The role of plasma in syngas tar cracking

Yamid Gómez Rueda · Lieve Helsen

Abstract Gasification of biomass and municipal solid waste is a technology that has been proposed as a dual-purpose solution for mitigating environmental impacts as well as for producing syngas, a very useful intermediary product for energy valorization and organic synthesis. However the presence of pollutants, notably tar, hamper this raw syngas (producer syngas) to be used in high-efficient energy applications such as jet engines, fuel cells or in Fischer-Tropsch synthesis, limiting its economic value. For reducing tar a lot of scientific and technical effort has been devoted. In this paper, the state-of-the-art of plasma tar removal from syngas is done, focusing on the use of plasma in tandem with existing technologies, underlining its advantages and the remaining challenges. The most promising ways to get a syngas with very low tar levels using plasma seem to be: (i) tandem tar cleaning techniques (e.g. secondary plasma enhanced catalytic unit) and (ii) secondary thermal plasma cracking units.

Keywords tar cracking · plasma · syngas cleaning

1 Introduction

The conversion of carbon-rich raw materials such as biomass and Municipal Solid Waste(MSW) into syngas has been proposed as the perfect solution for decreasing the amount of waste and byproducts discarded while obtaining a syngas that can be used for organic synthesis or for power generation with a reduced carbon footprint. However during the gasification process, apart from the syngas, a set of compounds called tar is generated (as shown in figure 1). The presence of tar in the syngas is considered the gasification Achilles' Heel [1, 2]. The presence of tar avoids the use of gasification for any applications except for boilers. Tar main problem is caused by its ease of condensation, making tar able to block small pipe fittings, such as reductions and injectors, causing also coking over downstream catalytic active sites even at high temperatures.

This condensation causes that the syngas cannot be used in applications that require high gas quality specifications. For instance in gas engines, gas turbines and fuel cells, the highest tar levels allowed for syngas are 50, 5 and 1 mg Nm^{-3}, respectively [3, 4], while the level of tars from gasifiers can range from hundreds of milligram per cubic meter (in fixed downdraft bed reactors) to hundreds of grams per cubic meter (fixed updraft bed reactors). If a technical solution could remove tar from syngas without compromising other quality parameters of the syngas, its market value would be increased.

However it still remains a challenge to develop a feasible way to strongly reduce tar levels in syngas without lessening gas quality, and plasma is a new tool that can help to achieve this goal in conjunction with existing solutions. From the available solutions proposed in scientific literature, we aim to present here a comparative study of plasma solutions currently investigated in order to envisage which role can play plasma in obtaining a syngas with very low tar levels.

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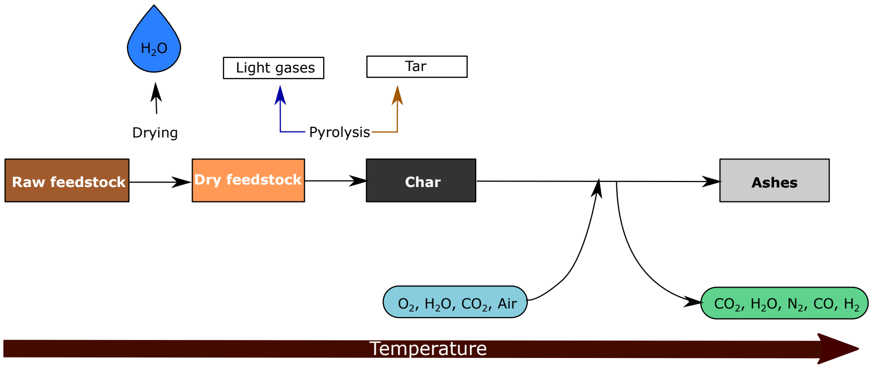

Fig. 1 Main steps occurring during a general gasification process.

2 Tar origin, formation, definition and classification

Tar is originated by the lack of equilibrium in gasification reactions, which also explains why they are not present in reactions where the chemical equilibrium is attained or close to be attained, like in combustion. This means that tar is present in any gasification processes, even with low-volatile feedstock. However, this does not mean that tar is a group of substances with a homogeneous set of properties, indeed it is the opposite. Tar includes molecules as diverse as pyridine or phenols, which are polar, water-soluble and reactive; and naphthalene and indene, which are in contrast non-polar, mostly hydrophobic and much less reactive.

The numerous compounds found in tar are a consequence of the different temperatures at which they are formed. Tar formation process has been studied by many authors [5, 6]and summarised by Materazzi et al. [7]. During gasification the degradation of the feedstock starts at 300-400°C by the formation of water and primary vapors; these primary vapors are mainly aliphatic compounds. After that, tar yield increases to temperatures up to 500-600°C, a point where cracking reactions start to be faster, resulting in a maximum tar production in this temperature range. However, this maximum tar yield point can vary depending on the chemical structure of the feedstock and it can fall outside the range proposed; tar compounds here are mostly paraffins, light hydrocarbons, and mixed oxygenated aromatics. Between these maximum and temperatures around 800°C, the tar composition changes, the oxygenated compounds start to disappear in order to give place to polyaromatic hydrocarbons (PAH). At temperatures higher than 800°C continuous cracking reactions result in the formation of smaller molecules, such as acetylene, CO, CO_2, H_2 and soot. A graph summarising this evolution is shown in figure 2.

