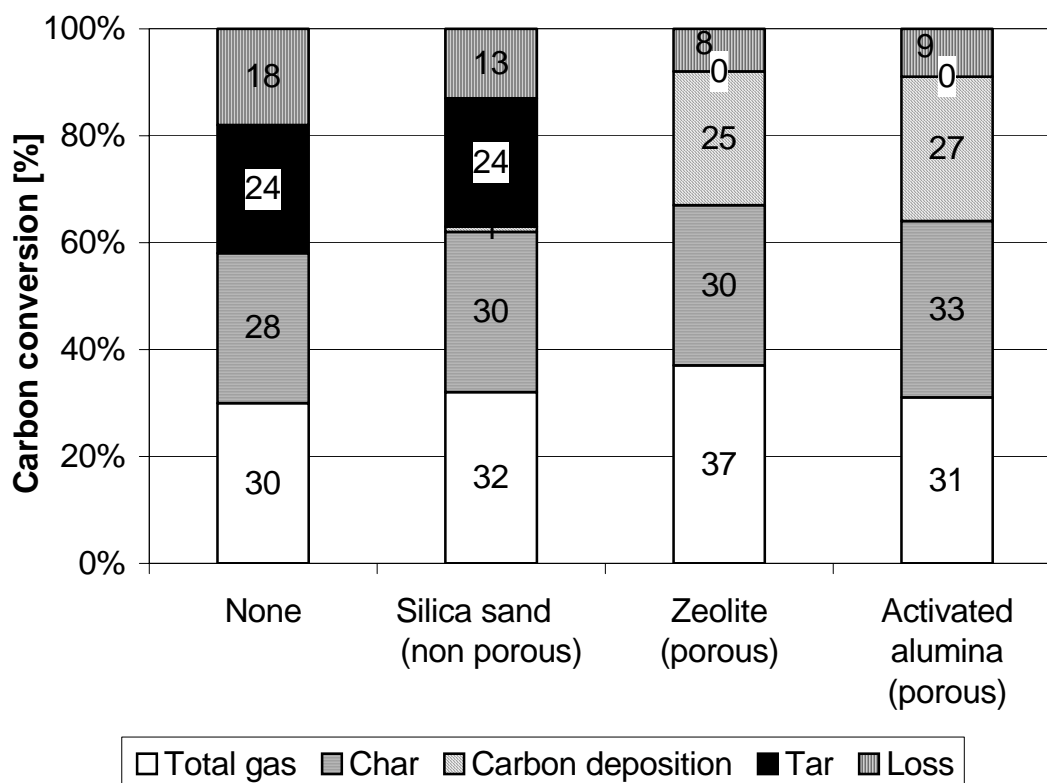


Figure 21. Carbon mass balance at 873 K (600°C) using four different bed materials.

Figure 21 shows the carbon distribution of the experiments for four cases; case 1 where no particles were employed, case 2 where quartz sand was employed as non porous particles, the case with zeolite (porous) and activated alumina (porous). Figure 21 shows that the porous particles can reduce the tar yield from 24 to 0 % (carbon basis) and the tar yield obtained without porous particles is nearly equal to the yield of carbon deposited on the porous particles at 600°C. This means that tar produced from pyrolysis is instantaneously absorbed on the surface of porous particles, and the residence time of tar in a gasification furnace is then prolonged. The tar is then pyrolyzed, carbonised and fixed on porous particles, so high tar reduction is achieved. [Namioka, 2003] added that the porous particles used may have a catalytic effect.

The use of porous particles had little effect on the total gas yield but an effect on carbon distribution; the use of porous particles decreased the amount of gaseous hydrocarbons and increased the amount of carbon monoxide and carbon dioxide. [Namioka, 2003] observed that the amount of benzene obtained with porous particles is higher than that obtained without porous particles, which may be caused by degradation of aromatic hydrocarbons.

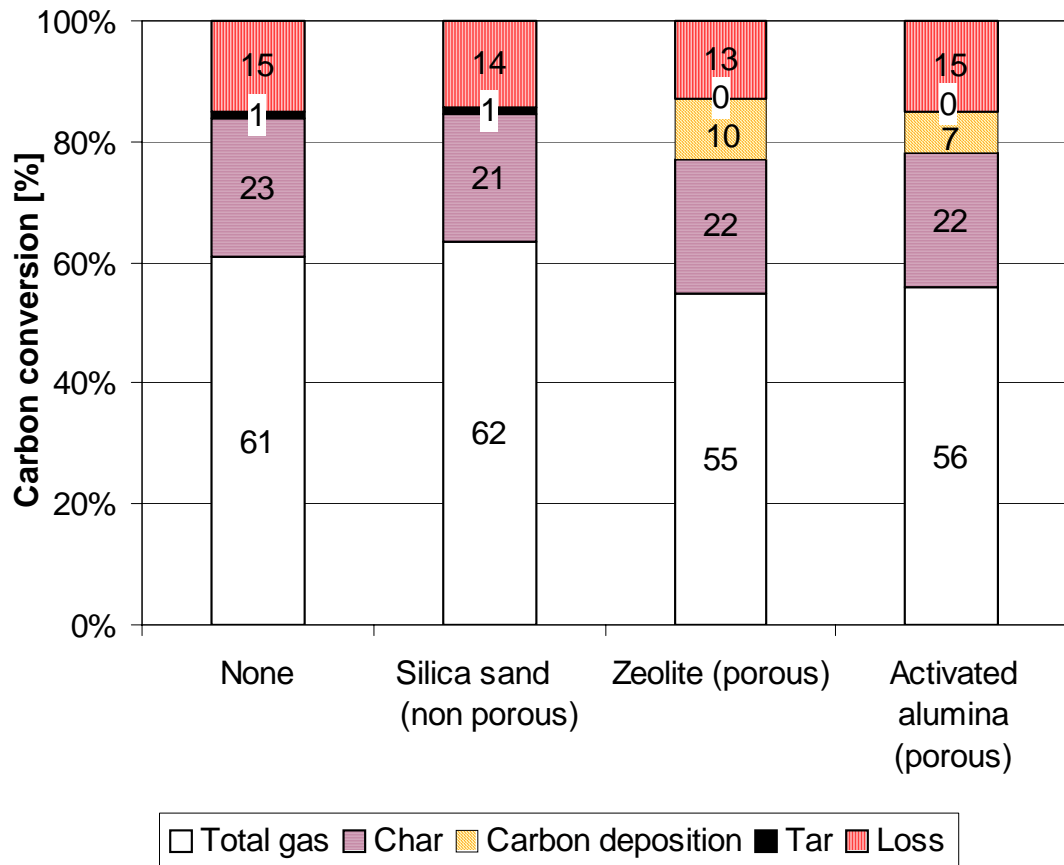


Figure 22. Carbon mass balance at 1073 K (800°C) using four different bed materials.

Figure 22 shows the carbon distribution at 800°C, as can be seen, the tar amount is just 1 % of the carbon for the base case at this temperature. The use of porous zeolite and alumina reduces the tar, however contrary to the results at 600°C, the tar yield without porous particles did not equal the yield of carbon deposition on the porous particles; the yield of carbon deposition is greater than that of tar. Figure 23 shows that the use of porous particles reduced the gaseous hydrocarbons, and the carbon in these reduced amounts is nearly equal to the carbon deposition on porous particles. According to [Namioka,2003] this means that porous particles capture not only tar, but also gaseous hydrocarbons, with a molecular weight lower than benzene.

