Strategies for Tar Reduction in Fuel-Gases and Synthesis-Gases from Biomass Gasification

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Abstract: Product gas components such as condensable substances, particles and, depending on the gas utilization, certain trace contaminants are responsible for the high gas cleaning demands in gasification technology. In this paper strategies to encounter this challenge are subject of discussion. Primary measures for tar reduction within the gasifier are covered as well as secondary steps for cleaning the produced gases downstream of the gasification reactor. In order to evaluate the success of these measures standardized tar measurement methods have to be used. A short overview about existing and new methods is given. The overall success of gasification technology for biomass feedstocks will depend on technological aspects discussed but also on the biomass supply ensuring all year round good quality and on infrastructure for heat (cold), gas and power transmission or storage respectively.

Keywords: biomass, tar, gasification, fuel gas, synthesis gas, gas cleaning, gas monitoring.

1. Introduction

Gasification is a promising but also very challenging technology for mainly decentralized energetic biomass utilization. At small to medium scale combined heat and power production is the main form of gas utilization. Conversion efficiencies to electricity are higher than in comparable combustion plants with steam generation and conversion into electricity by application of steam turbines or steam engines. Also the multiple varieties of synthesis gas application from producing methane, methanol or Fischer-Tropsch-fuels make gasification attractive. Several medium to large scale applications for synthetic fuel production, generation of SNG or for co-firing are in development or demonstration. Newer concepts of poly-generation [1] even propose different ways of gas utilization in one plant to achieve high overall efficiencies all year around. In figure 1 gasification and different pathways of gas utilization are depicted schematically.

Many reactor concepts for gasifiers exist which will not be covered in depth in this paper. The reader may be referred to the literature for reviewing the main gasifier plant concepts [2-4].

If the produced gases are used in industrial applications like cement plants or as reducing agents in chemical plants or in metallurgic processes gas cleaning can be very limited. Highest requirements are given, when catalysts come into use for gas synthesis or by application of e. g. low temperature fuel cells.

The drawback of gasification compared with other technologies like combustion is the high gas cleaning effort that has to be undertaken in order to maintain all functions of the plant over time for assuring economic operation. Anyhow the high specific investment cost especially for smaller plants question economics already in early stages of process development.

In this paper, different strategies for dealing with condensables, e.g. tar and water, are discussed. There is no single or one simple solution to overcome all challenges related with these substances. A successful application of gasification technology depends on several influencing parameters whose requirements have to be met.

2. Challenging components in biomass gasification product gases

The most problematic "substance" in gasification technologies is considered to be tar. When condensing together with tar water vapor in the gas can be troublesome as well because contaminated water is generated. Also by condensing within a washer, the amount of water that has to be dealt with increases.

Furthermore there is alkali components which are present as vapors at certain reaction temperatures and which are able to form deposits.

Also present in the gas in different quantities are solid particles like unreacted char or mineral components (ash). Together with the condensables these may form agglomerates within the system. When catalytic applications like tar reforming, use of fuel cells or gas synthesis are planned the gas has to be cleaned further from trace components containing sulfur, nitrogen or chlorine. For gas synthesizes further the stoichiometric ratio of hydrogen to carbon monoxide has to be adjusted by water gas shift reaction where also catalyst may be applied.

3. Tar

Tar is a synonym for a sticky, brownish to black, strong smelling highly viscous liquid or nearly solid substance which can be found within systems converting organic materials at high temperatures. In the following tar is considered. which evolves in biomass gasification installations.

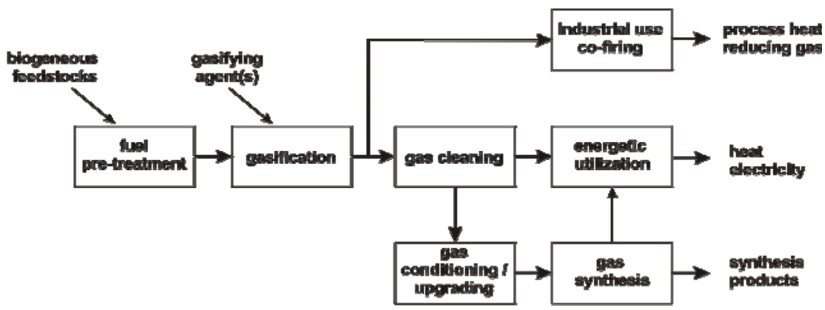

Figure 1. Gasification of biomass for different utilization pathways (adapted from Hofbauer 2009).

