

# **TAR FORMATION IN FLUIDISED-BED GASIFICATION - IMPACT OF GASIFIER OPERATING CONDITIONS**

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S.V.B. van Paasen  
J.H.A. Kiel





# TAR FORMATION IN FLUIDISED-BED GASIFICATION - IMPACT OF GASIFIER OPERATING CONDITIONS

S.V.B. van Paasen and J.H.A. Kiel

ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands, [vanpaasen@ecn.nl](mailto:vanpaasen@ecn.nl) and [kiel@ecn.nl](mailto:kiel@ecn.nl)

**ABSTRACT:** In fluidised-bed biomass gasification, the presence of heavy tars in gasifier product gas may cause fouling and soot formation in downstream processes, and tars with high water solubility may cause wastewater problems. The tar properties are influenced by gasifier operating conditions. Experiments reveal a decrease in total tar concentration by a factor of five with an increase in gasification temperature from 750°C to 950°C. Simultaneously, the tar composition shifts from alkyl-substituted Poly-Aromatic Hydrocarbons (PAHs) and oxygen and nitrogen containing tars to non-substituted PAHs. Above 800°C, the tars grow in molecular size leading to an increasing dewpoint with increasing temperature, despite the decrease in total tar concentration. In practical terms, increasing the gasification temperature appears not a general remedy against all tar-related problems. It may indeed lead to a strong decrease in heterocyclic tars like phenol, which may reduce wastewater problems drastically. On the other hand, it may lead to a considerable increase in tar dewpoint aggravating tar condensation and aerosol formation.

**Keywords:** tar, fluidised bed, gasification

## 1 INTRODUCTION

Gasification technologies are expected to play a key role in expanding the use of biomass as a major renewable energy source. The conversion of the solid feedstock to a gaseous product significantly increases its potential. The gas can be used for applications such as:

- Co-firing in coal- or natural gas-fired power plants,
- Electricity generation in stand-alone conversion devices (gas engines, gas turbines, fuel cells),
- Production of gaseous/liquid fuels or chemicals.

For all these applications, however, a more or less extensive cleaning of the product gas is required. And, although gasification of solid fuels is already an old technology and the specific volumes of gas to be treated are much smaller than after combustion, product gas cleaning appears to be a (and often *the*) major area of concern. In many applications, the tar content in the product gas has to be controlled to prevent a range of possible problems in downstream equipment, such as:

- Fouling and plugging due to tar condensation and soot formation,
- Difficulties in handling tar-water mixtures,
- Contamination of waste streams.

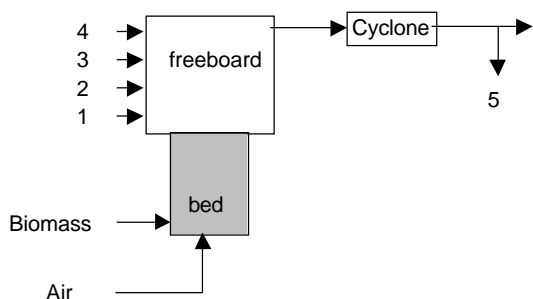
This tar production in itself is largely dependent on fuel properties and gasification conditions. In many previous studies, the focus has been mainly on total tar production. However, earlier work at ECN

has revealed already that often (changes in) the tar composition is the dominant factor, when looking at the impact on downstream equipment. The objective of the present work is to assist designers and operators of fluidised-bed biomass gasification based systems by providing detailed data concerning the impact of gasification temperature and gas residence time on tar composition and concentrations of specific tar compounds for commercially relevant conditions.

## 2 APPROACH

Experiments were conducted in a small-scale (1 kg/h) bubbling-fluidised-bed gasifier using woody biomass fuels. The experiments were carried out at different gasification temperatures and gas residence times, while the air to fuel ratio was adapted to the gasification temperature to mimic the conditions in a 50 MW<sub>th</sub> gasifier.

The gasifier is shown schematically in Figure 1. Gas samples can be taken at four places in the freeboard, equally distributed over the height representing differences in gas residence time. The fifth sampling point is located after the cyclone.