One additional discussion that arises from the previous description is about which of the substances formed during gasification can be considered a tar and which not. In an effort to solve this debate, a panel of experts of EU/IEA/US-DOE limited tar constituents to all organic compounds with a molecular weight larger than benzene [9]. Unfortunately, this definition is still too broad, from primary oxygenated products to heavy PAHs, which leads to further refined definitions. ECN in 2009 for instance, developed a very useful tar classification based on the tar properties and in typical tar components [10], which helps a lot to see trends in tar reduction when using different methods. Another tar classification frequently used in the literature is based on appearance and temperature range at which different compounds are found [11, 12]. Both classifications are summarised in table 1.

2.1 Tar removal reactions

When tar is removed by cracking, there are basically 5 reactions through which it can be transformed: partial oxidation (Equation 1), steam reforming (Equation 2), dry reforming (Equation 3) , hydrocracking (Equation 4) and thermal cracking (Equation 5). The extent of the reactions depend mainly on the temperature and of course of the gas composition.

The techniques used for tar cracking enhance the reactions either by an increase of temperature (eg. thermal cracking), a decrease of activation energy (eg. catalytic cracking), on both of which plasma can play an enhancing effect. While the effect of temperature and catalysts has been widely explored, the use of plasma is relatively new.

Tar reforming reactions

$$\mathrm{C}_n\mathrm{H}_m + \frac{n}{2}\mathrm{O}_2 \longrightarrow nCO + \frac{m}{2}\mathrm{H}_2 \tag{1}$$

$$\mathrm{C}_n\mathrm{H}_m + \mathrm{nH_2O} \longrightarrow \left(\frac{m}{2} + n\right)\mathrm{H}_2 + \mathrm{nCO} \tag{2}$$

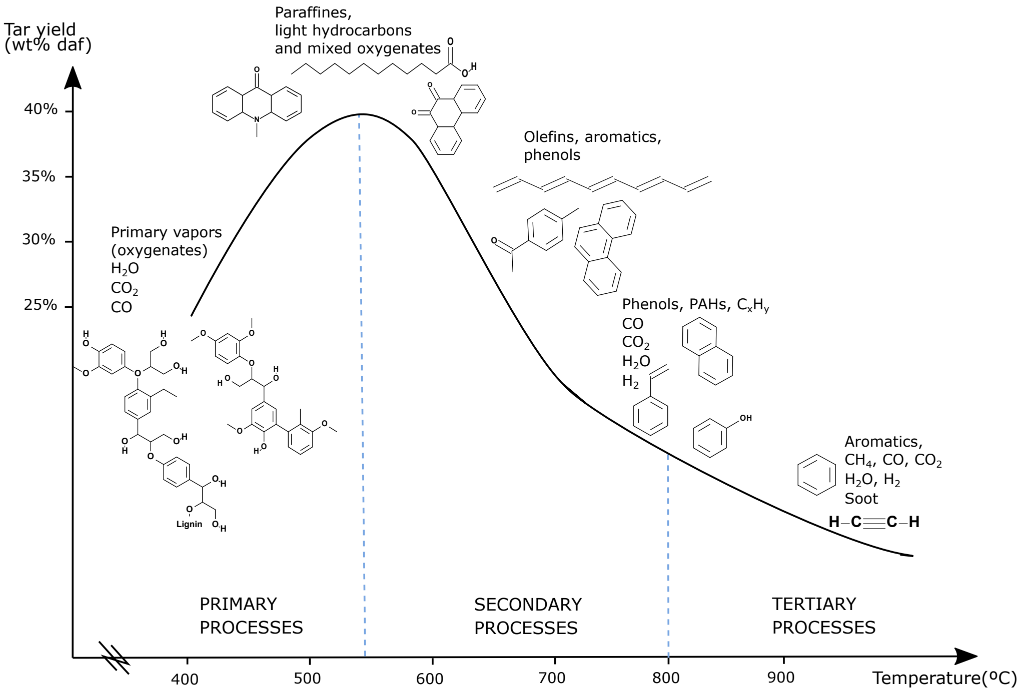

Fig. 2 Physicochemical transformations and conversion degrees of tar in a general gasification process. Reprinted from Fuel Processing Technology, Vol 128, Materazzi M.; Lettieri P.; Mazzei L.; Taylor R; Chapman C., Tar evolution in a two stage fluid bed—plasma gasification process for MSW valorization, p. 4-5, Copyright (2014), with permission from Elsevier [8].