It is a mixture of mainly hydrocarbons which condensed from the gas phase on cool surfaces or particles. The composition of tar depends on one hand on the properties of the fuel such as particle size and its distribution, the elemental composition, the content of minerals and water. It is further influenced by the reactor design and the gasification agent. Looking at a fuel particle entering the reactor tar evolution depends on how fast it heats up, on the maximum temperature it reaches, on the surrounding gaseous atmosphere to further react with (e.g. the amount of free oxygen, other reactive agents or the volatile components released from the particle. At higher reaction temperatures above 700°C aromatic and polycyclic aromatic hydrocarbons are formed in the gasifier. There are significant differences in tar from pyrolysis or updraft moving (fixed) bed gasifiers compared with tar generated in downdraft or fluidized bed gasifiers. The latter are generated at higher temperatures. They consist mainly of PAK and have less oxygen containing species. Carpenter et al. [5] show this temperature dependence clearly.

4. Strategies for dealing with tar in biomass gasification technology

The strategies for dealing with the challenge of tar are quite different. The easiest is the application of a high-temperature downstream process which is not affected by tar like co-firing [2,6], direct industrial use e.g. in cement plants [2,6] or the direct use in gas turbine combustors in pressurized systems [2,6-8]. Experiments with solid oxide fuel cells showed that these systems were surprisingly resistant against tar related fowling problems [9].

If the downstream gas utilization process would be negatively affected by depositions of tar two principle routes or combinations thereof are possible:

1. As little as possible tar generation in the reactor itself:
   a. Small, well designed downstream moving bed gasifiers with pilot filter
   b. Staged gasification systems,
   c. Use of catalytic active bed materials e. g. in fluidized bed gasifiers,
   d. “tar free” gasification by applying high temperatures e.g. entrained flow gasification.
2. Down-stream tar removal:
   e. Tar conversion / reforming with catalysts,
   f. Tar removal by gas washing or adsorption.

One approach of several researchers and developers is to produce as little tar as possible in the reactor. This can be done quite well in small downdraft gasifiers (30 to a few 100 kW) where an even distribution of air in the oxidizing zone is achieved and tar is successfully being converted. Such a system still needs a pilot filter that holds back remaining tar and requires regular maintenance.

Another approach is the application of staged gasification (Viking Gasifier [10-11], TK Energi AS [12], CleanSTGas [13], Xylowatt [14] and others). Here the primary pyrolysis process and the following oxidation and reduction reaction steps are separated spatially. This way very low concentration of condensable hydrocarbons can be achieved. The remaining species are also condensed on separated particles in the subsequent filter systems.

In fluidized bed gasifiers active bed material can be applied to achieve lower overall tar contents in the produced raw gases. Dolomite or olivine are naturally occurring minerals which are used for this purpose. There is quite substantial literature available about this topic [15-17].

Processes with two combined fluidized beds have gained interest in the past years [18-21]. Here solid inert material is transferred between a gasification and a combustion section as heat carrier. This is one way to perform allothermal steam gasification to produce nearly nitrogen free synthesis gas without using pure oxygen. The renewed interest refers more towards using reactive bed material which can introduce oxygen from the combustion section (oxygen donor process) or remove CO2 from the gasification section (CO_2 acceptor process or nowadays Adsorption Enhanced Reforming – AER [21]). Such processes are also referred to as chemical looping. In the AER process which is operated at rather low temperatures it was found that the bed material is not only capable of capturing CO_2, it also lowered the content of tar in the product gas. So the strategy of using two fluidized beds has good options to actively influence the reactions towards the desired products.

Catalytic conversion of tar can also be applied downstream of the gasifier. Corella et al. [22-23] recommend to lower the tar content in the gas with primary measures to less than 2 g/Nm³ in the product gas to avoid char deposits on the conversion catalysts. Larger scale testing with honeycomb catalysts has been carried out by Fraunhofer UMSICHT in Germany and at a plant in Austria [24]. There has been research with many catalytic active substances and also some long term tests but still there is no system available commercially. Some reviews about catalytic tar decomposition are available [15,25].

