Thermal tar cracking enhanced by cold plasma - a study of naphthalene as tar surrogate

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Abstract

Gasification has been proposed as a good solution for recovering energy from waste and biomass in the form of syngas. However, the presence of tar limits syngas applications. Tar model molecules have been removed by cold plasmas up to 400°C, but to avoid syngas cooling tar removal above 600°C is required. To investigate tar removal by cold plasma at higher temperatures, two sets of experiments were done, one to identify tar composition from MSW gasification, and a second one to crack in a nanosecond-pulsed corona plasma at high temperatures the most refractory tar compound found, naphthalene. In this paper, we report the first results of cold plasma for tar cracking at temperatures up to 1100°C, revealing that this tandem can remove naphthalene completely at 800°C, compared to the 1000°C needed in case of thermal cracking alone. The synergy between plasma and thermal cracking is driven by higher energy densities when temperatures increase. However, this synergy stops when thermal cracking reactions predominate.

Keywords: Gasification, Municipal Solid Waste, Cold Plasma, Tar Removal, Naphthalene

1. Introduction

Tar is a set of substances produced as a byproduct during the gasification of carbon-rich feedstock, such as Municipal Solid Waste (MSW), and its removal from syngas has been identified as one of the major challenges in gasification [1]. Although tar is a major factor in environmental pollution from gasification due to its toxic nature [2, 3], the main operational problem associated with tar is its capacity of condensing at high temperatures, which eventually causes clogging of piping and equipment, increasing maintenance times to inadmissible levels [4]. These maintenance times are critical for appliances such as gas turbines and engines, where the small injectors are prone to be blocked. Tar can also cause the deactivation of catalysts by coking, which hampers tar-polluted syngas to be used in fuel cells [5, 6, 7, 8], in methanation [9] and in Fischer-Tropsch synthesis.

Although there are some methods that take advantage of the ease of tar condensation to remove them, it is preferred to crack them to produce more syngas to avoid cooling (which is needed for condensation) in order to recover the sensible heat contained in the syngas. Cooling should be avoided if the downstream valorization processes are also carried out at high temperatures, such as in the case of methanation (operating at 500-700°C) [10] or Solid Oxide Fuel Cells (SOFCs operating between 750-950°C) [11]. Even if the subsequent valorization is carried out at lower temperatures, such as in Fischer-Tropsch or Proton-Exchange Membranes (PEM) fuel cells, cracking tar at the high temperature of the gasifier outlet is still beneficial since tar cracking reactions are endothermic.

So far, thermal and catalytic cracking have shown to be able to remove

tar to a high extent but the use of excessive temperatures in the former case (usually above 1000-1250°C) [12, 13, 14, 15], and the short lifetime due to coking [16], sulfur [17] or evaporation for the latter case does not allow them to be used extensively in the industry [18]. Some alternative approaches, like the addition of activated carbons and biochar, can be effectively used in certain lab conditions for tar removal [19, 20, 21], but not in real large-scale gasifiers due to carbon consumption by steam and oxygen reactions.

Therefore, plasma has arisen as a new solution for tar cracking. Thermal plasmas, which exhibit high temperatures (above 4000K) have been extensively used for MSW gasification in primary units [22, 23, 24, 25, 26] but also in secondary units for tar cracking. Materazzi et al. [27] have demonstrated that a thermal plasma secondary unit can convert tar into CO instead of soot, by using a plasma torch operating in a temperature range of 5500-–10,000°C. It has also been reported that the high temperatures alone are not able to remove some tar components such as naphthalene and benzene; naphthalene and benzene removal needs the combined effect of plasma excited species and high-temperature [28].

Although tar has been successfully removed with thermal-plasmas, the energy demand of such plasmas is large, making this technology feasible only when electricity is extremely cheap, or when difficult-to-treat inputs (such as dangerous waste) is used as feedstock [29]. For instance, Marias et al. [30] determined that a plasma torch of 240kW needed to produce a syngas with a power of 1616kW , which is an enormous amount of high quality energy (electricity) needed as input. The extreme gas heating up in thermal plasma cracking might require as well extra cooling down of the producer

3

gas for downstream applications. This has opened a window for using delete intensive plasmas, such as warm and cold plasmas which are less heated.

