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COLD PLASMAS FOR GASEOUS POLLUTANT CONTROL AS A BENCHMARK FOR THEIR USE IN TAR ABATEMENT IN SYNGAS

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Introduction

Gasification is a key tool for the valorisation of carbon-rich materials, which includes the organic fraction of wastes found in landfills. Because of that, in Enhanced Landfill Mining (ELFM) the production of high-quality syngas is crucial from the energetic, environmental and economic point of view. Currently the syngas produced from waste and biomass is generally co-fired in boilers, but an improvement on its quality could allow to use it in more efficient combustion processes such as gas engines, gas turbines or fuel cells and even in organic synthesis
processes such as Fischer-Tropsch. The most problematic barrier for producing high-quality syngas is the tar content.[17] Tars are condensable hydrocarbons generated as a by-product of gasification and are defined as all organic compounds with molecular weight greater than benzene.[6] The toxicity and condensation of tars cause lots of problems such as clogging in injectors, fouling in piping systems, and generation of additional waste streams reducing the operability of the processes and increasing dramatically maintenance costs.

Tars, PAHs and VOCs

In this paper, a review is made on Polyaromatic Hydrocarbons (PAHs), Volatile Organic Compounds (VOCs) and tars. First of all, tars are all organic substances with a molecular weight higher than benzene.[6] Most of the time, the tars of interest are not the same in different studies, because tar composition changes along with process variables in gasification processes, reactor configurations and type of feedstock used. Although benzene is not by definition a tar, in numerous studies focused on tar abatement, benzene is considered as a major component in order to determine the tar removal performance. The second family of compounds, PAHs, refers to compounds consisting of only carbon and hydrogen atoms, and comprising two or more benzene rings bonded in linear, cluster, or angular arrangements.[2,7] They consist of at least two single or fused aromatic rings with a pair of carbon atoms shared between rings.

Table 1: Different molecules classified as VOCs, PAHs and tars

Compound	VOC	PAH	Tar	Compound	VOC	PAH	Tar
Benzo-pyrene		x	x	Indeno[1,2,3-cd]pyrene		x	x
Acenaphthylene		x	x	5-Methyl chrysene		x	x
Anthracene		x	x	Phenanthrene		x	x
Benz[a]anthracene		x	x	Pyrene		x	x
Benzo[b]anthracene		x	x	Acenaphthene	x	x	x
Benzo[b]fluoranthene		x	x	Naphthalene	x	x	x
Benzo[j]fluoranthene		x	x	Ethylbenzene	x		x
Benzo[k]fluoranthene		x	x	Toluol	x		x
Benzo[c]fluorene		x	x	MBK	x		x
Benzo[ghi]perylene		x	x	Pyridine	x		x
Chrysene		x	x	Phenols	x		x
Cyclopenta		x	x	Xylene	x		x
Cyclopenta[cd]pyrene		x	x	Toluene	x		x
Dibenz[a,h]anthracene		x	x	Hexanal	x		
Dibenzo[a,e]pyrene		x	x	Ethanol	x		
Dibenzo[a,h]pyrene		x	x	2-propanol	x		
Dibenzo[a,i]pyrene		x	x	Acetone	x		
Dibenzo[a,l]pyrene		x	x	Formadehyde	x		
Fluoranthene		x	x	Butane	x		
Fluorene		x	x	Propane	x		

Although there are many PAHs, most regulations, analyses, and data reports focus on only a limited number of PAHs, typically between 14 and 20 individual PAH compounds (*cf.* Table 1).[1] The most extensively studied PAHs among the presented ones are 7, 12-dimethylbenzo anthracene (DMBA) and benzo(a) pyrene (BaP).[1,3] The last family of compounds are the VOCs. The US Environmental Protection Agency (EPA) defines them as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.[21] However, the European Union uses other criteria in its definition, defining them as any organic compound having an initial boiling point less than or equal to 250°C measured at a standard atmospheric pressure of 101.3 kPa.[9] Even when both definitions of VOCs are based on a different criterion (photo-chemistry and boiling point), all have a general character of low boiling point, high vapour pressure and strong photo-reactivity. Practically all the compounds that fall into one definition, fulfil the criteria of the other one.