The conventional form for tar removal is wet separation with washing agents. Historically water was used. This will be contaminated heavily with soluble components like phenols or ammonia but also by the mainly not soluble polycyclic aromatic hydrocarbons (PAK). Anyway this mixture needs to be separated and further treated before disposing it to the environment.

The danish Haboøre-project [6,26] uses an updraft gasifier which produces significant amounts of tar. This tar however is more comparable to pyrolysis liquids and contains less PAH than the more common downdraft of fluidized bed gasifiers. The rheology of that kind of tar is beneficial which makes handling easier compared with other tar residues. The tar water mixture is treated with a technology called TARWATC [27]. The separated tar fraction is stored and used for co-firing in the winter season to produce district heat.

Another way is proposed by the research center of the Netherlands (ECN) and the Dutch company Dahlman. Together they developed a tar cleaning system (OLGA) [28] which separates heavy and light tars and keeps them as much as possible away from the also condensing water. The system is comparably complex and therefore mainly suited for larger scale applications. It is intended to be combined with a two stage fluidized bed gasification system called MILENA [29] where steam gasification and combustion of solid residues are combined for syngas production. This system is optimized for a high cold gas efficiency and takes into account that higher levels of tar are present in the gas. The collected heavy tar might be recycled back together with the organic washing liquid to the combustor section of the reactor. This keeps the efficiency high and avoids hazardous material disposal.

Other recent developments applying gas washing also make use of organic solvents or washing agents like plant oil or biodiesel (fatty acid methyl ester (FAME) from plant oils). The FICFB (fast internally circulating fluidized bed) plant Güssing and Oberwart [1] in Austria and several projects on the way who use this technology make use of RME (rape seed oil methyl ester) washing.

In conventional gas scrubbers e. g. in coking plants for coal conversion an oil fraction from the separated tar is used in combination with water. This oily water seems to have good capabilities to wash out a large variety of species. Most probably this will be limited to larger applications where intensive gas cleaning and waste water treatment is affordable.

It has to be noticed once more that gasification is a multivariable process that reacts like a network of depending variables. If one variable is changed several other will be effected. Corella et al. [23] specify as one input variable of this system the operator because the success of the operation depends in many cases on the experience of the team running a plant.

5. Tar measurement and tar monitoring

The success of the primary and secondary methods to eliminate tar substances from the gas phase can only be determined by well working analytical methods. In order to achieve comparable results for measurements on different gasification systems throughout the world, the “tar guideline” [30] was developed and established as a European pre-normative standard (CEN/TS 15439) [31]. This method intends to get reproducible results by specifying setup, sampling and a laboratory analysis. It contains experience from several research groups and was adapted in a way to be applicable in many countries. It is not very easy to handle which might be one reason why it is still not so widely established. Nevertheless it is highly recommendable at least to compare other or new methods with the standard to know how much results differ from it.

Another way for tar sampling is the solid phase adsorption method (SPA) which was introduced by Brage et al. [32] Tar is condensed on an amino-phase adsorbent close to the sampling point. Sampling takes about one minute and is therefore much quicker than the guideline method which samples, depending on the tar species amount in the gas, for about 20 to 60 minutes (~30 min average for tar loads in the low gram range). The SPA-method allows for several subsequent samples to be taken and is rather easy to handle for the researcher in the field. The latter desorption of the analytes requires again skilled laboratory personal and if the sample can’t be transferred to the lab within a few hours information about lighter tar species is lost.

Online measurement tools for tar species in the gas phase were developed in the past ten years. Moersch et al. [33] proposed a measurement method using flame ionisation detection and two separate gas streams one being heated and one containing a cooled filter. Tar is adsorbed on the filter so that a differential signal can be evaluated from a tar loaded gas phase and a “tar-free” gas. Drawback of the method is a changing pressure drop with increasing tar deposits.

The research center of the Netherlands (ECN) proposed a different approach [34]. Here is not the tar content but the tar dew-point the value of interest. From a practical point of view the gas is well to handle if no tar will condense under normal operation conditions. This could be a measure for the effectiveness of gas cleaning devices or the process conditions of certain places within a plant.