$$\mathrm{C}_n\mathrm{H}_m + \mathrm{nCO}_2 \longrightarrow 2\,\mathrm{nCO} + \frac{m}{2}\mathrm{H}_2 \tag{3}$$

$$\mathrm{C}_n\mathrm{H}_m + \left(2n - \frac{m}{2}\right)\mathrm{H}_2 \longrightarrow \mathrm{nCH}_4 \tag{4}$$

$$\mathrm{pC}_n\mathrm{H}_m \longleftrightarrow \mathrm{qC}_x\mathrm{H}_y + \mathrm{rH}_2 \tag{5}$$

2.2 Tar dew point

The most important parameter regarding tar is the *tar dew point* which defines the point at which tar starts to condense, condensation that eventually derives in fouling/clogging. Tar dew point is defined as the temperature at which the total partial pressure of tar equals the saturation pressure of tar. The dew point of tar range from 150 to 350 °C, and it is crucial to remove tar before the gas temperature goes below this point. If not removed, tar can condense easily in process cold spots which can reach temperatures as low as 30 °C. The tar dew point is strongly influenced by the presence of tar classes 1, 4 and 5, because they are able to condense even at high temperatures. On the other hand, class 2 and 3 tar do not influence significantly the tar dew point, however they are water soluble, which can cause pollution problems in downstream gas cleaning equipment using water, being also problematic in catalytic treatments since they compete for active sites on the catalysts [13].

2.3 The complexity of tar minimisation

As it can be inferred from the previous section, the first challenge regarding tar minimization is related to the big amount of compounds considered as tar. The set of tar is composed of substances with diverse physicochemical properties which limit a lot the use of many technologies. For instance, nickel-based catalysts are good for reforming light aromatic hydrocarbons but get strongly deactivated by coking tar precursors [13] such anthracene and fluorene.

A second challenge for tar removal is its sampling. So far there is only one standard protocol for tar sampling, the *CEN BT/TF 143*, which consists of tar sampling by condensation/absorption over a set of bottles filled up with isopropanol. However, this method needs to take a lot of gas sample, requiring hours for one sampling. Therefore alternative methods have been developed, but none of them are yet standard, like SPA/SPE methods [15] or online methods such as UV spectrometry [16], optical methods [17], laser-induced fluorescence [18] among others. This makes quite difficult to compare the different removal methods, since each method has a different efficiency with respect to different substances, and report tar yield using a different classification. For instance, benzene cannot be determined by the standard protocol, but it can be detected with limited efficiency by SPA/SPE as well as when using UV-vis spec-

Basis of classification	Nomenclature	Description	Properties	Representative compounds
Molecular weight [10, 14]	Class 1	GC-undetectable	Very heavy tar; undetectable by GC	Biomass fragments; heaviest tar
	Class 2	Heterocyclic aromatics	Tar containing hetero atoms; highly water soluble	Pyridine, phenol, quinoline, isoquinoline, cresols
	Class 3	Light aromatics (1 ring)	Light hydrocarbons; do not pose condensation or solubility problems	Touene, ethylbenzene, xylenes, styrene
	Class 4	Light PAH compounds (2-3 rings)	Condense at intermediate temperatures at high concentrations	Indene, naphthalene, methylnaphthalene, phenanthrene, anthracene
	Class 5	Heavy PAH compounds ($\geq$ 4 rings)	Condense at high temperatures even at low concentrations	Fluoranthene, pyrene crysene,perylene, coronene
Appearance [12]	Primary	Oxygenated compounds	Found in the temperature range 400-700 °C	Syringols, guaiacols, furans
	Secondary	Aromatic compounds	Found in the temperature range 700-850 °C	Phenolics, olefins
	Tertiary	Complex aromatic compounds	Found in the temperature range 850-1000 °C	Toluene, indene, anthracene

Table 1 Tar compound classification. Acronyms: GC = Gas Chromatography, PAH = Polyaromatic Hydrocarbons. Modified from [10, 12, 14]

troscopy [19], which makes difficult to determine if a reported benzene level is due to the efficiency of the tar abatement technology used or is due to the efficiency of the detection of a specific sampling technique. A deeper look about tar measurement techniques can be made in the review of Dasappa [20].

A third factor that contributes to the complexity of the tar problem is the tar dew point. Even when it is the most important parameter regarding tar, it is hardly ever experimentally determined. This is mainly due to the fact that there is only one commercial device available, called *tar dew point analyzer* developed by ECN. Instead of determining tar dew point experimentally, some studies report a theoretical tar dew point based on tar composition and on a thermodynamic model. Since this can only be done by the tar protocol and the SPA/SPE method using a GC-FID or GC-MS, most of the scientific literature report tar yield instead of tar dew point, leaving a black spot on the tar condensation ability.