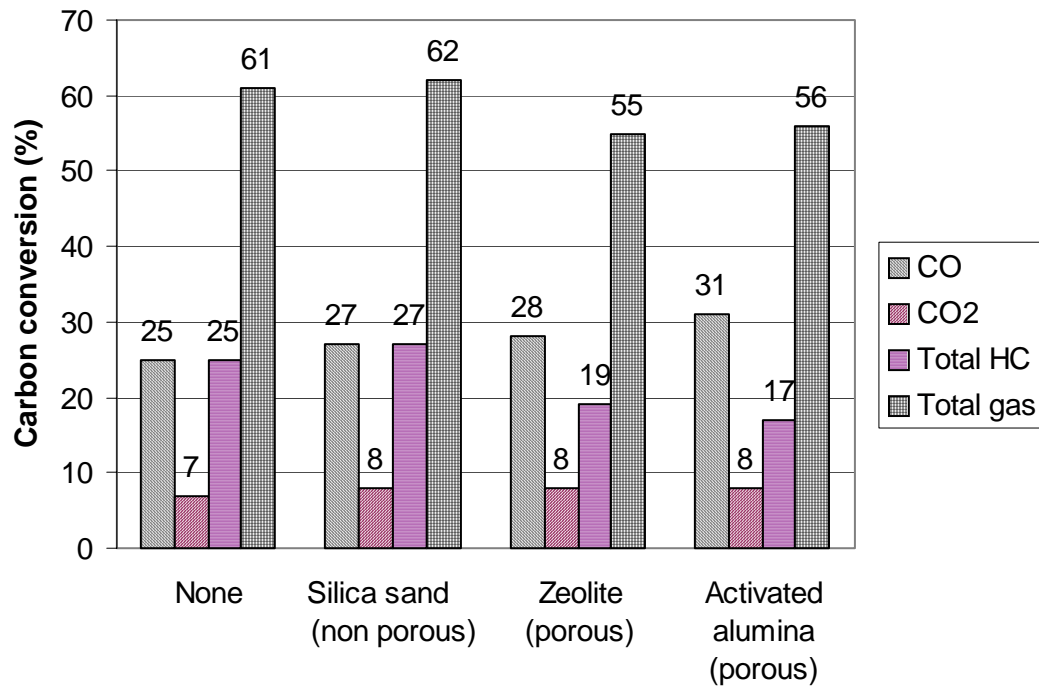


Figure 23. Carbon distribution in gas yields at 1073 K for four cases.

Because of the effect of holding gases, porous particles are also used as packing materials in gas chromatography, however the temperature in the GC column's is only about 200°C and there is thus no tar cracking.

The next section deals with the use of porous bed particles in a fluid bed combustor.

### Tar cracking using porous particles in a fluid bed combustor

[Franke,1999] has studied carbon burn-up of plastic in a fluid bed combustor using porous and non-porous particles. The reactor is shown in figure 24. Polystyrene pellets ( $C_8H_8$ )<sub>n</sub> were used as fuel, with a size of 2.1 mm x 3.3 mm x 3.4 mm and a weight of 19 mg. Three kinds of porous bed materials were used, MS-1B, activated bauxite and Galleonite 251. MS-1B, properties are listed in table 3.

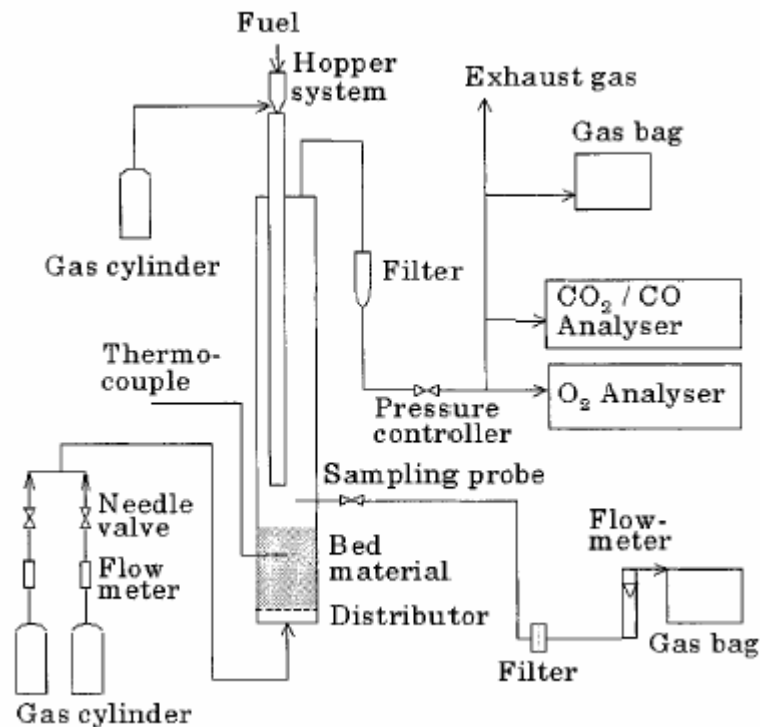


Figure 24. Schematic diagram of the bubbling fluidized bed combustor (BFBC)

Table 3. Property of porous particles used by [Franke,1999].

Composition [wt %]	MS-1B	Activated bauxite	Galleonite 251
Al <sub>2</sub> O <sub>3</sub>	84.7	69.4	12.8
SiO <sub>2</sub>	2.2	7.2	80.3
MgO	0.0	0.0	3.0
CaO	0.8	0.3	0.8
TiO <sub>2</sub>	1.1	13.0	0.0
Fe <sub>2</sub> O <sub>3</sub>	5.8	8.4	3.2
SO <sub>3</sub>	3.8	0.8	0.0
others	1.6	0.9	0.0
surface area [m <sup>2</sup> /g]	195	124	240
pore volume [cm <sup>3</sup> /g]	0.32	0.20	0.32

As can be seen from figure 25, the carbon conversion to CO<sub>2</sub> and total amount of gaseous carbon components was found higher for the porous MS-1B than quartz sand. According to [Franke,1999] porous particles in the bed capture carbon and tar and the increased residence time led to improved carbon conversion and reduced hydrocarbon emission.

According to [Franke,1999], with increasing amount of fuel fed, the difference became more significant.

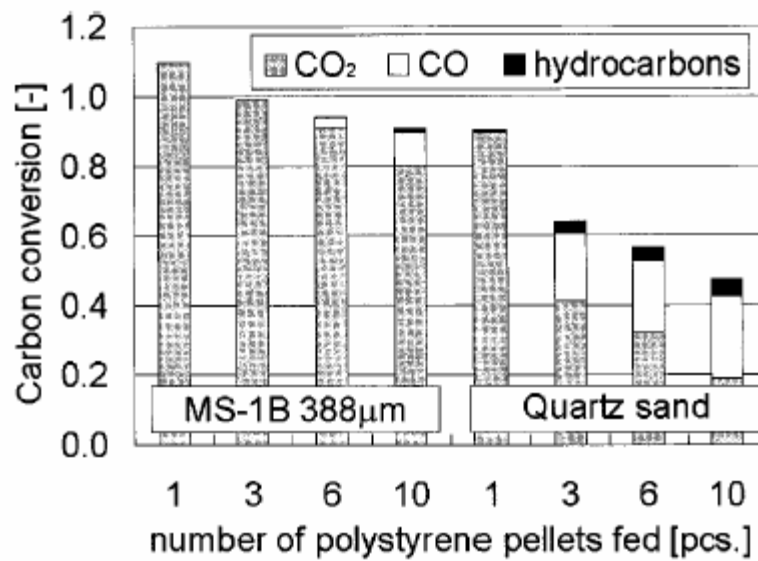


Figure 25. Emissions from combustion of polystyrene pellets in a Bubbling Fluid Bed Combustor (BFBC) using quartz sand and MS-1B as bed material.

Thus porous particles can thus reduce the tar amount in a fluid bed combustor, in the next section the effect of porous activated carbon particles will be tested.