The main difference between cold plasmas and thermal plasmas is the equilibrium temperature of the plasma species. While in thermal plasmas all species are in thermal equilibrium, in cold plasmas the electron temperature is higher than the temperature of the other species. This means that the gas is not heated-up by the plasma, but it is still exposed to high-energy electrons, generating excited molecules, ions, and UV radiation. In the case of warm plasmas, there is still a non-equilibrium temperature among all the species, but some degree of heating is achieved. In tar cracking, Dielectric Barrier Discharge (DBD) and corona plasmas are the main cold plasma technologies used, and gliding arc discharge (GAD) is the main warm-plasma technology used.

Although GADs have shown to be effective for tar model compounds removal alone [10, 31, 32, 33, 34] or in combination with catalysts [35, 36, 37], the need of syngas cooling after such units is still there. However, by using cold plasmas (DBD and corona) there is a negligible gas heating, discarding the need of any downstream syngas cooling.

The main difference between the two cold plasma technologies mentioned lies in the type of voltage source used: while DBD uses AC, corona uses DC. This has many implications, one is that while DBD plasmas need a dielectric material around one or two of the electrodes, corona plasmas do not need any dielectric. Unfortunately, corona plasmas can easily transit towards a spark and are more difficult to control. The other main difference is that DBD plasmas are naturally pulsed due to the AC energy source, while

corona plasmas need an extra unit in order to generate a pulsed discharge.

DBD plasma units have been the most explored cold plasma technologies in lab-scale experiments for tar removal, either alone or in combination with catalysts. Although some authors have studied the DBD plasma alone, like Saleem et al. [38], for the removal of benzene, or Wu et al. [39] in the removal of naphthalene, most of the studies have been performed using plasma in combination with catalysts. For instance, Liu et al. showed that an M1Al3 catalyst in a plasma reactor can achieve toluene conversions higher than 95% with benzene and ethylbenzene as main reaction products [40]. Similar works using a plasma combined with in-situ Ni/Al_2O_3 and Ni/ZSM show an enhanced conversion of toluene with a simultaneous soot reduction [41, 42] when compared to plasma cracking alone. Naphthalene has been also successfully removed in similar plasma-catalytic systems [36, 43, 44].

Corona plasmas have been used in few cases for the conversion of naphthalene and hydrocarbons. Nair et al. were able to remove naphthalene at 400°C at residence times of 3 min [45] and Bityurin et al. demonstrated that carbon monoxide reduced naphthalene cracking activity when compared to a pure nitrogen atmosphere [46]. The reduced use of corona plasma with respect to DBD is due to the difficult generation of pulses, which requires the use of high voltage resistors to limit the current, requiring careful design to avoid sparks in the HV system. However, the lack of any dielectric material in corona plasmas makes them interesting for using them at the high temperatures found at the exit of gasifiers.

However, removing tar at low temperatures has very little advantage in comparison to wet scrubbing using organic solvents (except that liquid waste

5

streams are avoided), because it forces the gas exiting the gasifier to be cooled-down for cleaning, requiring a reheating after the cleaning process for ultimate valorization. So far the highest reported operating temperature on which a cold-plasma cracking unit has operated is 400°C for corona plasma [45]and 400°C for DBD plasmas [47].

There is thus a need for operating cold plasma systems at higher temperatures. In this paper, two sets of experiments are described in order to evaluate a nanosecond pulsed corona plasma for tar removal at high temperatures. The first set of experiments focused on the characterization of tar resulting from gasification of MSW from steam and air atmospheres. In this analysis it is used the standard definition of tar given by the EU/IEA/US-DOE panel, which considers as tar as all the organic compounds of a higher molecular weight than benzene [48], and it is also used the tar classification made by the Energy Research Center of the Netherlands (ECN) [49] showed in table 1 in order to understand tar evolution. The second set of experiments focused on cracking the most stable tar molecule identified in the first part in a nanosecond pulsed corona plasma under a nitrogen atmosphere.

2. Experimental

The feedstock for the first set of experiments was a MSW sample with the fraction and composition given in table 2. The gasification reactor consists of a stainless-steel 316 cylinder with two temperature zones, one cold and one hot. The MSW sample was kept in the cold zone, around 20°C, while the hot zone of the reactor reached the desired temperature. The reactor was kept under a flow of N_2 while heating-up. The sample was then moved to the

6

Table 1: Tar compound classification according to ECN [49]. Acronyms: GC = Gas Chromatography, PAH = Polyaromatic Hydrocarbons.

