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Teerbildung und Teerkonversion bei der Biomassevergasung - Anwendung der nasschemischen Teerbestimmung nach CEN-Standard



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Abstract

Introduction

The gasification of solid, liquid or gaseous fuels to a synthesis gas for utilisation in energetic, thermic or chemical processes is not a new technology. After a short wide spread use in Germany due to energy limitations in second world war, gasification has been used to produce synthetic diesel (Fisher-Tropsch-Synthesis) in South Africa since the 1950's. Currently there's an installed capacity of about 60 GW_{th} of synthesis gas power world-wide. Products are preferably liquid fuels, ammonia, methanol, hydrogen and also electricity. For fuel, mainly coal, waste from crude oil refineries and natural gas is used. In this case biomass has only a negligible share.

The first patents on gasification were already issued in the 17th and 18th century. In the 19th century, the first peat and coal driven gasifiers were used for iron production in France on a commercial scale. In 1945 biomass gasification was of particular interest, a company called *Imbert* produced more than 500,000 wood gasifiers, largely used in the transportation sector for driving cars and trucks.

Since the oil crisis in the 80's, the acceptance of the Kyoto-Protocol and the related declarations to reduce CO₂-emissions globally, biomass gasification came again in the focus of research and partly also of the industry.

The main advantage of biomass gasification compared to combustion and the utilisation in a conventional steam turbine process is the higher efficiency and the simultaneous generation of electricity and heat and the decentralised use in small scale facilities even below 100 KW_{el}. In the range up to 20 MW_{el} there's the potential to achieve an efficiency of 41 % with a pressurised fluidised-bed gasifier. A conventional modern wood-fired steam power plant would only achieve an efficiency of 34 %. Also in the small scale of about 500 KW_{el} an efficiency of 30 % is possible. Here gas engines are used instead of gas turbines.

To this day a commercial break-through of biomass gasification was not realized. Both technical and economical reasons have to be mentioned:

- Coal is at present considerably cheaper compared to the distributed biomass fuel sources. Besides the general problem to introduce new processes in a rather conservative branch of industry this is a major disadvantage.
- The utilisation of the synthesis gas in gas engines or turbines requires a complex gas cleaning process for the removal of the condensable hydrocarbons that are formed during gasification. The spectrum of these mainly aromatic chemicals is generally called tar. When the dew point of these compounds is undershot, it can result in the formation of deposits and fouling, what makes a reliable, unmanned operation of the plant impossible. The gas cleanup systems from large coal gasifiers can be hardly used here and are usually also too expensive and too complex.

Therefore the research and development focuses on gas cleaning. In recent years various primary and secondary methods for different biomass gasifiers have been evaluated and to a minor degree also successfully operated during several years.

Problem formulation

One basic problem for all investigations on the efficiency of tar reduction measures was actually the determination of the tar content itself. Completely different procedures of the multiple institutes for the primarily wet-chemical sampling and likewise for the following analysis of the tar solution led to different results. Among other things, the solvent and the temperature of the cooling bath, in which the impinger bottles sit, is to be mentioned. The results were not comparable and conclusive statements on the gas quality were not feasible. This had an impact on warranty claims of manufacturers of gas engines and turbines who demanded very low tar limits in the producer gas.

A project of the European Union addressed this problem since 1998 and since then, a detailed method was developed. This standard for tar measurement, also known as the *Tar Guideline*, is available since 2001 and is in the process to become a CEN-Standard. CEN is the abbreviation for ‘Comité Européen de Normalisation’. In English it’s known as ‘European Committee for Standardization’. This committee was founded in 1961 by the national institutes for standardization to produce technical standards on an European level.

With this standard for tar measurement, it is now possible to get an insight into the

partly unexplained phenomena of tar formation and tar conversion and to do important basic research to achieve conclusions for the successful operation and design of gas cleaning systems.

Objective

On the basis of the preliminary standard for tar measurement and the possibilities offered by it, the tasks of work were defined within two chronological steps.

The first task addresses issues of construction and testing of the tar measurement method:

- How can the measurement system be constructed as a reliable, simple and transportable unit ?
- How can the measurement system be extended for the requirements regarding steam gasification of biomass (so far the standardisation only addressed the gasification with air) ?
- In which order of magnitude is the measurement error ?