Last but not least, the close correlation between all the parameters in gasification, especially in strategies in-situ (i.e. when tar is removed in the same reactor where the gasification takes place), add an element of complexity to tar abatement. For instance, an increase in gasification temperature can decrease tar yield, but at the same time changes the gas composition, and increases char gasification rate so that the change in tar yield is caused by a combination of temperature and gas composition instead of only temperature. The gas equilibrium reactions and tar reduction are simultaneously affected by almost all the parameters inside the gasifier so that these two phenomena cannot be completely separated, although the interaction can be limited by using a first gasification unit to maximize carbon conversion, and a secondary unit devoted to tar reduction.

In summary, we can say that a method for tar reduction should not only remove tar, but also increase the other quality parameters of syngas, without transforming tar into products that can increase the tar dew point or into soot.

3 The potential of plasma in tar minimisation

Plasma is a state of matter that is the consequence of exposing a gas or mixture of gases to a high electromagnetic field. A plasma consists of a set of free radicals, electrons, ions and excited molecules that create a highly reactive atmosphere [21]. The reactive species in the plasma and the UV radiation generated carry enough energy to initiate tar decomposition reactions.

So far, plasma has been widely explored as an alternative technology to improve the conversion and selectivities for reactions such as hydrocarbon reforming [22, 23], hydrocarbon partial oxidation [24, 25] and CO_2 hydrogenation [26, 27]. The use of plasma in these reforming reactions is focused on process intensification by increasing reaction rates and by reducing the reforming reaction temperatures, which would allow to reduce the CO_2 footprint as well as the costs associated with high-temperature equipment. Since these reforming reactions are quite similar to tar reforming/cracking reactions, the use of plasma can also enhance the reaction rate of tar abatement reactions. The type of plasma used in the mentioned applications is called cold-plasma, on which the temperature of the gas is not (or marginally) affected by the effect of plasma because the electron temperature(Te) is not in equilibrium with the gas temperature (Tg). But apart from cold plasmas, thermal plasmas can also be used for tar cracking

Hot or thermal plasmas work at very high temperatures (higher than 4000 °C) where Te and Tg are close to the equilibrium. They have been explored mainly as a heat source for applications such as combustion and gasification of hazardous waste. They have been also explored in secondary units downstream a traditional gasifier for syngas cleaning.

3.1 Plasma gasifiers: gasification and tar cleaning in one unit

Plasma gasifiers are plasma units where a thermal (or hot) plasma is the source of heat in contrast to traditional auto-thermal gasifiers where the heat comes exclusively from the partial oxidation of the feedstock. The high temperature produced by hot plasmas helps to destroy dangerous molecules and toxic substances, which is practical to treat medical waste [28, 29], sewage sludge [30] and even waste with certain levels of radioactivity [31].

There are several plasma gasifier configurations, but the most usual for gasification uses a plasma torch, on which the solid waste is impacted by a plasma gas at the bottom of a reactor, reaching temperatures up to 2000°C, while the heart of the plasma is beyond 4000°C. In this configuration, the lower part of the reactor is at a high temperature while the upper part of the reactor is at a much lower temperature, as it is shown in figure 3. The feedstock is fed from the side or the top, and a molten residue is recovered from the bottom while the syngas is recovered from the top as well. One advantage of this configuration is the possibility of melting and separating metals and inorganic materials, helping to recover some materials for further valorization such as metals for catalysis [28] or inorganics as plasma stone for building materials [32, 33]. An additional advantage is that the hydrogen content is relatively high, caused primarily by the action of the high temperature. The Cold Gas Efficiency is also higher compared with traditional gasifiers like entrained flow [34].

Another advantage is the relatively low tar content of the syngas produced. Although tar is generated in the pyrolysis zone and leave the reactor before they can pass through the gasification zone in most configurations, tar-yields as high as 543 mg Nm^{-3} [35], and as low as <10 mg Nm^{-3} have been reported [36]. This is a tar-content much lower than the one found in fluidized gasifiers, where the tar yield is in the range of 1-100 g Nm^{-3}.

With respect to drawbacks, the main one is the high costs associated with a plasma gasifier installation, which makes it economically feasible only when dangerous waste at big scales needs to be treated [37], although technically it can treat any type of carbon-rich feedstock. An idea of the plasma gasification costs compared to traditional thermal treatment was made by Sikarwar et al. in a case-study scenario with a 680 tonne per day waste, a plasma gasification plant would cost an estimated 97 million to construct, which is almost three times the cost of other waste treatment facilities (e.g. incineration) [38]. This is mainly due to the high energy input required, as demonstrated by Marias et al. In their work, they found that a plasma torch 240 kW is needed for a gasifier producing a gas with a power 1660 kW, which is a big energy demand taking into account that only around one-third of the 1660 kW can be recovered as the electrical energy required for the plasma torch [39].