Nomenclature	Description	Properties	Representative compounds
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 aromatic (1 ring)	Light hydrocarbons; do not pose condensation or solubility problems	Toluene, ethylbenzene, xylenes, styrene
Class 4	Light PAH compunds (2-3 rings)	Condense at intermediate temperatures at high concentrations	Indene, naphthalene, methylnaphthalene, phenanthrene, anthracene
Class 5	Heavy PAH compunds ($\geq$ 4 rings)	Condense at high temperatures even at low concentrations	Fluoranthene, pyrene crysene, perylene, coronene

hot-zone and kept under a flow of air for 60 min, with an Equivalence Ratio (ER) of 0.3 for air gasification experiments with and air flow of 95ml/min and a steam-to-waste ratio of 0.5 for steam gasification experiments.

The sample weight during all the experiments was 5 g. The steam was injected by a boiler unit connected by a three-way valve to the main reactor. The steam was injected once the boiler steady-state was reached and checked by measuring the steam condensation in a parallel process. The tar generated was sampled by the Solid-phase Adsorption - Solid-phase Extraction (SPA/SPE) method as stated by Brage et al. [50] and the gas released was collected in a Tedlar-gas bag for being analyzed off-line by a micro-GC. A scheme of the experimental setup is presented in figure 1.

For the second part of the experiments, only one tar model molecule was chosen based on the results of the first series of experiments. The equipment
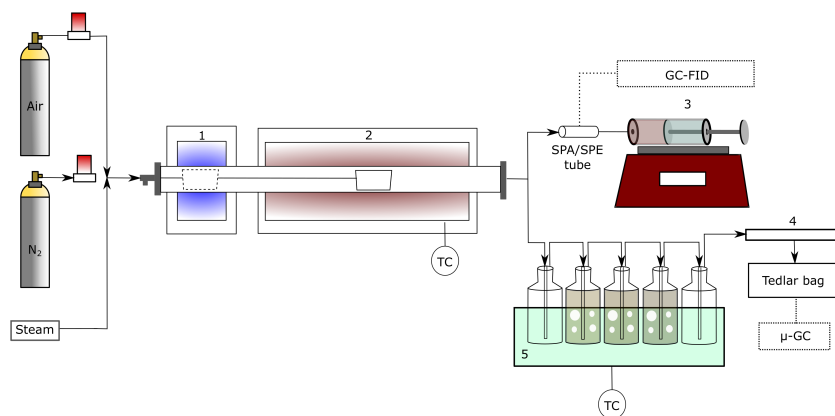
Figure 1: Gasification reactor. Parts: 1. Reactor cold zone. 2. Reactor hot-zone. 3. SPA/SPE sampling setup 4. Glass wool filter. 5. Series of bottles for tar condensation, three of them contain acetone while the other two are empty.

used in this part consists of a High-Voltage Direct-current (HV DC) power unit with 24kV voltage and 5mA current connected to an RC-circuit which allows producing short DC pulses by using a spark-gap switch filled-up with nitrogen. The pulses are then transmitted through a coaxial cable to a reactor that is placed inside a three-zone oven. The reactor consist of a FeCrAl pipe of 1.27m length and 64mm diameter.

Upstream of the reactor, a saturator filled up with the objective molecule is kept at a temperature of $70 \pm 1°C$. A carrier nitrogen stream of 2NL/min (normal liter per minute) passes trough the saturator which is mixed-up with a second nitrogen stream of 2NL/min before entering the plasma reactor. The residence time in the plasma reactor is set to 30s in order to obtain an appreciable energy density (see equation 2). Between each temperature test, the reactor was flushed with air for 20 min to remove the soot produced and then again purged with nitrogen for 10 min. The tar concentration

Table 2: Waste fractions, proximate and ultimate analysis of the MSW samples used in gasification tests

Proximate composition (wt.%, db)	
Volatile matter	55.3
Fixed carbon	1.8
Ash	46.5

Waste fraction	Fraction (wt%, dry basis)
Wood	1
Paper	4
Textile	9
2D plastics	39
3D plastics	5
Other combustible	11
Fines	31

Ultimate composition (wt.%, db)	
C	40.5
H	6.1
N	1.1
O	4.3
S	0.2
Cl	1.2
LHV (MJ/kg, db)	22.9

was evaluated by the SPA/SPE method, by sampling 100ml of gas at the bottom of the reactor after each test, with a blank test taken before each test. Between three to five samples were taken for each experiment after 25-30 minutes of achieving steady-state. All gas lines, including the SPA sampling lines, are heated at a temperature between 105-110°C. A scheme of the experimental setup is shown in figure 2. The plasma discharge was followed by a Handyscope HS4 DIFF from the company TiePie.