## Tar cracking using activated carbon

[Griffits,1967] studied the cracking of tars from a pyrolysis reactor on an activated carbon (type 207C) column maintained at 350-900°C. 20 g of coal sample (volatile matter 37.3 % daf, ash 1.7 %) was pyrolyzed at 10°C/min up to 500°C and then maintained at that temperature for 30 minutes. The volatile products then passed through a cracking tube containing activated carbon and maintained at a definite temperature throughout the process. The tar and liquor products were condensed in a trap at 0°C; residual moisture was removed in a drying tube and residual hydrocarbons were finally condensed by a trap at 80°C. The gaseous products were collected and analysed by GC.

The pyrolysis products passed through a 7.6 cm column of activated carbon at a definite temperature shown on figure 26.

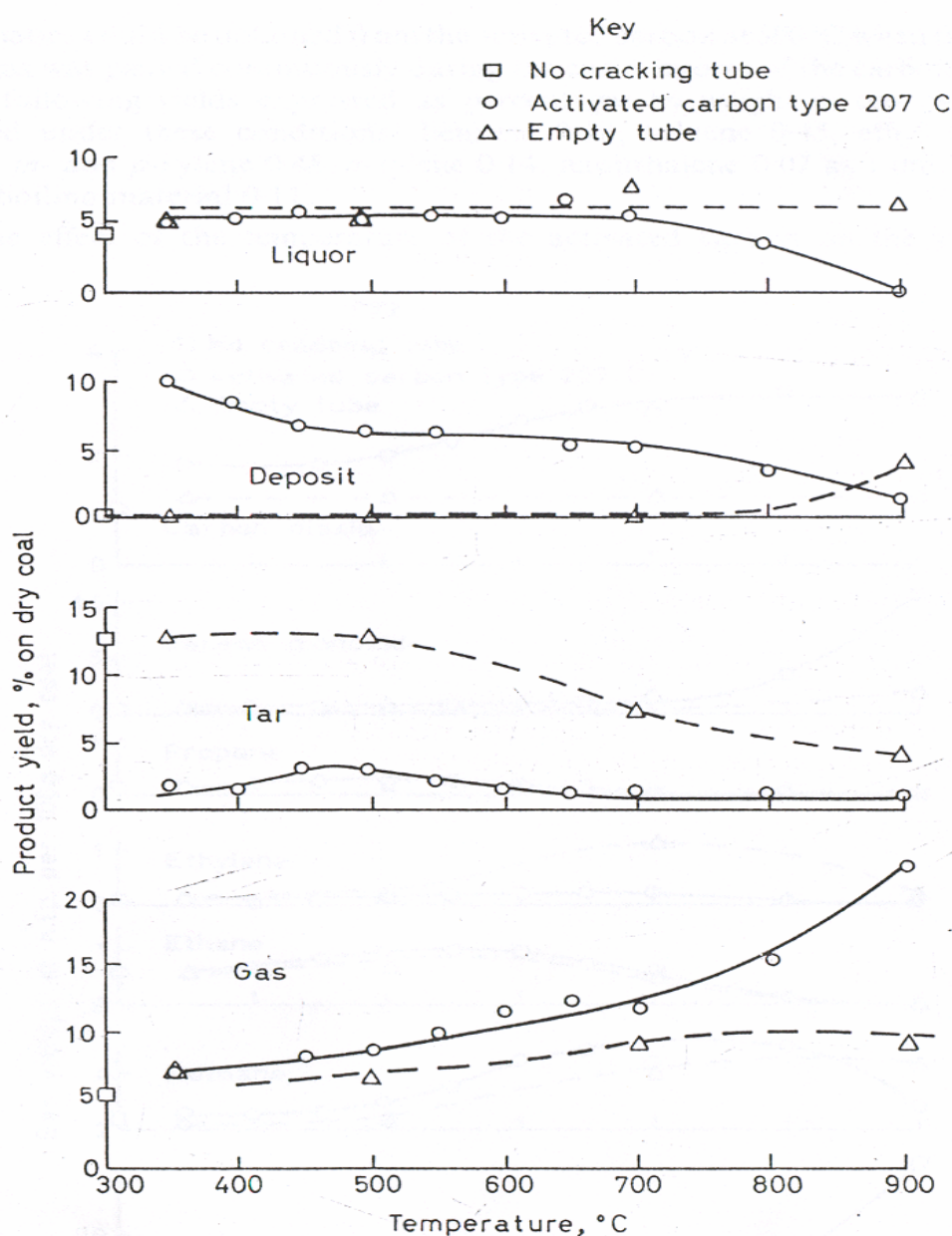


Figure 26. Effect of cracking temperature on yield of products.

As can be seen from figure 26 the tar obtained was considerably smaller than that obtained without a cracking tube and passed through a maximum (3 wt % of coal) at 500°C. Below 700°C the decrease in tar yield was mainly due to retention of the tar by the carbon as shown by the weight of the deposit.

The results obtained when various aromatic compounds were vaporized and carried in nitrogen through a column with activated carbon at 500°C can be seen in table 4. For the alkyl benzene the decomposition increases with molecular weight. The decomposition of benzene was negligible and that of toluene small. Aromatic compounds passed more slowly than the alkyl benzene through the column at 500°C and formed considerable deposits. The methylnaphthalene gave deposits up to 37 wt %. The 9,10 dihydroanthracene gave a deposit of 85 wt %, the rest leaving mainly as athracene and gas [Griffits,1967].

Tabel 4. Cracking of aromatic compounds on activated carbon type 207C. Length of column 7.8 cm; temperature 500°C; nitrogen flow 100 ml/min. Tar class from [Milne,1998].

Reactants			Products (wt %)			
Compound	Tar class	MW g/mol	Deposit	Parent compound and isomer	Lower boiling compounds detected	Gas
Benzene	4	78,11	Negligible	99	Negligible	Negligible
Toluene	3	92,14	4	94	2	Negligible
o-Xylene	3	106,17	7	83	6	1
n-Propyl benzene	3	120,19	11	51	32	4
Sec-Butyl benzene	3	134,22	16	33	41	5
1-Methyl naphthalene	3	142,2	27	45	16	5
1,6-Dimethyl naphthalene	3	156,23	37	24	25	4
Phenanthrene	4	178,23	65	Not estimated	Not estimated	Not estimated
9,10-dihydroanthracene	3	180,25	84.5	Negligible	11.8	2.9
Phenol	2	94,11	24	64.5	5.3	1.6
p-Cresol	2	108,14	43	1	44	3.5
1-Naphthol	2	144,17	76	Not estimated	14	1.8

The data from table 4 are plotted in figure 27 as a function of molecular weight for the different tar classes using the Milne classification system. The line for class 4 has only 2 points. As can be seen the deposit increases with MW for each tar class. If the curves for class 2 and 3 are extrapolated to zero deposit, they cross the x-axes close to the molecular weight of benzene (78 g/mole). The class 2 tars (phenol, cresol, naphthol) tend to give higher deposit than the other tar classes.