To summarise, the terms Polyaromatic Hydrocarbons (PAHs), Volatile Organic Compounds (VOCs) and tars, encompass families of compounds, comprising hundreds of different molecules. Some substances can be considered to belong just to one of these definitions, while others may belong to two or three families at the same time (*cf.* Table 1). The classification could appear ambiguous, especially since there is no consensus concerning the exact definition of PAHs, VOCs and tars. Howver, some common points of interest are defined. The most recent results of non-thermal plasma (NTP) techniques used for PAHs, VOCs and tar removal will be presented, underlying the remaining challenge of NTP for being used as a removal technique for tars.

Non-thermal plasma (NTP) technologies

There are two main NTP techniques for plasma removal of pollutants: Dielectric Barrier Discharge (DBD) and Corona. DBD plasma is built using an AC plasma source and a barrier discharge in one of the electrodes, while Corona uses a DC plasma source and a high-voltage pulse generation circuit (*cf.* Figure 1). When catalysts are added to these configurations, they can be attached in pellets forming a packed-bed, or as a powder in a thin layer coating one of the electrodes.[22] Cylindrical DBD configurations as well as pulsed corona discharges in VOCs removal have been demonstrated in numerous occasions in literature, especially with TCE[8], benzene[5,18,23], and toluene[5,16,24,26], as well as for NOx and SOx.[13,15] On the other hand, the examples of NTP for PAHs removal are scarcer, but they tend to examine groups of PAHs rather than an individual PAH, usually including acenaphthene and anthracene.[4,25] The most recent research has been focused on combining NTP with biofilters[19] and catalysts.[8]

As it was already mentioned, some compounds are considered to belong to different families, like toluene that is a VOC and a tar. Toluene has been extensively studied using NTP removal technologies as a VOC[5,16,24,26], but toluene is also removed using NTP, considering it as a model tar compound.[10-12] However, the conditions at which tar removal processes occur are very different compared to the ones for VOC removal The same goes for naphthalene and benzene removal. Tar removal happens at gasification conditions, which means very high temperatures (usually above 800°C) and different atmospheres (including large amounts of CH_4, CO, CO_2 and H_2O). The difference in the process conditions does not allow to directly extrapolate results from one study to another, which poses the challenge of evaluating NTP technologies for VOCs and PAHs removal in gasification conditions that are more extreme.

The removal of heavy tars seems to be a second challenge with NTP technologies, because the compounds investigated in the literature are usually light compared with

many tar components that are problematic, like gravimetric tars. Two other factors that represent a challenge to adapt NTP technologies to tars are the concentrations of pollutants (that are much higher than the ones considered in PAHs and VOCs removal) and the very heterogeneous chemistry of tars (compared with the chemistry of VOCs and PAHs), which could affect the performance of NTP removal.