2.1. Performance indicators

In order to evaluate the thermal-plasma tar removal process, multiple indicators need to be calculated. One of these performance indicators is the energy per pulse delivered by the plasma, which is determined by equation 1 from the voltage-current curves presented in figure 3.
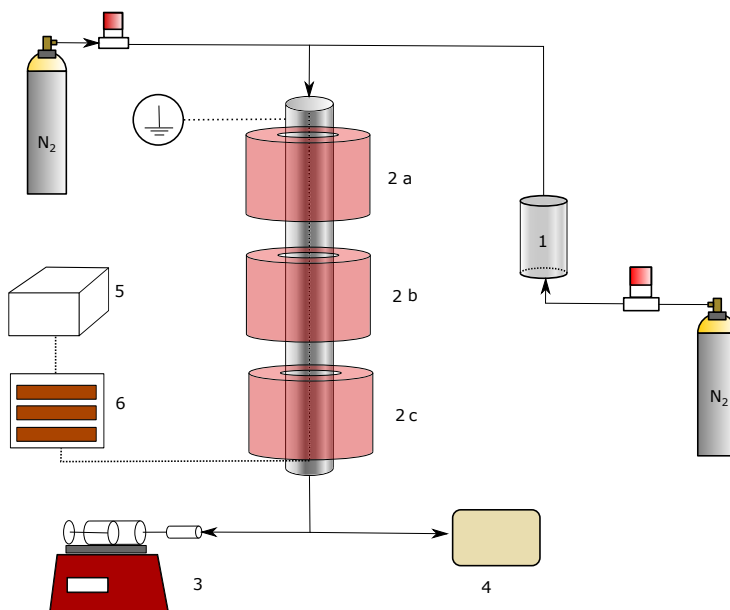
Figure 2: HV nanosecond pulsed corona plasma reactor setup. Parts: 1. Tar model molecule saturator. 2a,b,c. Three-zone convection oven. 3. SPA/SPE sampling 4. Exhaust. 5. HV DC power supply. 6. Pulse generator

$$Ep = \int_0^{t=500ns} U(t)I(t)dt \tag{1}$$

where E_p is the energy per pulse in mJ per pulse, U(t) represents the instantaneous voltage in V and I(t) represents the instantaneous current in A. Another parameter for evaluating the tar removal efficiency is the specific energy input (SEI) or energy density, which is calculated using equation 2 where E_p is the energy per pulse determined by equation 1 in mJ per pulse, ν is the frequency of the pulses in pulses per second, and $\dot{Q}$ is the volumetric flow of nitrogen carrying the tar model molecule in normal liters per minute. The SEI units are J/L.

$$SEI = \frac{E_p * \nu * 60}{\dot{Q} * 1000} \tag{2}$$

The conversion of the tar model molecule in the plasma tar cracking experiments is determined by using equation 3 where C_o represents the initial concentration of the model compound, which was taken when the reactor was heated at 100°C , while C_f represents the final concentration.

$$\eta(\%) = \frac{C_o - C_f}{C_o} * 100 \tag{3}$$

The energy efficiency or energy removal efficiency, (EE) of the plasma process is evaluated by equation 4, where $[C]_{on}$ and $[C]_{off}$ are the concentrations leaving the reactor when the corona plasma is on and off respectively,

$$EE = \frac{[C]_{\text{off}} - [C]_{\text{on}}}{SEI} \tag{4}$$

A final significant parameter is the energy efficiency parameter β (also known as characteristic energy or energy cost) of the model molecule destruction process. It is calculated from plotting the exponential decrease of the model molecule concentration versus SEI, as in equation 5 [51, 52] where β and the SEI are given in J/L.