**Figure 1:** Schematic of the 1 kg/h bubbling-fluidised-bed gasifier (WOB) at ECN.

The gas analysis comprises the measurement of permanent gases as well as tar compounds. The concentration of CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, benzene and toluene is measured on-line every minute with gas monitors and/or a micro-GC. The concentration of tar compounds has been determined with the Guideline method just above the fluidised bed and after the cyclone.

The Guideline method resulted from a broad international effort co-ordinated by ECN to arrive at a widely-accepted, standard tar measurement method [1]. During sampling, tars are dissolved in isopropanol using six impinger bottles. Two types of tar concentrations can be obtained, *viz.* the concentration of gravimetric tar and concentrations of individual organic compounds. **Gravimetric tar** is defined as the evaporation residue of a part of the bulk solution, at given and standard conditions. Concentrations of **individual organic compounds** are determined by GC-analysis of the bulk solution. The full version of the Guideline as well as a description of the further development into a CEN standard can be found on the dedicated web-site [www.tarweb.net](http://www.tarweb.net) and in [1].

The gravimetric tars include GC-detectable as well as GC-undetectable (class 1) tar compounds. Therefore, the gravimetric tars partly overlap with the GC-detectable tars. The GC-undetectable tar concentration can be obtained by the determination of the GC-detectable fraction in the gravimetric tar sample (after redissolution) and subtracting this from the gravimetric tar concentration. Furthermore, HPLC analysis of the gravimetric tars allows the analysis of

individual heavy hydrocarbons with a molecular mass higher than coronene.

### 3 PRESENTATION OF RESULTS

#### 3.1 Tar classification

The impact of tar formation on the performance of downstream processes mostly is not related to the lump-sum tar content (expressed, e.g., in g/m<sup>3</sup> “tar”), but problems are merely caused by specific tar fractions or tar compounds. Therefore, much emphasis has been given to the determination of the tar *composition* by measuring individual tar compounds. Based on the behaviour of the tar compounds in downstream processes, the classification system was derived as presented in Table 1.

Class 1 tars are compounds that cannot be detected with a GC and include tar compounds heavier than coronene. Class 2 tars are aromatic compounds with hetero atoms (*e.g.* oxygen and nitrogen), and are compounds with a high water solubility. Class 3 tars are light compounds with 1 aromatic ring, which do not contribute to tar related problems. Class 4 tars are compounds with 2 or 3 aromatic rings and class 5 tars are compounds with 4 to 7 aromatic rings. Both class 4 and class 5 tars (partly) condense when the gas is cooled down to 20°C.

**Table 1:** Tar classification system.

	Name	Tar compounds
Class 1	GC-undetectable	Determined by subtracting the GC-detectable tar fraction from the total gravimetric tar.
Class 2	heterocyclic aromatics	pyridine, phenol, cresol, quinoline
Class 3	aromatics (1 ring)	xylene, styrene, toluene
Class 4	light PAH compounds (2-3 ring)	naphtalene, biphenyl, acenaphthylene, fluorene, phenanthrene, anthracene
Class 5	heavy PAH compounds (4-7 ring)	fluoranthene, pyrene, chrysene, benzo-fluoranthene, benzo-pyrene, perylene,

#### 3.2 Tar condensation

An important thermodynamic property for condensation is the tar dewpoint. The tar dewpoint is the temperature at which the real

total partial pressure of tar equals the saturation pressure of tar. ECN developed a dewpoint model for the calculation of tar dewpoints from a given tar composition (for more information see [www.thersites.nl](http://www.thersites.nl)). The model includes vapour/liquid equilibrium data for the tar compounds in the product gas from a downdraft or fluidised-bed gasifier. The calculation is based on ideal gas behaviour. Raoult's law is applied for the calculation of a mixture of hydrocarbons, using the vapour pressure data of individual compounds. The tar dewpoint is calculated from the measured tar composition, i.e. tars with a molecular size between toluene and coronene. Heavier tars are not considered, but they may be expected to have a relatively high dewpoint at low concentration. Therefore, generally, the calculated tar dewpoint should be considered as an underestimate, the actual dewpoint probably being (somewhat) higher.