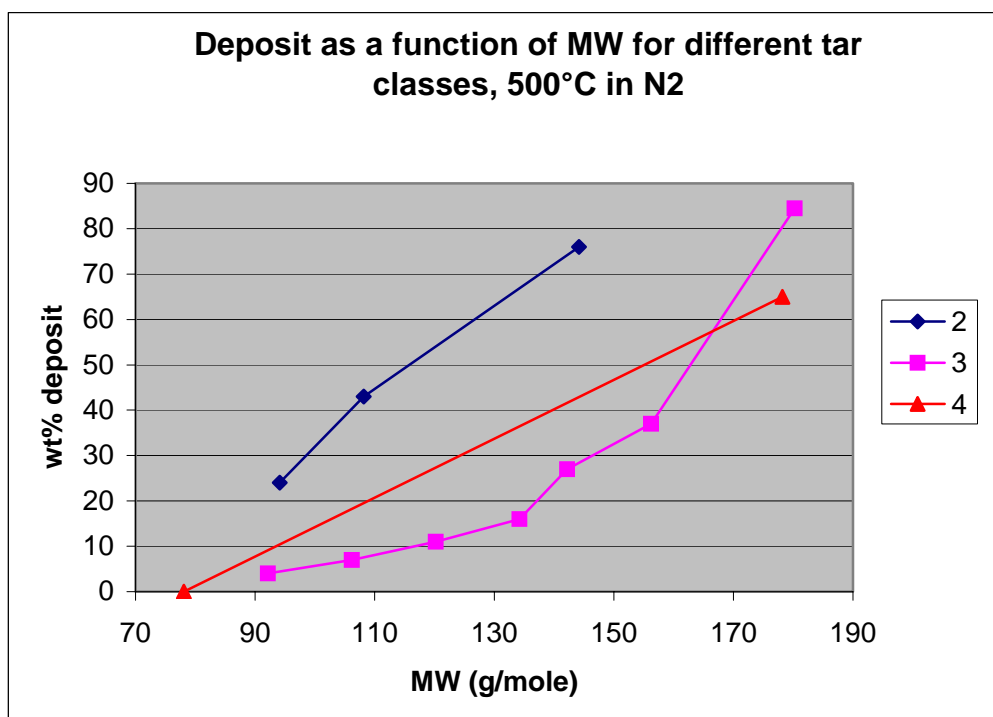


Figure 27. Deposit from tar as a function of molecular weight for different tar classes.

The effect of column length was tested by varying the length of the column from 3.8 to 12.8 cm, the corresponding weight ratios of activated carbon to coal carbonised being 0.28 and 1.7, respectively. Figure 28 shows the variation with column length of the yields of individual hydrocarbons in the tar. For benzene, toluene and xylenes the yields passed through a maximum with column length, the maximum at about 10 cm. Griffiths give no explanation to the maxima with respect to column lengths.

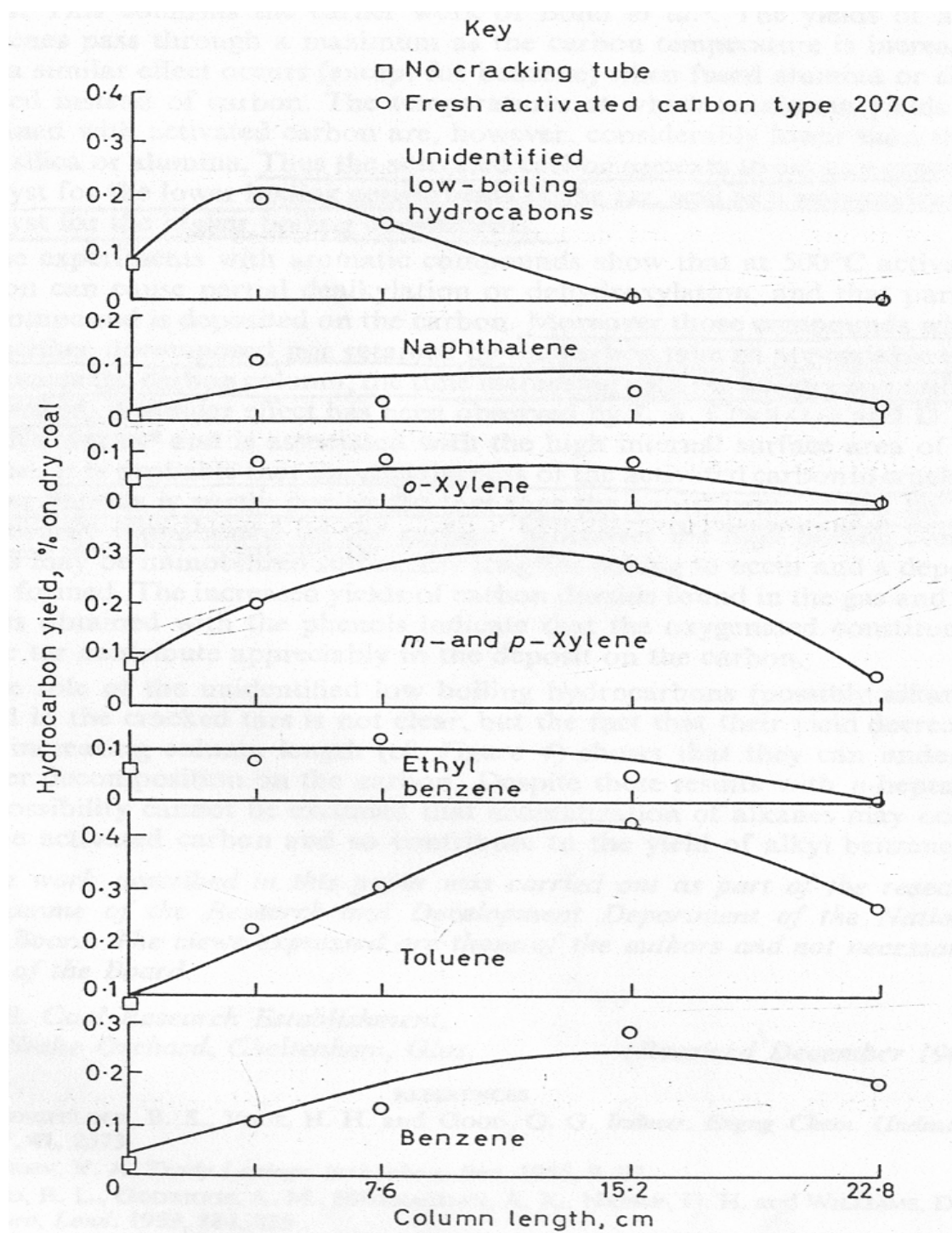


Figure 28. Effect of column length at 500°C on yield of hydrocarbons.

Griffiths found that the retention time of the tars was proportional to the lengths of the column and increased with the boiling point of the compound. For a 7.8 cm carbon (activated carbon type 207C) column at 500°C, the retention time ranged from one minute for benzene to seven minute for 1-methyl naphthalene. Griffith further adds that the dependence of retention time on boiling point is similar to that found in gas-liquid chromatography.

The next section describes tar cracking using char and activated char at a short residence time.

## Tar cracking using char and activated char, short residence time

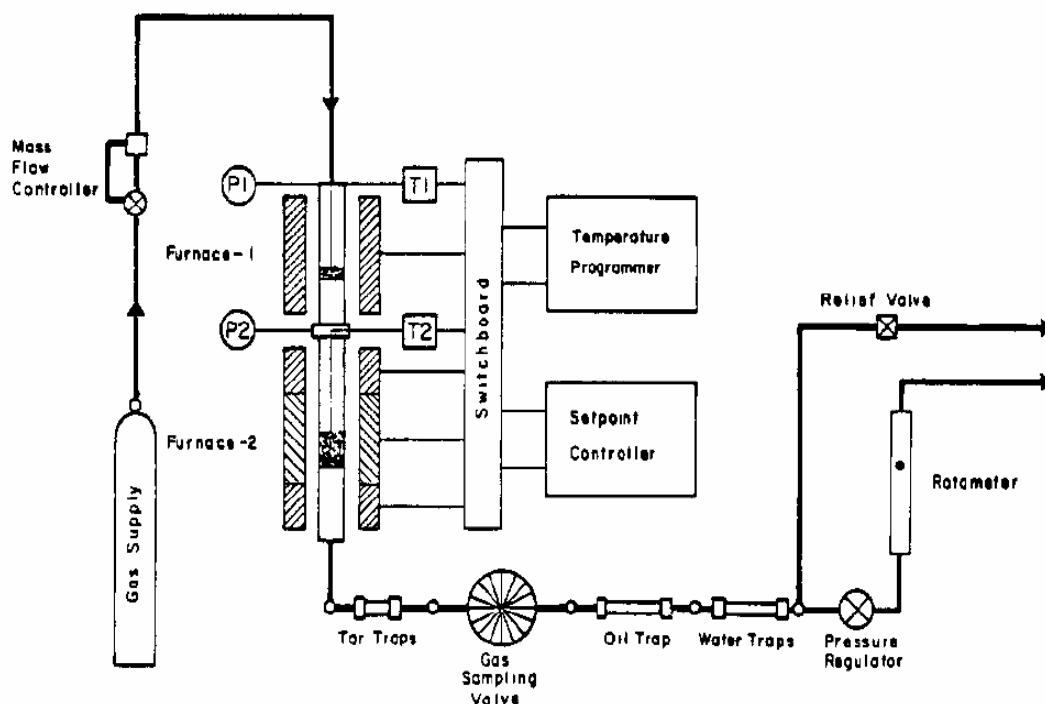


Figure 29. Two-stage reactor system.