$$\frac{[C]_{on}}{[C]_{off}} = exp\left(\frac{SEI}{-\beta}\right) \tag{5}$$

3. Results and discussion

3.1. Identification of tar representative molecules

The first part of the experiments consists of gasification experiments using air and steam for the light MSW fraction in the setup described in figure

11

Table 3: Gasification experimental matrix

Gas agent	Temperature	Sample ID
Air	800°C	Air-800
	1100°C	Air-1100
Steam	800°C	Steam-800
	1100°C	Steam-1100

1. The experimental matrix is shown in table 3. The objective of this experimental program is to evaluate the tar speciation at different temperatures and using different gas agents, but also to determine which compounds are more difficult to remove by thermal cracking.

The tar composition of these experiments is presented in tables 4 and 5 which are analyzed with respect to total tar, phenolic compounds concentration, and aromatic compounds distribution. At first sight, the temperature increase causes a reduction in the total tar yield. For air gasification, the effect is evident, but not for steam. Although total tar yield is almost the same in both experiments with steam, at 1100°C the presence of benzene is much higher. Considering that benzene is quantified but it does not enter into the definition of tar, then the tar yield reduction is more clear.

Regarding phenolic compounds, presented in table 5, they are present in very low quantities at 800°C, and totally disappear at 1100°C. Due to these two reasons, we can leave out of consideration these compounds in the second set of experiments.

The aromatic compounds represent between 97 and 100% of the total tar yield in all experiments. At 800°C, besides benzene the two most abun-

dant compounds are toluene and naphthalene for air and o-xylene, naphthalene and indene for steam. At high temperatures, the most representative molecules are naphthalene and acenaphthylene for air and naphthalene and benzene for steam. In all cases naphthalene appears as one of the most representative tar molecules, especially at high temperatures where it is by far the most abundant compound in both air and steam gasification. This makes naphthalene the most interesting molecule to be chosen for the second part of the experiments, which coincides with previous studies that have chosen naphthalene as tar model molecule in biomass and coal gasification [35, 53, 54].

Other molecules that can be problematic are the polyaromatic hydrocarbons (PAHs) such as acenaphthylene, phenanthrene, fluoranthene, and pyrene. During the experiments, PAHs compounds concentration increases with temperature, and although their concentration is still very low with respect to other compounds, PAHs have a higher impact in tar dew point. This means that the tar remaining after tar cracking at high temperatures is more stable and more prone to condensation than the tar remaining at low temperatures.

The tar composition presented here differs from the tar composition presented in other publications using other types of feedstock such lignite [55], bituminous coal [56], woody biomass [57], sewage sludge [58, 59]. Even compared with other MSW, [60, 61] tar composition is very different, mainly due to the MSW composition. However, in most of the studies, naphthalene is among the most abundant tar molecules [57, 58, 59, 60, 62, 63, 64] and the most difficult aromatic compound to be destroyed by thermal cracking, after

13

Table 4: Aromatic compounds found during steam and air gasification of MSW. Concentrations are given in μg/100ml. ND = Not detected (below the limit of detection)
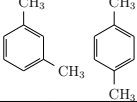
| Structure	Temperature	800°C	1100°C	800 °C	1100°C
	Gasification agent	Air	Air	Steam	Steam
	Benzene	10.45	2.38	N.D	5.24
	Toluene	18.77	1.42	0.73	1.56
	m/p-Xylene	2.83	0.37	1.33	N.D
	o-Xylene	2.18	2.9	6.3	2.16
	Indan	0.42	N.D	0.32	0.04
	Indene	3.59	1.63	2.42	1.1
	Naphthalene	6.59	13.59	4.02	5.24
	2-Methylnaphthalene	1.91	0.24	1.37	0.13
	1-Methylnaphthalene	1.25	0.16	0.86	0.11
	Biphenyl	0.69	0.81	0.53	0.37
	Acenaphthylene	1.12	3.93	0.65	1.33
	Acenaphthene	0.2	0.1	0.2	0.03
	Fluorene	0.56	0.53	0.41	0.22
	Phenanthrene	0.73	2.53	0.49	0.87
	Anthracene	0.23	0.54	0.16	0.2
	Fluoranthene	0.07	1.19	0.05	0.46
	Pyrene	0.16	1.41	0.1	0.38
Total tar	(Phenolic + Aromatic)	51.92	33.81	20.33	19.99

Table 5: Phenolic compounds found during steam and air gasification of MSW. Concentrations are given in µg/100ml. ND = Not detected (below the limit of detection).