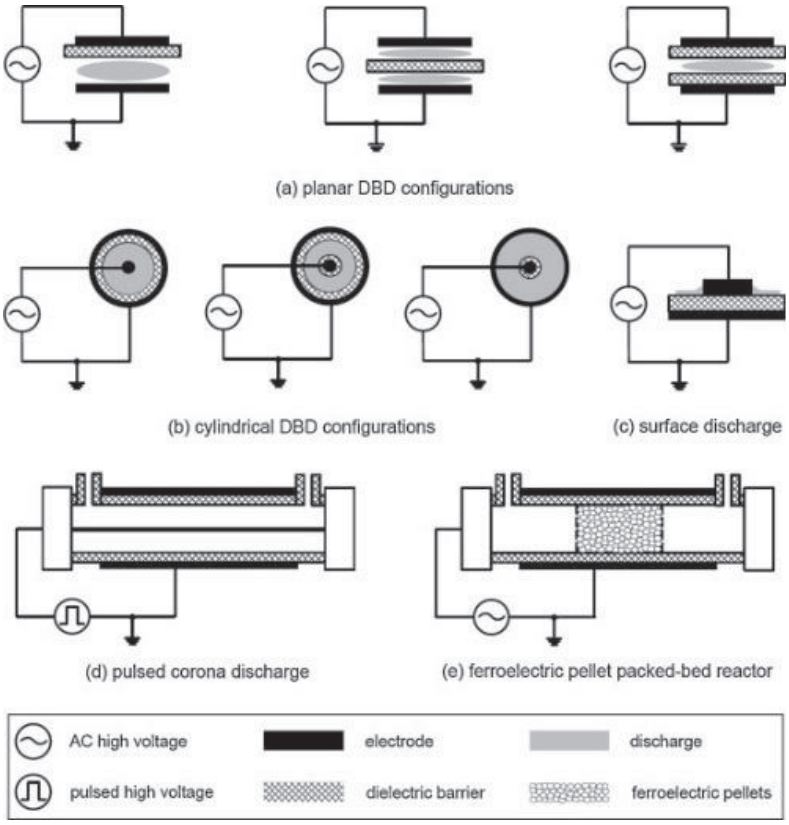

Figure 1: Different types of plasma configurations. Modified from Vandenbroucke *et al.*[22]

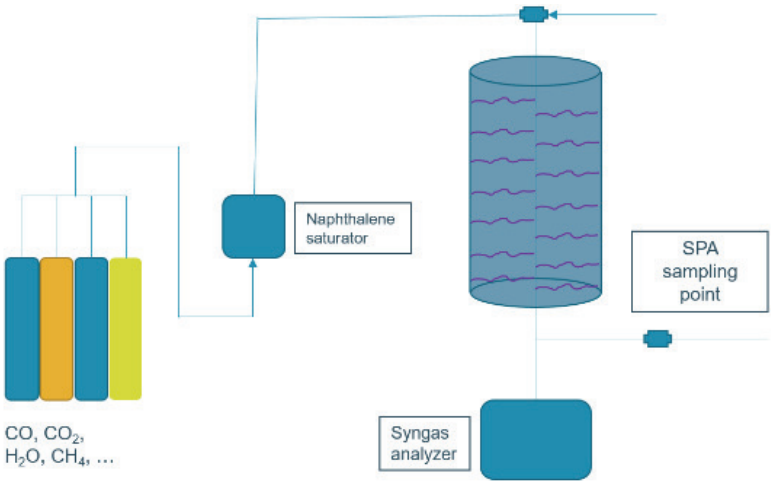

Figure 2: Corona plasma experimental setup

Due to the reasons given above, at KU Leuven a Corona Plasma unit able to reproduce the conditions at the exit of gasifiers has been built. The main idea is to evaluate if a corona plasma could be used in a secondary unit for tar removal just at the exit of the gasifier, and to evaluate the process parameters on which tars are better eliminated, focusing on an energy-efficient tar removal. The setup is presented in Figure 2. Model tar compounds will be used at the beginning, in a simple atmosphere increasing stepwise the complexity of the atmosphere and the tar composition in order to get an understanding of the influence of the different compounds on the plasma removal efficiency.

Conclusion

PAH and VOCs are two families of compounds of special interest because of their toxicity and reactivity, and NTP techniques have been used to remove some compounds belonging to these families. The previous results with specific compounds, that also belong to the category of tars, show the potential of non-thermal plasmas for removing tar-like compounds. However, there must be studies more focused on removing such pollutants in real gasification conditions, on which tars are found, and which are completely different from the ones used for PAHs and VOCs removal. There are two main challenges for NTP technologies for tar removal. The first one is to remove tars under real gasification conditions, and the second one is to remove a broader range of compounds, going beyond the VOCs and the PAHs studied, focusing on high-molecular weight compounds. Technical aspects also play a role, especially the ones related with scalability and energy consumption. The scalability is crucial for gasification processes because the facilities intended to be used are large-scale and the concentration of the pollutants will thus be variable and much higher than the concentrations presented in toxicology and environmental studies. Secondly, the amount of energy used by the tar removal unit should be low enough to have a revenue in a gasification process.

Hence, VOCs and PAHs can be eliminated using NTP technologies, but at conditions which are drastically different from the ones presented in a gasifier. Although the results are promising, improved technologies should be built to evaluate if NTP could be a suitable tool to abate tars under gasification conditions. The evaluation should include also a broader range of compounds, going beyond the VOCs and PAHs already studied, keeping also an eye in the variation levels of the concentration.

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