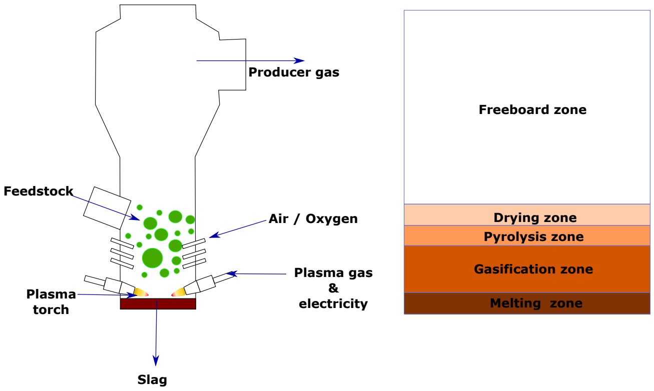

Fig. 3 Scheme of a plasma gasifier and temperature zones

3.2 Hot plasmas in secondary tar cracking units

Apart from plasma gasifiers, thermal plasma units can be used in a secondary unit downstream a traditional gasifier, like a fluidized-bed. In this case, hot plasmas are used in a different configuration compared to plasma gasifiers, because in this type of units the goal is to heat up the gas, instead of the feedstock. The main advantage of this process is that it reduces tar while simultaneously melts the fly ashes and the dragged bed material from the gasifier. In an arc-plasma secondary unit, as the shown in figure 4, Materazzi et al. demonstrated that the plasma can reduce tar to undetectable levels [7, 8], while recovering inorganics in a sintered material called plasmarok. Variations of the configuration used by Materazzi et al. [8], like the one shown in figure 5 claim the same type of advantages.

In secondary units, in contrast to plasma gasifiers, tar is exposed to the high temperatures of the plasma for a more prolonged time with respect to plasma gasifiers. However, the cracking of some surrogates like naphthalene seems to be affected not only by plasma temperature but by the interaction of plasma temperature, plasma ionization, electron impact, and UV radiation [7]. Naphthalene and benzene also seem to be the most difficult molecules to crack in a similar secondary thermal plasma unit used by Striugas et al., who reported tar levels as low as 90 mg Nm^{-3} [40].

Another type of plasma used in secondary units is gliding arc, mostly at a laboratory level and with model molecules. This type of plasma is sometimes called warm-plasma because it has a temperature lower than the plasma used in plasma torches. It has been proved to reduce the levels of toluene under a nitrogen atmosphere [41]. Gliding arc has been also proved to be efficient in steam reforming of toluene [42, 43] and naphthalene [43] with higher conversions for toluene than for naphthalene, and conversion over 90% reported by Nunnally et al. for toluene [43]. Partial oxidation performed with gliding arc has been also applied over heavier compounds such as acenaphthene, fluorene and anthracene [44] with conversions over 80%.

The main disadvantage of secondary hot plasma units is again related with the high-energy demand, making it only feasible for big scale units.

3.3 Cold plasmas in hybrid units: Secondary refining units

Plasma technologies have the asset of being able to work simultaneously with thermal reforming and catalytic reforming reactions, thus making plasma a technology that can enhance the already existing alternatives. Due to the less aggressive conditions, cold plasmas are the ones that allow using simultaneously other tar reduction methods. Among the different cold plasmas used in secondary units the two most important are corona, which uses DC sources, and dielectric-barrier discharge (DBD) plasmas, which use AC sources.

These cold plasmas can be combined with two other techniques for tar reduction: with a thermal cracking unit [46, 47] to enhance thermal cracking; and with catalysts, to enhance catalytic steam or dry tar reforming [48, 49, 50, 51, 52, 53, 54] , which is the most popular.

The combination of a cold plasma unit with a convection heater has been explored in a few studies. For instance, Nair et al. [47, 55] observed that naphthalene could be cracked from syngas using a pulsed corona plasma using temperatures as low as 400 °C. In a more recent study it was found that toluene can be converted to lower hydrocarbons under a hydrogen atmosphere at 400 °C using a DBD plasma [46]. Similar conclusions have been drawn for benzene [56]. The temperature at which the tar cracking takes place using thermal cracking alone is around 800-1200°C, which means that plasma strongly reduces the need for extreme temperatures. There is still a lack of research for polyaromatic molecules at higher temperatures using cold plasmas, mainly due to the technical difficulties of operating high voltage equipment at high temperatures. Taking into account that in gasification there is a need of working at temperatures higher than 600°C to avoid gas cooling, this is still a weak point of cold-plasma technologies.

The combination of plasma with catalysts is one of the most explored synergy technique for tar abatement. The use of a secondary catalytic tar cracking unit alone allows decreasing the amount of tar at temperatures lower than the used in thermal cracking [38].

When considering a catalyst for tar abatement, it should combine high selectivity at temperatures lower than 700°C, resistance to deactivation, high mechanical resistance, and low-cost [57, 58, 59, 60, 61, 62]. However, there is no catalyst that can fulfill all these requirements and because of that, a combination of different catalysts or plasma-enhanced catalysis has been explored. There are two ways of performing plasma-enhanced catalysis: one, where the plasma and the catalyst are placed in the same reactor, or in plasma configuration (IPC); and the second one where a plasma reactor is followed by a catalyst, or post-plasma configuration (PPC).