[Borson,1989] has studied tar cracking in a two-stage reactor system, see figure 26. The work was performed to study the effect of thermal treatment with or without a wood char bed. Wood tar vapors were generated in reactor 1 by pyrolysis of sweet gum hardwood particles with a size range of 45-250  $\mu\text{m}$ . The wood particles are heated in reactor 1 from 30 to 450°C with a rate of 12°C/min; the holding time is 30 min at the final temperature. The tar vapors are then diluted in a helium carrier gas and then passed to a cracking reactor, where they are cracked with or without 0.2 – 12 cm deep beds of char from pyrolysis of the same wood. The temperature is 400-600°C with a residence time of 2.5 to 100 ms.

The data from Borson show average char surface area for the whole bed decreasing from 14 to 8.7 and 3.4  $\text{m}^2/\text{g}$ , after 0, 1 and 3 consecutive exposures to fresh tar. The declining surface area is ascribed to accumulation of coke deposits produced by continued conversion of the tar over the char.

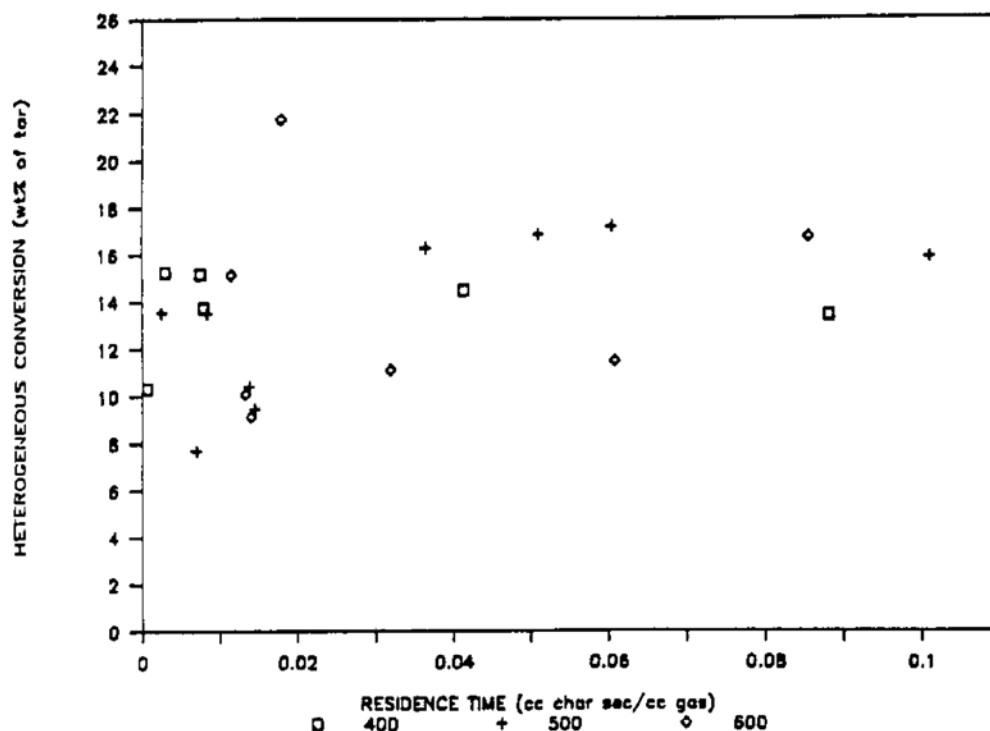


Figure 30. Tar conversion (y-axes “Heterogeneous conversion”) of wood pyrolysis tar induced by wood pyrolysis char at various temperatures (400, 500 and 600°C) and residence-time (x-axes) of 2.5-100 ms.

Figure 30 shows that the char-induced tar conversion was about  $14 \pm 7$  wt % of tar using temperatures of 400, 500 and 600°C and space time of 2.5-100 ms. To investigate whether the tar conversion was affected by the carbon form in the char, experiments were performed with activated carbon at 500°C and two different residence time (400 and 1200 ms), see table 5

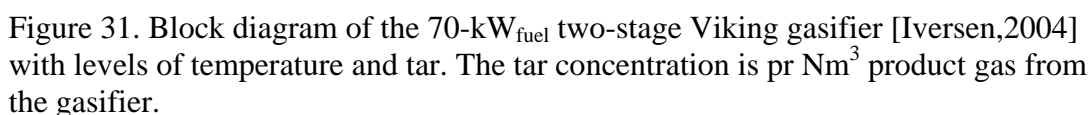
Table 5. Tar conversion over activated charcoal at 500°C and two-residence time.

Residence time (ms)	Wt % tar conversion
400	19.6
1200	15.8

Despite the longer residence time using the charcoal, the charcoal-induced conversion of 16-20 wt % of tar is within the  $14 \pm 7$  wt % conversion (of tar) induced by wood char (figure 30). Thus the tar cracking using charcoal is similar to the tar cracking using char.

The next section describes the use of char as tar cracker in a two stage reactor.

[Iversen,2004] describes the two-stage reactor with separate pyrolysis and gasification stage, see figure 31.



40

components. The amount of heavy tar was determined gravimetrically. The tar content after the partial oxidation and after the char bed can be seen in table 6 and 7 respectively. Only tertiary tars are found in the test series 2. Unfortunately the condensates were not analysed for phenols. However using a parallel gas sampling with acetone as absorbent, the amount of phenol was determined to be less than 0.05 mg/Nm<sup>3</sup> or less than 1% of the amount of naphthalene [Brandt,2000].

As can be seen the total amount of light tar is reduced from 2100 mg after the partial oxidation to 40 and 6.4 mg/kg dry wood for the experiments at the 9/9 and the 10/9, respectively. This is a reduction factor of 53 and 328, respectively. The reduction factor increases from naphthalene (two aromatic rings) to phenanthrene (three aromatic rings) to pyrene (four aromatic rings), thus the reduction increases from the light to the heavy PAH's (table 8) Thus the char bed also here has selectivity in reducing the higher tar components. The total reduction factor is close to the reduction factor for naphthalene, because naphthalene is a dominating component.

Table 6. Tar content of the gas after partial oxidation [mg/kg dry wood chip].  
Test series 2.

Component \ Date	9/9-98	10/9-98
Naphthalene	480	580
Phenanthrene	340	350
Pyrene	580	460
Total light tar	2100	2100
Heavy tar	840	1300

Table 7. Tar content of the gas after passing bed of char [mg/kg dry wood chip].  
Test series 2.

Component \ Date	9/9-98	10/9-98
Naphthalene	7.4	1.83
Phenanthrene	0.21	0.006
Pyrene	0.09	< 0.005
Total light tar	40	6.4
Heavy tar	1)	1)

1) Indicate concentration below detection level

Table 8. Reduction factor = (tar amount before char bed)/(tar amount after char bed).  
Test series 2.

Component \ Reduction factor	9/9-98	10/9-98
Naphthalene	64.9	316.9
Phenanthrene	1619	58333
Pyrene	6444	>92000
Total light tar	52.5	328

The gas residence time in the bed is about 1s. [Brandt,2000] concludes that a high surface area of the char and a temperature of above 750°C are necessary to avoid a decrease in activity due to carbon deposition on the char surface. [Bentzen,1999] measured the surface area of the char to be as high as 625-867 m<sup>2</sup>/g. The advantage of using

a char bed, as cracker is that the char is available insitu in the reactor and a separate tar-cracking reactor can thus be avoided.