After addressing these issues, investigations at various gasifiers should be carried out. Here, a practical approach was chosen. It was focused on basic research, but always related to the practicable limitations and possibilities to adapt real gasifier systems and gas cleaning devices. The following important questions regarding tar formation and conversion during biomass gasification were to be answered:

- What is the influence of fuel characteristics ?
- What is the influence of gasification parameters on the different reactor types, like temperature, gasification agent, air ratio and, if applicable, additives with catalytic properties ?
- What is the influence of secondary tar reduction measures such as scrubbers and catalysts ?

Finally, with those results the basics of tar formation and tar conversion during biomass gasification should be compiled. For example, how the tar formation in the reactors is taking place; when and how high tar concentrations can be expected; what can be done for the minimisation; where are the limits of the reactors themselves and finally how

successful secondary measures can be adopted to work efficiently.

Summary of the results

The developed tar sampling according to the CEN-Standard proved as a reliable tool to extract and trap the tars with a wet-chemical method in a solvent from the synthesis gas of various gasification processes. The extension of the measurement system for biomass steam gasification was successfully accomplished. An additional cooling bath and the extension of the cooling coil in the liquid quench proved to be sufficient and easy to handle. Furthermore the uncertainties which can be expected for the two methods of analysis were evaluated and calculated.

In the test program, the tar formation and tar conversion in different reactor types was examined. The varied parameters were the reactor temperature (from 400 to 1000 °C), different gasification agents, catalysts and the use of secondary reduction measures. Together with the knowledge from literature the experiments resulted in explanations for many open questions on biomass gasification and showed issues that can be addressed in the different types of reactors. Thanks to the standardized tar sampling and analysis procedure, the values are internally and internationally comparable.

The introduction of a tar index, that describes the ratio of tar determined by gravimetric analysis and GC-MS analysis, proved itself as a useful value for the interpretation of the results.

The main findings are:

Basic Insights on tar formation and tar conversion

The most important influence on the composition of the GC-MS detectable tars is the *local temperature* the tars are “exposed“ to. At temperatures below 700 °C (if no catalysts are present) most tars are macromolecular, so called primary tars that can be analysed only gravimetrically. As identifiable tar substances at these temperatures phenol, toluene and partly guaiacol and 4-methylguaiacol have to be mentioned. At temperatures above 800 °C up to 1000 °C the primary tars are thermally unstable and decompose into non condensable gases or form new secondary or tertiary tar compounds from the products of decomposition. The most important secondary tars that

can be identified are indene, naphthalene and phenanthrene.

The *residence time* of the tars in the respective temperature range is also of major importance. For a sufficient reduction of tar without any additional catalyst, residence times far above of 0,2 seconds and temperatures of above 1000 °C are necessary. In literature it can be found that residence times in the range of above 3 seconds and temperatures of above 1100 °C should be chosen.

In practical gasification applications the *fuel characteristics* of typical wood-like biomass hardly affect the tar formation. A higher content of *cellulose* in the fuel could have small tar-reducing effects. A higher *content of water* affects the tars only indirectly via the heat balance in the reactor and the hereby changed temperatures.

Tars do not only originate from the *lignin share* in the biomass but also from the conversion products of *cellulose*. Guaiacol and 4-methylguaiacol are however substances that derive only directly from lignin.

Catalysts like CaO - based minerals can reduce tars effectively at an order of magnitude. The GC-MS detectable tars are *not selectively* but uniformly reduced. Furthermore, the introduction of a tar index illustrates that catalysts *preferably reduce* the high-molecular *primary tars*, that are not detectable with GC-MS analysis. The application of this finding in fluidised bed technology works at typical operating temperatures, as well as in the new AER-Process at approx. 650 to 670 °C. This proves the effect of CaO as a catalyst. As soon as CaO is present predominantly as CaCO₃, the tar reduction is no longer given.

The difference between steam or air as a *gasification agent* has got a more crucial effect on the non-condensable gases, than on the total tar quantity produced. A higher air ratio provides a non-selective tar reduction, but reduces the heating value of the synthesis gas.