The most popular catalysts for tar abatement in both IPC and PPC configuration are nickel-based, and the synergistic effect of plasma and nickel catalysts has been demonstrated. For instance, Liu et al. showed that Ni/ZSM5 can reduce toluene at 300°C with a conversion close to 80%. Using the same catalyst under an IPC they reported an increased conversion of 85%, and a less evident synergistic effect was reported for PPC [49]. Similar enhancing effects have been published by Yuan et al. using a plasma jet over a Pt/Al_2O_3 catalyst for naphthalene cracking [63]. However the effect of plasma over nickel is also dependent on the type of support, for instance, Liu et al. reported a negligible effect of plasma over Ni/CaO and Ni/SiO_2 for toluene cracking[49].

The plasma enhancing effect over toluene was also demonstrated by Tao et al, showing that plasma-enhanced catalysis has superior performance than the thermal, plasma and catalytic cracking alone [50].

Titanium-based catalysts have been also studied coupled with plasma. While TiO_2 is not considered as a material able to catalyze tar-cracking reactions, the UV radiation of plasma can induce photocatalytic activity, transforming TiO_2 into an active catalytic material for tar removal. Sun et al. demonstrated that with microwave induced plasma over a gas enriched with Ar an increase in toluene conversion from 90 to 95 % us-

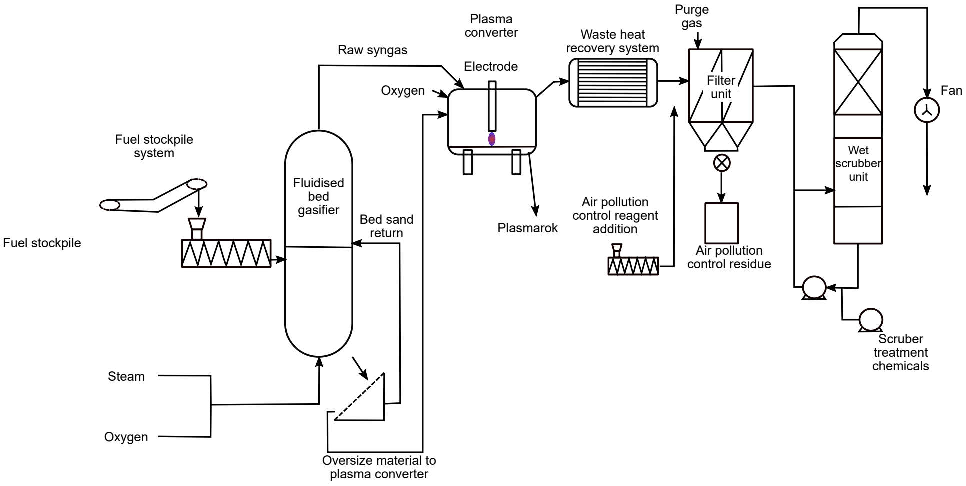

Fig. 4 APP thermal plasma cleaning design. Taken from Materazzi et al [8].. Reprinted from Fuel Processing Technology, Vol 128, Materazzi M.; Lettieri P.; Mazzei L.; Taylor R; Chapman C., Tar evolution in a two stage fluid bed—plasma gasification process for waste valorization, p. 4-5, Copyright (2014), with permission from Elsevier.

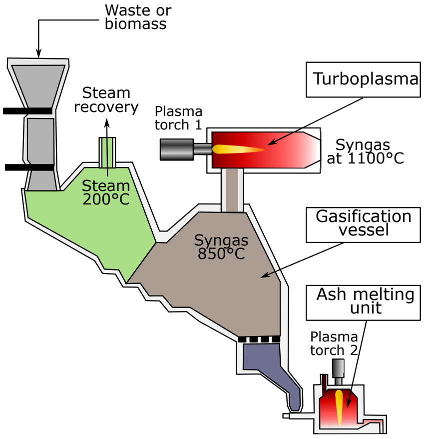

Fig. 5 Europlasma gasifcation design. Taken from Deyder et al [45] Reprinted from Biomass and Bioenergy, Vol 35, A.Deydiera; F.Marias; P.Bernada; F.Couture; U.Michon, Equilibrium model for a travelling bed gasifier, Pages 133-145, Copyright (2011), with permission from Elsevier.

ing a combination of steam with TiO_2 [64, 65]. Similar conclusions were made by Huang et al. over Toluene in a plasma-assisted catalytic oxidation process using $TiO_2/Al_2O_3/Ni$ catalyst [48], and by Wu et al. during photocatalytic naphthalene oxidation cracking using TiO_2/diatomite together with a DBD plasma in an IPC configuration [66]. Some of the results mentioned above have been summarised in figure 6.

An additional advantage of plasma-photocatalytic systems is that it decreases the coking rates, like in the reported results of Fan et al over a Ti/HZSM catalytic bed [73]. This effect could potentially improve the lifetime of catalysts such as Rh, Ru, Pd, Pt which are currently unsuitable for a commercial plant despite their high tar removal capacity [60].