## Discussion and conclusion

Tar is formed during the pyrolysis process by the thermal breakdown of the polymers cellulose, hemicellulose and lignin. The tar consists of various organic compounds, which can condense and thus be troublesome for the subsequent processes.

The tars can be removed using physical removal, thermal cracking, catalytic cracking, partial oxidation or using a bed of porous particles. For the physical tar removal a new absorption process named OLGA is potential able to remove almost all tar at a low temperature using a downstream absorption process. Thermal tar cracking needs a very high temperature to be effective. Literature data shows that thermal cracking of updraft gasifier tar needs a temperature of 1290°C to be accomplished within 0.5 s.

Partial oxidation can be used to reduce the tar level. The literature shows that the lighter compounds are cracked to heavier tars, the concentrations of some of these actually increase during the partial oxidation. The tar concentration versus lambda can have a maximum for some of the heavier tars; the maximum tar level is at lambda 0.3-0.6 for some of the heavy tars. One of the references shows that if the partial oxidation is performed using a primary and a secondary stage, there may be a specific ratio between the primary and secondary airflows, which minimizes tar amount. The optimal ratio depends on the fuel, but literature values of 0.1-0.2 secondary to primary flow rate have been found. Theoretical calculations using the Chemkin model indicate that the tar is cracked by H<sup>•</sup> free radicals produced in the oxidation of the fuel gas. Model calculations indicate that equilibrium is reached after about 1 s. This means that equilibrium is not reached during the mentioned partial oxidation process.

Tar cracking using catalyst can also be used. These can be dolomite, olivine or Ni catalyst. Olivine has a favourable attrition resistance compared to dolomite. Ni catalyst can be used if special precautions are taken with respect to deactivation. It is best to use Ni catalyst in an external fixed bed reactor. Catalytic cracking using Ni is described using first order kinetics. Several commercial Ni catalytic crackers have emerged.

The literature shows that tar cracking can be accomplished using porous particles such as char. The tar is adsorbed on the surface of the porous particles and the residence time of tar in the gasifier is then prolonged. The tar is then pyrolyzed, carbonised and fixed on the porous particles. Tar cracking can be accomplished at low temperature (even 500°C) if the residence-/retention time is sufficiently high (minutes). For a given column and tar class, the tar decomposition to deposit increases with molecular weight. The tar decomposition depends also on the tar class; class 2 tars are easier to crack than class 3 and 4.

Very high tar cracking can be accomplished using char with a large surface area. The tar cracking can be accomplished in both a fluid bed and a fixed bed. When cracking using char is combined with cracking using partial oxidation in a two staged fixed bed gasifier, the tar level can be reduced to less than 5 mg/Nm<sup>3</sup> from the gasifier. The tar level can be further reduced to less than 1 mg/Nm<sup>3</sup> using coolers and simple filters.

It is advantageous to use a combination of a partial oxidation and a char bed to crack the tars in staged gasifiers because the partial oxidation cracks the lighter tars and increases the heavier tars while the char bed selectively reduces the heavier tars. The literature shows that the char bed reduces tars heavier than benzene.

Experiments have shown that if wood chips have been slowly and uniformly pyrolysed to a pyrolysis end-temperature above 500 °C the residual tar content in the char will be negligible. In staged gasifiers, where the pyrolysis takes place in a separate reactor, this will mean that all the produced tars from the pyrolysis will be cracked in the partial oxidation zone and in the char bed.

Further studies with tar cracking using porous char particles should focus on investigating the tar adsorption, cracking and desorption of products from porous particles. Parameters like surface area, pore distribution and size of char, enthalpies of adsorption/-desorption and retention time of tar molecules etc. can be important for the rate of tar cracking on porous char particles. Models or correlations are needed to describe the tar cracking on porous particles.

## References

Jesper Ahrenfeldt, Benny Gøbel, Ulrik Henriksen, Jan Fjellerup. "EXPERIMENTAL CHARACTERISATION OF RESIDUAL-TAR IN WOOD CHAR". DTU, MEK-ET-2005-06, April 2005, ISBN 87-7475-330-4.

Jens Dall Bentzen, Peder Brandt, Benny Gøbel, Claus Hindsgaul Hansen and Ulrik Henriksen. "Optimering af 100 kW tottrinsforgasningsanlæg på DTU". DTU, MEK, August 1999, ET-ES-99-02 (in Danish).

Colomba Di Blasi. "Modeling Intra- and Extra-Particle Processes of Wood Fast Pyrolysis". AIChe Journal, October 2002, Vol. 48, No.10, p. 2386-2397.

Colomba Di Blasi, and Carmen Branca. "Kinetics of Primary Product Formation from Wood Pyrolysis". Ind. Eng. Chem. Res., 40, 5547, 2001.

Boerrichter, H.. "Gas cleaning at ECN – Lessons learned and results achieved". ECN Biomass contribution to the GasNet & IEA Bioenergy Agreement Meeting Strasbourg, France, 2-3 October 2002.

Michael L. Boroson, Jack B. Howard, John P. Longwell, and William A. Peters. "Heterogeneous Cracking of Wood Pyrolysis Tars over Fresh Wood Char Surfaces". Energy & Fuels 1989, 3, p. 735-740.

Peder Brandt og Ulrik Henriksen. "Tjærekrakning ved partiel oxidation af pyrolysegas fra halm. Delrapport 1. Forsøg ved 800 og 900°C". DTU, Institut for Energiteknik, ET-ES-98-08, Juni 1998, ISBN 87-7475-200-6 (in Danish).

Peder Brandt and Ulrik Henriksen. "Decomposition of Tar in Gas from Updraft Gasifiers by Thermal Cracking". Proceedings of 1<sup>st</sup> World Conference on Biomass for Energy and Industry, Sevilla, Spain, June 5-9, 2000. London, James & James (Science Publishers) Ltd.

Peder Brandt, Elfinn Larsen, Ulrik Henriksen. "High Tar Reduction in a Two-Stage Gasifier". Energy & Fuels 2000, 14, p. 816-819.

Carmen Branca, Paola Giudicianni, and Colomba Di Brasi. "GC/MS Characterization of Liquids Generated from Low-Temperature Pyrolysis of Wood. Ind. Eng. Chem. Res. 2003, 42, 3190-3202.

BTG: Homepage: Tar and Tar removal,  
Date: 10/5-2004 <http://www.btgworld.com/technologies/tar-removal.html#reverse-flow-operation>

J. Corella, J. Herguido, J. González-Sáiz, Rodríguez-Trujillo. "Fluidized Bed Steam Gasification of Biomass with Dolomite and with a commercial FCC Catalyst". Research in Thermochemical Biomass Conversion 1988. Edited by A.V. Bridgwater, J.L. Kuester. London: Elsevier Applied Science, p. 754-765.

D. Dayton. "A Review of the Literature on Catalytic Biomass Tar Destruction". Milestone Completion Report. December 2002. NREL/TP-510-32815.

National Renewable Energy Laboratory.

L. Devi, K.J. Ptasinski, Frans J.J.G. Janssen. "A review of the primary measures for tar elimination in biomass gasification processes". Biomass and Bioenergy 24, 2003, p. 125-140.

ECN. Source for the two figures and the quotation is located at the homepage of ECN under OLGA technology, date: 22/4-2004:

<http://www.ecn.nl/biomassa/products/experiments/olga.en.html>

Robert J. Evans and Thomas A. Milne. "Molecular Characterization of the Pyrolysis of Biomass 1. Fundamentals". Energy & Fuels volume 1, Number 2, Marts/April 1987, p.123-137.