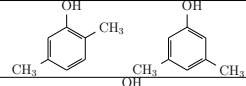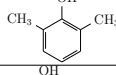|	Temperature	800°C	1100°C	800 °C	1100°C
Structure	Gasification agent	Air	Air	Steam	Steam
	Phenol	0.13	0.08	0.13	0.55
	o-Cresol	0.01	N.D	0.1	N.D
	m-Cresol	0.01	N.D	N.D	N.D
	p-Cresol	0	N.D	0.09	N.D
	2.4-Xylenol	N.D	N.D	N.D	N.D
	2.5/3.5-Xylenol	N.D	N.D	N.D	N.D
	2.6-Xylenol	0.01	N.D	0.07	N.D
	2.3-Xylenol	N.D	N.D	N.D	N.D
	3.4-Xylenol	0.01	N.D	N.D	N.D

benzene [65, 27].

3.2. Plasma cracking experiments

3.2.1. Characterisation of the plasma discharges

The plasma pulses were kept between 70-72 pps (pulses per second) throughout the whole temperature range. The voltage and current pulses shapes were very similar during all discharges. The voltage pulse had an oscillating behavior, with a peak voltage of 20kV, with a duration of 30ns

²³⁸ and two more peaks of a similar duration but characterized by lower voltage.
²³⁹ These characteristics can be seen in the voltage-current curves at different
²⁴⁰ temperatures presented in figure 3.
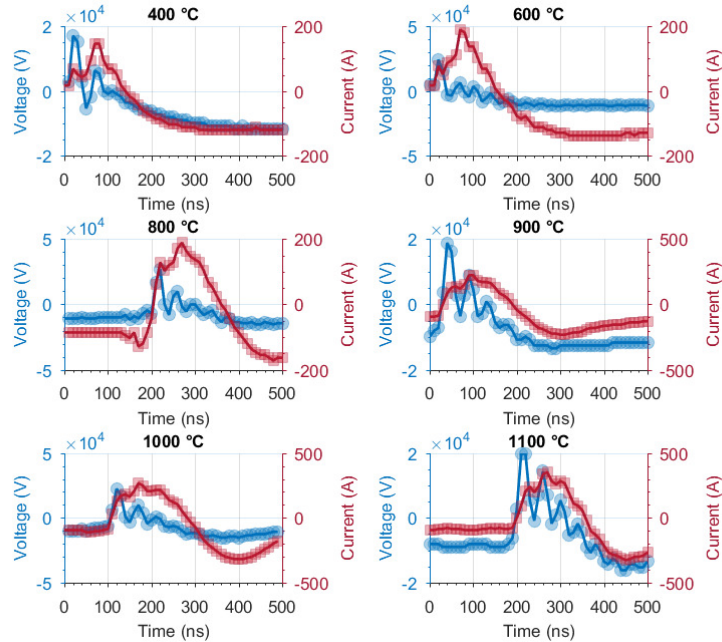
Figure 3: Plasma discharges over nitrogen polluted with naphthalene at different temperatures. Blue represents Voltage and Red represents Current.

²⁴¹   The energy per pulse at each temperature can be calculated from the
²⁴² voltage-current curves by using the equation 1, in a similar way as used
²⁴³ in previous publications [31]. By using equation 2 the SIE variation with
²⁴⁴ temperature can be calculated. The calculated SEI at each temperature is
²⁴⁵ shown in figure 4.

²⁴⁶   There is a direct proportionality between SEI and temperature, however,
²⁴⁷ it is not clear whether it follows a linear or exponential trend. The evolution

16
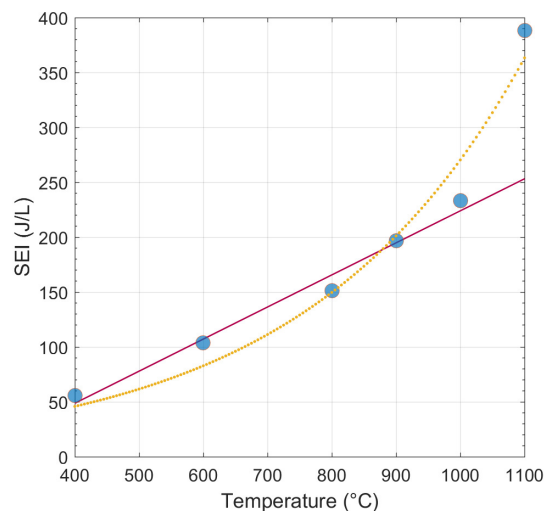
Figure 4: SEI variation with temperature. Points represent experiments, the yellow dotted line is an exponential regression, the red solid line is a linear regression (excluding the last point).