However, the hybrid plasma-catalytic units are in a very early stage of exploration. Most of the tar cracking catalysts studied in tandem with plasma are nickel or noble-metal supported catalysts. Traditional tar cracking catalysts such as dolomite[74, 75, 76], olivine [77, 78, 79], K_2CO_3 [80, 81], CaO [82, 83, 84], iron oxides [85] and chars [86, 87, 88] are yet to be explored. Indeed most of the catalysts found in many tar removal reviews [13, 38, 57, 58] have been unexplored in tandem with plasma.

4 Plasma tar cracking compared with other removal strategies and future trends

Tar problem is as old as the solutions proposed to reduce them. Plasma is so far a novel technique that needs a lot of research and effort in order to be a viable solu-

Technique	Tar compound	Scale-up level	T(°C)	Tar inlet concentration $\left(\frac{mg}{Nm^{-3}}\right)$	Tar outlet concentration $\left(\frac{mg}{Nm^{-3}}\right)$	Removal efficiency (%)	Ref
Mechanical and physical removal methods							
OLGA wet scrubbing	Real tar	Industrial	400	8680-3240	680-630	80-92%	[67]
Cyclone separator	Toluene	Industrial	–	7500-6600	2582-1827	66-72%	[68]
Wet scrubber	Toluene	Industrial	–	2582-1827	1048-676	59-63%	[68]
Sand bed filter	Real tar	Industrial	10-20	–	–	50-97%	[69]
Wash tower	Real tar	Industrial	50-60	–	–	10-25%	[69]
Venturi Scrubber	Real tar	Industrial	–	–	–	50-90%	[69]
Wet electrostatic precipitator(ESP)	Real tar	Industrial	40-50	–	–	0-60%	[69]
Fabric filter	Real tar	Industrial	∼200	–	–	0-50%	[69]
Cracking methods							
Catalytic tar cracking. (dolomite, olivine)	Real tar	Industrial	700-900	8600	57	>95%	[70]
Thermal tar cracking (secondary air inlet, partial oxidation)	Real tar	Industrial	>1100	50,52	12,9	74%	[71]
Thermal plasma cracking (plasma gasifier, primary unit)	Real tar	Pilot plant^a	1127-1327	-	132-543	-	[35]
Thermal plasma cracking (plasma gasifier, primary unit)	Real tar	Pilot plant^a	1100-1400^b	-	<10	-	[36]
Thermal plasma cracking (secondary unit)	Real tar^c	Pilot plant	1200-1250^b	115,3	<9,5	86,46-99%	[7]
DBD plasma	Naphthalene	Lab scale	20-25	50	3	95%	[72]
Corona	Naphthalene	Lab scale	400	3000-4000	60	>98%	[55]
DBD+Ni/Al_2O_3	Toluene	Lab scale	300	26100	2610	∼90%	[23]
DBD+CuO nanowires	Toluene	Lab scale	25-30^d	26100	0	100%	[54]

Table 2 Different tar removal methods efficiency and tar exit levels.^{a} The scale-up level corresponds to the one reported in the reference, but industrial plants are already in operation. ^{b} This temperature refers to the gas exit temperature, the plasma core is above 5000K. ^{c} Toluene, benzene and naphthalene not taken into account.^{d} Temperature not reported, but due to the nature of the plasma and the absence of heating, ambient temperature is inferred.

tion for tar reduction in gasification, but it has advantages over most the technical solutions already studied.

The main advantage of plasma units over other technologies is its superior tar conversion, which can only be compared with catalytic tar cracking, as it can be seen in figure 3.3. For cold plasmas, there is the additional advantage of having the capability to be combined with catalysts and thermal cracking in secondary units showing superior cracking activities (cf. figure 6). The main disadvantage of plasma is associated with its high energy input which makes them very inefficient, and difficult to scale-up, especially for hot plasma units on which the energy input is in the order of hundreds of kW, although with cold plasmas there is room for overcoming this barrier.

Comparing all plasma techniques with scrubber and solvent extraction, plasma techniques have the big advantage of recovering tar as gases and char. In contrast, in scrubbers tar is recovered in a liquid state, posing a new problem of treatment of byproduct streams, losing the calorific value of tar at the same time. Furthermore, if we compare any plasma device presented here