#### 4 EXPERIMENTAL RESULTS

Both the temperature as well as the gas residence time in a gasifier strongly influences the tar composition and concentration in the product gas. The tar composition is a result of multiple consecutive reactions. Each reaction has a certain reaction time for completion. The gas residence time determines how many, and to what extent, consecutive reactions can take place at a certain temperature. The relation between tar formation and the gasifier temperature and gas residence time at constant fuel to air ratio is discussed in [2]. In this section, tar formation in relation to the gasification temperature with variations in the ER will be discussed.

##### 4.1 Temperature with variation in ER

In order to obtain results that are more representative for gasifiers at commercial scale, the ER - temperature relation for a 50 MW<sub>th</sub> atmospheric, air-blown fluidised-bed gasifier, operated on woody biomass, has been determined and was used for the experiments. This means that the airflow was increased according to this relation when the gasification temperature was increased. The following assumptions were

made for the calculation of the ER - temperature relation, given in Table 2:

- Commercial scale: 50 MW<sub>th</sub>
- Carbon conversion = 93 %
- Air pre-heating = 100°C
- Heat loss = 2.7 % (LHV basis)
- Biomass moisture content = 9.5 wt%
- Gas composition calculated with an in-house model.

**Table 2:** ER - temperature relation for a 50 MW<sub>th</sub> atmospheric, air-blown fluidised-bed gasifier.

Test	Gasification temperature	ER
1	750°C	0.22
2	800°C	0.24
3	850°C	0.25
4	900°C	0.27
5	950°C	0.28

**Table 3:** Impact of gasification temperature at varying ER: experimental conditions

	1	2	3	4	5
ER [-]	0.23	0.24	0.26	0.27	0.29
Bed temp. [°C]	759	807	854	906	955
Freeboard temp. [°C]	721	770	823	874	924

**Table 4:** Impact of gasification temperature at varying ER: experimental results

Bed temp °C	759	807	854	906	955
Tar dewpoint °C	194	188	195	207	220
Tar total g/m <sub>n</sub> <sup>3</sup>	54.1	26.2	19.6	14.4	11.8
Unknown mg/m <sub>n</sub> <sup>3</sup>	14527	6951	5063	3177	2452
Class 1 mg/m <sub>n</sub> <sup>3</sup>	17504	6367	4173	2152	1865
Class 2 mg/m <sub>n</sub> <sup>3</sup>	7301	1579	186	41	17
Class 3 mg/m <sub>n</sub> <sup>3</sup>	7015	4967	3314	1596	541
Class 4 mg/m <sub>n</sub> <sup>3</sup>	6900	5413	5912	6231	5401
Class 5 mg/m <sub>n</sub> <sup>3</sup>	466	492	753	1070	1522

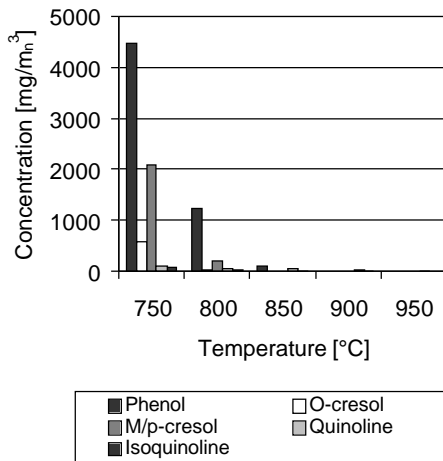
Gas samples taken after the cyclone; concentrations on dry basis; tar data correspond to a single measurement.

Table 4 reveals a decrease in total tar concentration by a factor of five, when the gasification temperature is increased from 750 to 950°C. Both the class 2 tars, compounds that exhibit high water solubility, and the class 1 tars decrease in concentration with increasing gasification temperature. The class 4 and class 5 tar concentrations, however, increase with increasing gasifier temperature, resulting in an increase in the tar dewpoint.