Secondary tar reduction measures, like a *diesel scrubber* and a *combination of fixed bed catalysts* based on CaO and Ni successfully demonstrate how tars can be removed or catalytically converted to non-condensable gases. A suitable control of the reduction system and an already reduced tar concentration at the gas inlet of the system is important for a reliable operation.

Implications for existing types of gasifiers and secondary measures

With the achieved results the tar composition and tar quantity in the different types of gasifiers can be retraced.

The *fixed bed co-current gasifier* provides a tar content below 2 g/Nm³ in practical conditions. The high temperature and the flow through a hot fixed bed of catalytically active charcoal makes this possible. This happens only as long as no streaks of tereous gases from colder areas are passing by. Therefore special attention has to be put on particle size and air distribution to keep an optimal flow field.

For the *fixed bed counter-current gasifier* tar contents far over 10 g/Nm³ and a completely different tar composition exists due to the different local reaction guidance and reaction areas. The hot gas from the combustion zone flows into the pyrolysis zone and takes large quantities of primary tars with itself. A primary tar reduction in this reactor is not possible. However, the primary tars are often simpler to separate from the synthesis gas than the tertiary tars, since for example the primary and/or secondary tar component toluene can serve as a solvent for heavier components.

The results show, that the *entrained flow reactor* is only useful for gasification at very high temperatures with steam and especially oxygen as a gasification agent, like it was demonstrated on an industrial scale with coal as a fuel. For biomass air gasification and lower temperatures, this type of reactor was only successfully used within two-stage reactor systems. These systems consist normally of a primary pyrolysis reactor and a kind of entrained flow reactor. With two of these systems, a clean synthesis gas that can be directly used in gas engines was created without any secondary tar minimisation measures.

Because of the limitation of operating temperatures (approx. 850 to 900 °C due to possible bed agglomeration), the *fluidised-bed technology* offers no possibility for a sufficient thermal tar reduction. However, tar-reducing catalytic additives can be added to the fluidised bed or a catalytically active material can replace the bed completely. In the test runs, especially CaO-based substances like calcite showed promising performance. Regarding the tar reduction, almost a factor of 10 was reached compared to silicate sand. From literature further effective materials are known such as olivine. The absorption enhanced reforming process with steam (AER) at temperatures of 650 to 700 °C with calcined bed materials on CaO-basis shows high contents of hydrogen with comparable tar contents as in high temperature fluidised beds (approx. 850 to

900 °C) without catalysts.

In general it can be said that so far only with the two-stage reactors a tar quantity level was achieved that doesn't necessitate secondary tar reduction measures. Scrubbers with rapeseed oil methyl ester or diesel work both in the test runs and in plant operation for many years. The tar minimisation achieved with fixed bed catalysts on CaO and Ni-basis likewise promises success for reaching the required tar quantity levels, but is very expensive, particularly when Ni-materials are used.

Outlook

The wet-chemical tar sampling and analysis method proved to be a good tool for the evaluation of gasifiers and gas cleanup facilities for synthesis gas.

The *limitation of the method* was shown regarding its use to determine the usability of the synthesis gas in chemical processes. In such processes, hydrocarbons can play a role that don't fall under the definition of tar, e.g. benzene. Benzene is considered likewise as a soot precursor and can be present among others in a typical gasification process in higher quantities than all other aromatic compounds. This can be important for the downstream conversion of the synthesis gas to liquid or gaseous fuels in catalytic reactors. For such applications the sampling and the analysis method must be modified accordingly, in order to sufficiently detect also these substances. Aside from the tars, catalyst poisons such as H₂S have to be considered. This and other more or less relevant trace materials are formed also during biomass gasification, depending on the fuel and the gasification parameters.

For the use of alternative *catalytic bed materials* in fluidised bed reactors *long term test runs* with a focus on mechanical and chemical stability have to be carried out. Only these can supply sufficient information about their suitability.

A further insufficiently clarified open question is the determined dependence of the tar formation and tar conversion on the *residence time*. Here further investigations, primarily not with model substances, but with real tars, are necessary in order to gain further insight. A temperature range from 400 to 1300 °C and residence times less than 100 milliseconds up to 10 seconds or more would be useful.