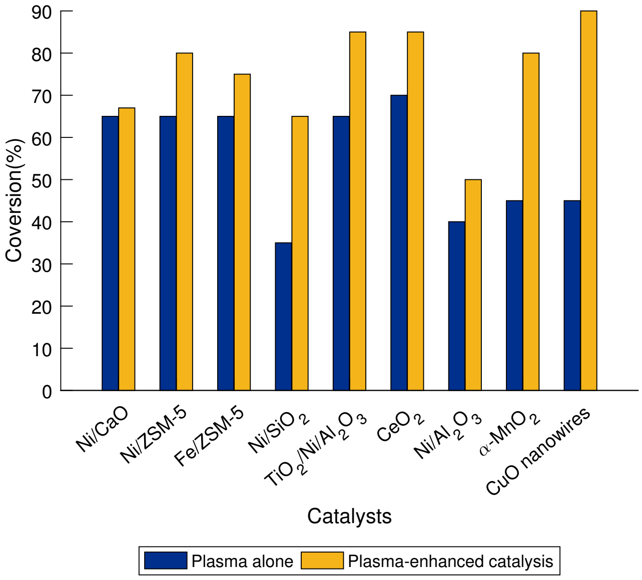

Fig. 6 Plasma cracking vs plasma-enhanced catalytic cracking of toluene. Data taken from [48, 49, 50, 51, 52, 53, 54]

with train scrubber systems like OLGA, plasma can remove tar at temperatures higher than 400°C, which is the highest operating temperature of the OLGA system [89].

Apart from operating at higher temperatures, tar removal efficiencies are $\geq$ 95% in plasma tar cleaning systems, while mechanical and physical methods, rarely reach efficiencies above 90%[69]. The biggest advantage of mechanical and physical methods is that their implementation is well known at industrial scale (cf. scale-up in table 3.3). The scaling-up and industrial recognition are two of the weakest points of any new tar cleaning technology, including plasma.

With respect to thermal cracking, the main advantage of thermal plasma units is their ability to produce temperatures much higher than the ones produced in traditional thermal cracking units, being, therefore, more effective for tar cracking. Apart from the already mentioned high energy input of thermal plasmas, another drawback of plasma units with respect to thermal plasmas is the easy scalability and implementation of thermal cracking units, especially the ones with secondary oxidant inlets. Implementation and scalability is also a big advantage of thermal cracking units vis-à-vis cold plasmas, however, instead of being competitive technologies they could work in tandem, but the demonstration of cold plasmas at temperatures higher than 400-500°C is yet to be done.

The only tar reducing method that has removal efficiencies comparable with plasma is catalytic tar cracking. Despite its high tar conversion, catalysts have problems of a reduced lifetime due to deactivation by coking, by HCl and by H_2S [58], a problem that cannot occur with plasma due to its working principle. Another problem of catalysts is that they seem to be effective only for a set of tar compounds, but get deactivated by other tar compounds, while plasma is able to remove most of the tar compounds. When compared with cold plasmas, catalysts show similar advantages, including their ability to crack tar at temperatures much lower than the ones required in thermal tar cracking, but catalytic tar cracking have the additional advantage of being already used at small-scale industrial level. A deeper comparison between catalytic and cold-plasma tar cleaning is difficult to perform, due to the lack of data regarding long-run catalytic tests in one side and the lack of data of pilot cold plasma units in the other side.

In summary, the energy input has been the main drawback of plasmas in gasification so far, however, the use of cold plasmas in secondary units have shown promising results in reducing the energy input. Unfortunately, cold plasma units (as well as hybrid cold-plasma units) have been proved only at lab-scale and with tar model molecules, and there is a need of scaling-up these units with real tar issued from gasification. The biggest challenge for doing this is the operation of high-voltage equipment at elevated temperatures since the materials used limit (especially in DBD plasmas) either the voltage applied, or the operating temperature.

On top of that, the use of plasma in gasification has to overcome some bad news of industrial projects that been abandoned, like the one canceled in Teesside UK in April 2016 [90], or the one halted in Ottawa CA in 2015 [91]. Although all the big investment projects are linked with plasma gasifiers, the bad reputation of plasma in gasification due to the unsuccessful projects will surely affect the scaling-up of cold plasmas in secondary units. Adapting cold plasmas to already existing thermal and/or catalytic secondary units could offer a faster scaling-up, due to the good performances shown by lab-scale experiments of plasma-enhanced catalytic (and thermal) units.

5 Conclusions

Although plasma is a relatively new player and tar is a complex problem, plasma shows competitive characteristics to produce a tar-clean syngas, like showing a long lifetime and capacity to transform tar into lighter hydrocarbons. So far, in secondary units, only thermal plasma units have demonstrated to be effective for tar cracking at pilot scale, but cold-plasma units have shown promising results at lab-scale, which makes them worthy for further research.

Cold-plasmas capacity to work inside a catalytic or thermal cracking unit is the most appealing characteristic of this technology. The effect of plasma is able to enhance the catalytic and thermal activity while reducing coking in many cases, showing superior capacity for tar removal when compared with the catalytic and plasma cracking alone.

Regarding future trends, so far cold plasma hybrid units have been used to crack tar model molecules at low to moderate temperatures (up to 400°C). However, there is a need of research focused on obtaining information about the behavior of cold plasmas operating at temperatures higher than 400°C with and without catalysts for tar cracking in order to avoid unnecessary gas cooling. On top of that, there is a lack of exploration of real tar abatement using cold plasmas, because most of the studies have been focused on model molecules such as benzene, naphthalene, and toluene.

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