D.C. Elliot. "Relation of Reaction Time and Temperature to Chemical Composition of Pyrolysis Oils", ACS Symposion Series 376, Pyrolysis Oils from Biomass". Edited by E.J. Soltes and T.A. Milne. Denver, CO. April 1987.

R.J. Evans, T.A. Milne. "Molecular Characterization of the Pyrolysis of Biomass. 1. Fundamentals", Energy & Fuels 1 (2), p. 123-138, 1987.

Hans-Jürgen Franke, Tadaaki Shimizu, Akire Nishio, Hiroyuki Nishikawa, Makato Inagaki and Watari Ibashi. "Improvement of Carbon Burn-up during Fluidized Bed Incineration of Plastic by Using Porous Bed Materials". Energy & Fuels 1999, 13, p. 773-777.

L. Garcia, R. French, S. Czernik, E. Chornet. "Catalytic steam reforming of bio-oils for the production of hydrogen: effect of catalyst composition". Applied Catalysis A: General 201, p.225-239.

D.M. Griffith and J.S.R. Mainhood. "The Cracking of Tar Vapour and Aromatic Compounds on Activated Carbon". Fuel A journal of fuel science 1967, 46, p. 167-176.

Jun-Ichiro Hayashi, Masahiro Iwatsuki, Kayoka Morishita, Atsushi Tsutsumi, Chun-Zhu Li, Tadatosh Chiba. "Roles of inherent metallic species in secondary reactions of tar and char during rapid pyrolysis of brown coals in a drop-tube reactor". Fuel 81 (2002) p.1977-1987.

Ulrik Henriksen, Erik Kofoed, Ole Christensen. "Heat Transfer in Straw". Department of Energy Engineering, DTU. In proceedings of the conference: "Advances in Thermochemical Biomass Conversion". Interlaken, Switzerland. May 1992. Vol.2. p. 1110-1121.

Hermann Hofbauer, Reinhard Rauch, Klaus Bosch, Reinhard Koch and Christian Aichernig. "Biomass CHP Plant Güssing – A Success Story". Published in A.V. Bridgwater "Pyrolysis and Gasification of Biomass and Waste". Proceedings of an Expert Meeting, Strasbourg, 30 September-1 October 2002.

T.A. Hoeven, H.C. de Lange, A.A. van Steenhoven. "Ex-situ Removal on Tar of Small-Scale Biomass Gasification by Partial Oxidation". 2<sup>nd</sup> World Conference on Biomass for Energy, Industri and Climate Protection, 10-14 May 2004, Rome, Italy.

Marja Petra Houben. "Analysis of tar removal in a partial oxidation burner", -Eindhoven Technische Universiteit Eindhoven, 2004. Proefschrift.- ISBN 90-386-2845-5.

[Ising et al.]:

[1]: Technische und Wirtschaftliche Optimierung der Vergasung von Holz in der zirkulierenden Wirbelschicht, Abschlussbericht, Fördererkennzeichen 00 NR 178, by Dr. - Ing . M. Ising, Dipl.-Chem. Dr. C. Unger, Dipl.-Ing. F. Heunemann, Dipl.-Ing. L. Dinkelbach, December 2002 located on the internet at:  
[http://www.umsicht.fhg.de/WWW/UMSICHT/Produkte/ET/Bio\\_Bsp.html](http://www.umsicht.fhg.de/WWW/UMSICHT/Produkte/ET/Bio_Bsp.html)

[2]: Cogeneration from biomass gasification by producer gas-driven block heat and power plants, M. Ising, Chr. Unger, A. Heniz, W. Althaus. 12<sup>th</sup> European biomass conference and exhibition 17-21 June 2002 Amsterdam, the Netherlands

[3]: Gasification of biomass in a circulation fluidised bed with special respect to tar reduction, Markus Ising, Dr. Javier Gil, Dr. Christoph Unger. 1<sup>st</sup> world conference and exhibition on biomass for energy and industry, 5-9 June 2000; Sevilla, Spain.

Henrik Laudal Iversen and Benny Gøbel. "Update on gas cleaning technologies for biomass gasification gas for different applications". Biomass Gasification Group, Department of Mechanical Engineering, Technical University of Denmark, June 2004.

T.A. Milne, N. Abatzoglou, R.J. Evans, "Biomass Gasifier "Tars": Their Nature, Formation and Conversion". National Renewable Energy Laboratory. NREL/TP-570-25357; NREL: Golden, Co, 1998.

Michael Morris. "Catalytic cracking of tar in product gas from wood gasification". TPS Termiske Processer AB, 2004.

Tomoaki Namioka, Kunio Yoshikawa, Hiroyuki Hatano and Yoshizo Suzuki. "High Tar Reduction With Porous Particles for Low Temperature Biomass Gasification: Effects of Porous Particles on Tar and Gas Yields during Sawdust Pyrolysis". Journal of Chemical Engineering of Japan, Vol. 36, No 12, p.1440-1448, 2003.

JPA Neeft, HAM Knoef, P. Onaji. "Behavior of tar in biomass gasification systems. Tar related problems and their solutions". Novem report No. 9919. Energy from Waste and Biomass" (EWAB), The Netherlands, 1999.

S.V.B. Van Paasen, L.P.L.M. Rabou, R. Bär et al. "Tar removal with wet ESP. Parametric study". Paper presented at Rome 2004 conference on biomass.

Y.G. Pan, X. Roca, E. Velo, L. Puigjaner. "Removal of tar by secondary air in fluidised bed gasification of residual biomass and coal". Fuel 78, 1999, p. 1703-1709.

Karsten Pedersen og Elfinn Larsen. "Karakterisering af tjære i gas fra termisk forgasning af biomasse" Teknologisk Institut og Forskningscenter Risø. Marts 1999.

K.J. Ptasinski, L. Devi, F.J.J.G. Janssen. "Olivine as a Tar Removal Catalyst for Biomass Gasifiers". 2<sup>nd</sup> World Conference on Biomass for Energy, Industri and Climate Protection". 10-14 May 2004, Rome, Italy.

S. Rapagná, N. Jand, A. Kinnemann, PU Foscolo. "Steam-gasification of biomass in a fluidised-bed of olivine particles". Biomass and Bioenergy 2000; 19; p.187-97.

Shafizadeh, F. and P.P.S. Chin, "Thermal Deterioration of Wood". ACS Symp. Ser., 43, 57 (1977).

Chirag Sathe, Jun-Ichiro Hayashi, Chun-Zhu Li, Tadatoshi Chiba. "Combined effects of pressure and ion-exchangeable metallic species on pyrolysis of Victorian lignite". Fuel 82 (2003) p.343-350.

Pekka A. Simell, Jukka K. Leppälahti and Esa A. Kurkela. "Tar-decomposing activity of carbonate rocks under high CO<sub>2</sub> partial pressure". Fuel Vol.74 No. 6, p.938-945, 1995.

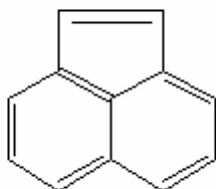
Pekka Simell, Esa Kurkela, Pekka Ståhlberg, Jouko Hepola. "Catalytic hot gas cleaning of gasification gas". Catalysis Today 27, 1996, p. 55-62.

P. Simell, P. Ståhlberg, Y. Solantausta, J. Hepola and E. Kurkela. "Gasification gas cleaning with nickel monolith catalyst. Published in A.V. Bridgwater and D.G.B. Boocock (eds.). Developments in Thermochemical Biomass Conversion, vol.2, 1997, Blackie, London, UK.