##### 4.2 Tar composition

In order to better understand the mechanisms of tar formation and decomposition inside the gasifier, the tar

compounds have been regrouped in the following 3 groups: alkyl-substituted tar compounds, heterocyclic tar compounds and PAH compounds without substituted groups. This grouping corresponds to the division made by Milne and Evans: primary tars, secondary tars, tertiary tars. In the scope of tar related problems of waste water production and tar condensation, the formation of PAH compounds and heterocyclic tar compounds are most interesting.

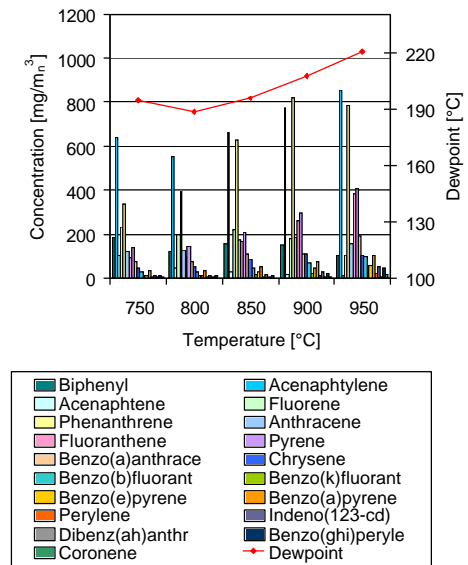


**Figure 2:** Heterocyclic tar compounds sampled after the cyclone at different gasification temperatures.

The results for the heterocyclic tar compounds are given in Figure 2. At 750°C, heterocyclic tars are produced in the freeboard of the gasifier. At 800°C, the conversion rate becomes appreciable, resulting in a decrease in heterocyclic tar concentrations in the freeboard. Already at a temperature of 850°C and a gas residence time of approx. 4 s (sampling after the cyclone), the heterocyclic tars are completely decomposed. At a residence time of approx. 1.3 s (sampling just above the bed), the temperature should be increased to 950°C to obtain the same effect.

The results for the PAH tar compounds without substituted groups are given in Figure 3. It appears that most PAH compounds are formed with increasing temperature from 750 to 900°C. Above 900°C, the concentration of large PAH compounds (pyrene-coronene) further increases, but the concentration of small PAH compounds like biphenyl and phenanthrene levels off or starts to decrease.

The naphthalene concentration (not shown because of its high values) continuously increases from 2 g/m<sup>3</sup> at 750°C to 3.5 g/m<sup>3</sup> at 900°C, and levels off to 3 g/m<sup>3</sup> at 950°C.

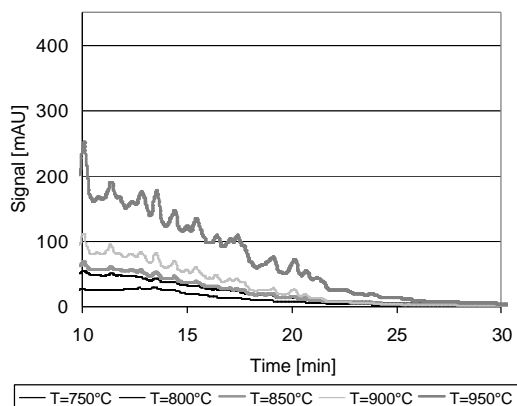


**Figure 3:** PAH tar compounds without substituted group sampled after the cyclone at different gasification temperatures.

#### 4.3 Mechanism of heavy tar formation

Two mechanisms may be responsible for the observed production of class 4 and class 5 tar compounds in Table 4 and the PAH compounds in Figure 3. On the one hand, class 5 tars could be the products from the cracking of even heavier tar compounds that form part of the GC-undetectable class 1 tars. This seems not to be contradicted by the experimental results, as it appears that the increase in class 5 tars is accompanied by a decrease in class 1 tars. On the other hand, the class 5 tars could also be the products of PAH growth reactions involving small PAH compounds or unsaturated hydrocarbons.

In order to verify the occurrence and importance of class 5 tar formation through the decomposition of class 1 tars, a HPLC analysis of the gravimetric tar fraction has been performed. This HPLC analysis allowed a qualitative analysis of PAH compounds with a molecular mass larger than coronene (i.e., tars heavier than class 5 tars). Figures 4 gives the response of the UV detector of the HPLC analyser as function of the retention time, starting after the elution of coronene at a retention time of 10 minutes.