For several applications especially in research and development more detailed information about the tar species are subject of interest. Mass spectrometers are for instance applied for analysis of catalytic tar decomposition [35].

For quantitative measurements the combination of gas chromatography (GC) and mass spectrometry (MS) is very useful. The time for the analysis is longer (~30 min) compared with parts of seconds in the MBMS [35] or time of flight MS but the individual substances can be calibrated well. The GC/MS system adapted by Neubauer [36] further has the possibility to work with photon ionization to shorten the MS separation and to allow for short analysis times as well with the same instrument. Mass spectrometers are very versatile tools in gasification research but they are very expensive.

For being able to measure at gasifiers in commercial operation, more rugged and easy to handle tools are necessary. Tar dew point analyzer, tar Analyzer by University of Stuttgart were first approaches. In the past years development of tools based on laser induced fluorescence was carried out at TU Berlin [37-38], TU Graz [39] and TU Munich [40] in different research projects. Due to ongoing developments in optical technology rather small and affordable tools can be expected for the near future.

6. Use of analytical tools for research in tar reduction strategies

In the last two sections approaches to minimize the tar content in gasification product gases for utilization as fuel or for further gas synthesis were presented. In this section some results from a recent project incorporating a liquid quench and a wet ESP for tar separation from the gas will be shown. Van Paasen et al. [41] published a parametric study of such a system. The ESP used in the ERA-NET project [42] was somewhat smaller. Here the already mentioned GC/MS was connected directly to the plant for online tar analysis. Samples were taken before and after the quench/ESP System.

In Figure 2 two ion-chromatograms are shown. In the upper one the peaks from tar substances in the raw gas are visible. From the left to the right the molecular mass increases in the same way as the number of aromatic rings. The largest Peak on the left hand side is benzene, followed by mono-aromatic up to retention time of about 8 minutes where naphthalene, the smallest PAK, eluates. Comparing with the lower chromatogram of the cleaned gas the naphthalene peak is smaller. The total tar content has decreased and especially the heavy tars, PAK larger than Naphthalene have disappeared nearly completely. It can further be observed that the light tar components and especially the benzene are not very much affected by the gas cleaning applied.

Further both methods for online tar analysis (GC/MS) and for online tar monitoring (LIF-based CON-TAR) are used for further ongoing research in tar reduction. One approach under examination is the use of char which was generated in the gasification process or as previously mentioned generated in a separate pyrolysis step apart from the gasification reactor. Char is known to be able to lower tar concentrations when letting gas passing over hot beds of char. The char inventory in a fluidized bed is influencing the gasification reactions [43].

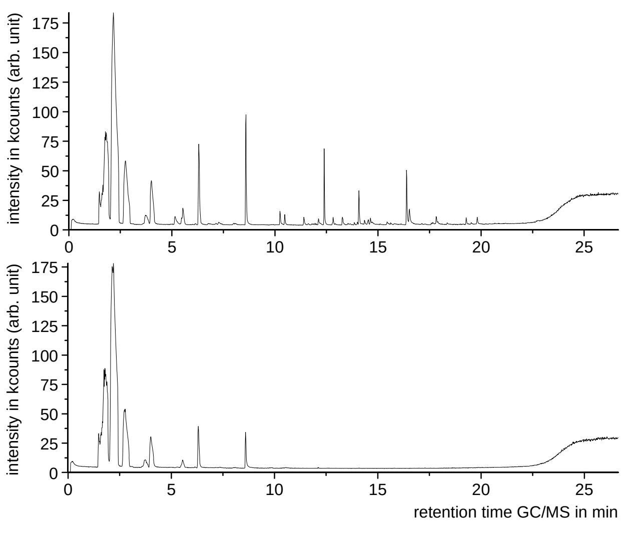

Figure 2. GC/MS spectra from online tar-measurements before and after a wet ESP.

7. Conclusion

Summarizing it can be said that there is no single solution or strategy to solve tar related challenges in biomass gasification. Solutions depend on gas utilization planned, desired scale of the plant from the kW to the tens of MW range, and from the right choice of a gasification reactor concept fitting the points above and being suitable for the available feedstock. Analytical tools are necessary for further development of gasification technology to become successful and to fulfill the high expectations.

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