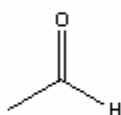
## APPENDICES WITH TAR COMPONENTS

<u>TAR NAME: FORMULA</u>	<u>CLASS</u>
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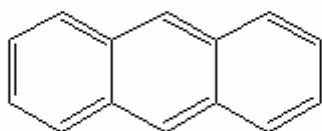
Acenaphthylene: $C_{12}H_8$	3
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Acetaldehyd: $C_2H_4O$	1
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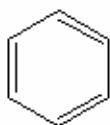


Anthracene: $C_{14}H_{10}$	4
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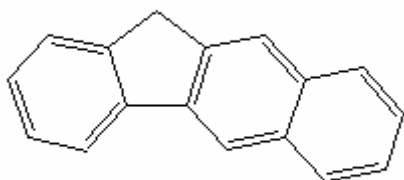
**Benzene:  $C_6H_6$**

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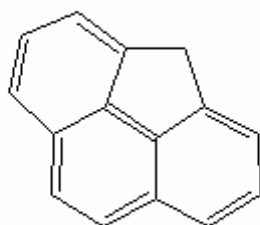
**Benzofluorene:  $C_{17}H_{12}$**

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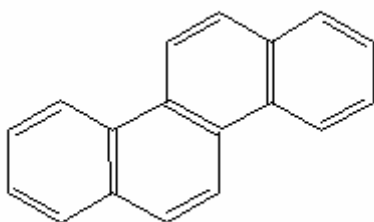
**Benzofluorentene:  $C_{20}H_{12}$**

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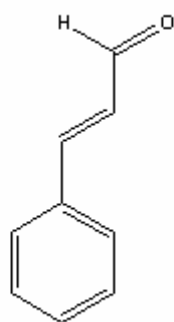
**Chrysene:  $C_{18}H_{12}$**

**4**



**Cinnamaldehyde (danish "kanelaldehyde"):  $C_9H_8O$**

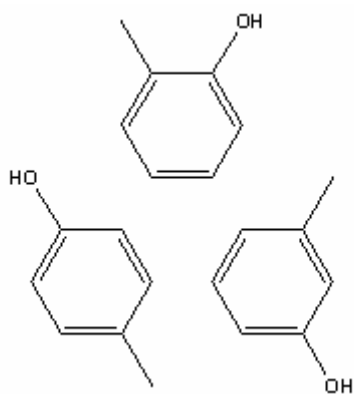
**1**



**Cresol:  $C_7H_8O$**

**2**

**ortho**

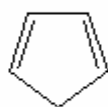


**para**

**meta**

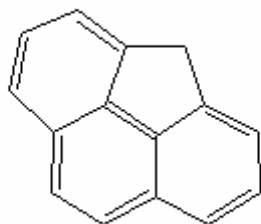
**Cyclopentadiene:  $C_5H_6$**

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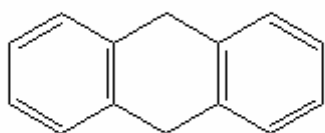
**Cyclopentaphenanthrene: C<sub>15</sub>H<sub>10</sub>**

**3**



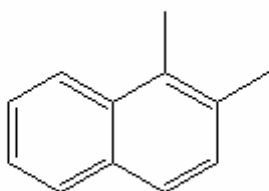
**9,10 Dihydroanthracene: C<sub>14</sub>H<sub>12</sub>**

**3**



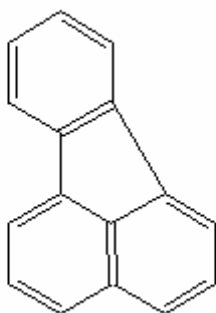
**Dimethylnaphthalene: C<sub>12</sub>H<sub>12</sub>**

**3**



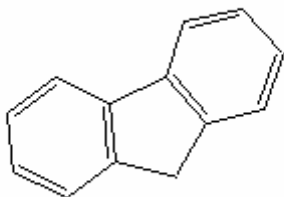
**Fluoranthene: C<sub>16</sub>H<sub>10</sub>**

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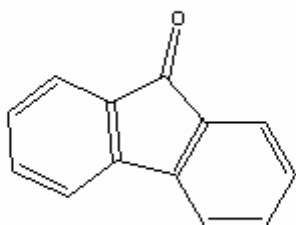
**Fluorene:  $C_{13}H_{10}$**

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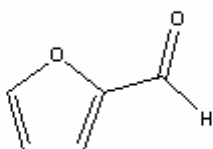
**9-Fluorenone:  $C_{13}H_8O$**

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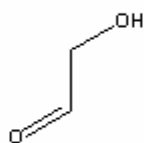
**Furfural:  $C_5H_4O_2$**

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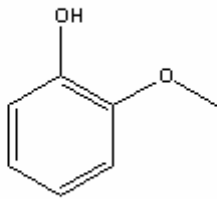
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**1**



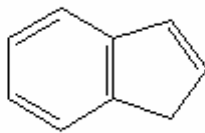
**Guaiacol or methoxyphenol:  $C_7H_8O_2$**

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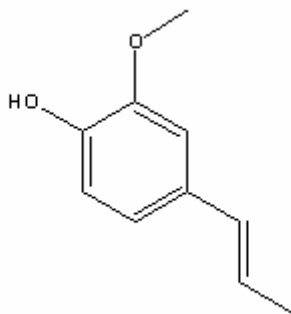
**Indene:  $C_9H_8$**

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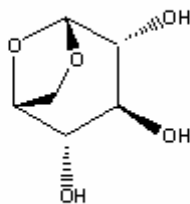
**Isoeugenol:  $C_{10}H_{12}O_2$**

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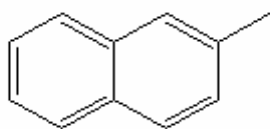
**Levoglucosan:  $C_6H_{10}O_5$**

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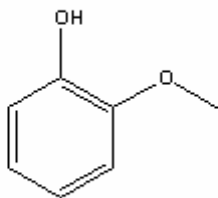
**Methylnaphtalene:  $C_{11}H_{10}$**

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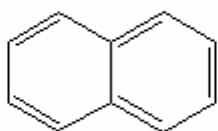
**Methoxyphenol:  $C_7H_8O_2$**

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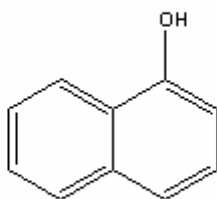
**Naphtalene:  $C_{10}H_8$**

**4**



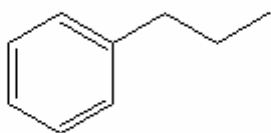
**Naphthol:  $C_{10}H_8O$**

**2**



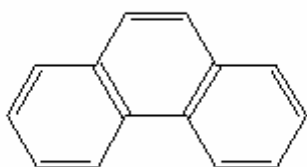
**n-Propylbenzene:  $C_9H_{12}$**

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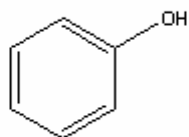
**Phenanthrene:  $C_{14}H_{10}$**

**4**



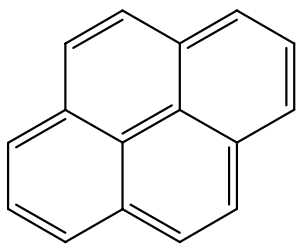
**Phenol:  $C_6H_6O$**

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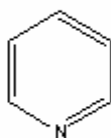
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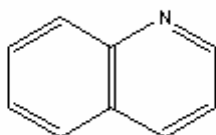
**Pyridine:  $C_5H_5N$**

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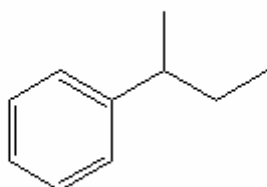
**Quinoline:  $C_9H_7N$**

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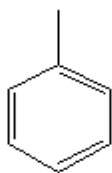
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**3**



**Toluene:  $C_7H_8$**

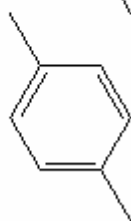
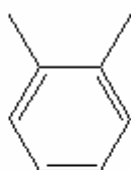
**3**



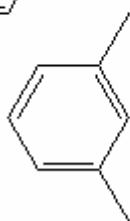
**Xylenes:  $C_8H_{10}$  for each**

**3**

**ortho**



**para**



**meta**





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