**Figure 4:** HPLC analysis of gravimetric tar sampled after the cyclone at different gasification temperatures.

The ‘hill’ in the HPLC diagrams of Figures 4 is due to the presence of a fairly high concentration of light hydrocarbons in the gravimetric tar sample. Generally, these hydrocarbons have a lower retention time than coronene. Due to the high concentration, however, the hydrocarbons elute also at higher retention time, disturbing the diagram. The peaks on the ‘hills’ are of most interest, since they indicate the presence of hydrocarbons with a lower polarity than coronene, like large PAH compounds.

The absence of these peaks in the HPLC diagrams for the gravimetric tar samples taken at 750-800°C is an indication that at low temperature, large PAH compounds are hardly present in the tar sample. Above 850°C, the peaks increase considerably in height with increasing gasifier temperature. Apparently, above 850°C large PAH compounds (larger than coronene) are produced by the PAH growth reaction mechanism.

The increasing production of heavy PAH compounds with increasing temperature seems in conflict with the decreasing class 1 tar concentration. The class 1 tars were defined as tars that cannot be detected with a GC. Heavy non-polar PAH compounds stick on the non-polar GC column and are not eluted which makes the measurement of these compounds with the current GC method not possible. It was expected that these non-polar heavy PAH compounds would dominate the class 1 tar composition. However, the high concentration of class 1 tars at low gasification temperatures seems

not in agreement with the low concentration of heavy PAH compounds at these temperatures. It appears that the class 1 tar comprises a second group of tar compounds.

#### 4.4 Class 1 tar composition

It is postulated that this second group consists of primary and secondary tars according to the classification of Evans and Milne. The composition of primary tars is close to the composition of the biomass itself, and is determined by the monomer structures of the lignocellulose components in the biomass. Secondary tars are decomposition products of primary tars. Due to the high oxygen (and nitrogen) content of woody biomass, the primary and secondary tars will both have a relatively high oxygen (and nitrogen) content as well.

Furthermore, the primary and secondary tars, containing hetero-elements, generally have a high polarity, which makes them difficult to analyse with both GC-FID equipped with a non-polar column and with the applied HPLC method.

To verify this hypothesis, the gravimetric tars have been subjected to an ultimate analysis. The oxygen content of the class 1 tar was estimated from the gravimetric tar by subtracting the contribution of GC detectable tars to the oxygen content of the gravimetric tars. The oxygen content in the class 1 tars is higher than in the gravimetric tars in all cases, and remains constant or even increases with increasing bed temperature. Apparently, the oxygen content in the GC-detectable tar fraction of the gravimetric tars is considerably lower than in the class 1 tars.

In conclusion, class 1 tar indeed appears to contain a substantial fraction of hetero-elements containing compounds, which are likely to be primary or secondary tars. This also implies that the water solubility of tars may be underestimated considerably when the evaluation is based on the class 2 tar content only.

## 6 CONCLUSION AND APPLICATION

The application of the product gas is determining the use of a primary measure. In indirect co-firing, the product gas fired in the main (coal-fired) boiler. Generally, the

product gas temperature is kept as high as possible to prevent tar-induced problems. In that case, the gas will not be cooled to temperatures below the water dewpoint. Therefore, tars with a high water solubility (class 2) do not pose a problem. However, the gas cooling will require in most cases a mild control of the heavy PAH content in the product gas to prevent fouling.

More advanced applications, such as firing the product gas in a gas engine or a gas turbine, or using the product gas for the production of gaseous or liquid fuels, generally require a much cleaner product gas and often require the product gas to be cooled down to (near-) ambient temperature, below the water dewpoint. In these cases, generally, primary measures may be applied to optimise the tar composition for secondary removal processes or for subsequent gas cleaning processes in general. For example, if water scrubbing is applied, primary measures may be used to fully decompose the highly water-soluble class 2 tars, leading to a considerable reduction in wastewater treatment cost.

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