before 1000°C suggest a linear dependency (with a R^2=0.98) which was also found by other authors [45, 46, 66] but the high SEI value at 1100°C indicates that an exponential trend (with an R^2=0.95) can also describe this evolution.

3.2.2. Naphthalene cracking experiments

The plasma setup, described in the Experimental section and shown in figure 2 is used to crack naphthalene at temperatures between 400°C and 1100°C. The initial concentration of naphthalene was set at 1.6 g/Nm³ (Nm³ refers to Normal cubic meters) or around 300 ppm.

These experiments confirm that naphthalene requires temperatures higher than 1000°C in order to be fully cracked by thermal cracking. This tempera- ture is slightly lower than the temperatures already reported for naphthalene

17

cracking [15, 65] due to the longer residence time used in this study together with a possible catalytic effect of the FeCrAl oxide present in the inner walls of the reactor. The use of plasma reduces this temperature to 800°C which means that a clean gas could be obtained by introducing a plasma at a lower temperature. The results of naphthalene cracking are shown in figure 6a, showing a clearer trend than previously published results [67].

An additional observation in figure 6a, which can be confirmed by observing figure 6b, is that there is a point (around 900 °C) where thermal cracking reactions are more extensive than plasma cracking reactions. In figure 6b where energy efficiency(EE) is plotted against temperature, it can be observed that below 800°C the EE increases with temperature, but beyond this point, EE drops sharply. This behavior can also be seen in the variation of energy cost (β), which varies inversely with EE, showing its lowest value at 800°C. (see figure 5).

An explanation can be found in the fact that up to 800°C the amount of naphthalene present in the gas is high enough to allow all (or most of) the reactive plasma species to be consumed by reacting with naphthalene (reaction R2, see next section). Above this point, the naphthalene concentration is reduced mainly by thermal cracking, making the excited species to be consumed by collisions with bulk gas molecules, reactor walls and other excited molecules (reaction R3 and R4, see next section), which consequently reduces the energy efficiency. The EE drop is enhanced by the fact that the SEI increases with temperature.
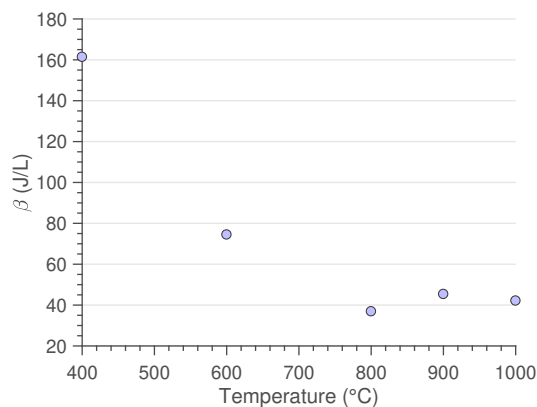
Figure 5: Specific energy cost β variation with temperature

3.2.3. Kinetics of plasma naphthalene cracking

In order to evaluate the efficiency of the plasma removal process, the 0D-global kinetics approach for pollutant removal proposed by Yan et al. [68] is adapted to the nanosecond pulsed naphthalene removal process. According to this approach the naphthalene plasma removal process can be described by the reactions R1 to R4. In these reactions N_2^* represents reactive radicals, and N_2 represents the bulk gas, which consists mainly of ground-state nitrogen molecules ($N_2(X^1\Sigma_g^+)$)

The process starts with reaction R1 by the production of reactive radicals. The following three reactions represent 3 possible ways in which the reactive radicals can be consumed:

- Reaction R2 represents the radical consumption due to reaction with naphthalene

- Reaction R3 represents the consumption of nitrogen radicals by quenching with bulk gas molecules producing non-reactive radicals that do not react with any naphthalene molecule.

19
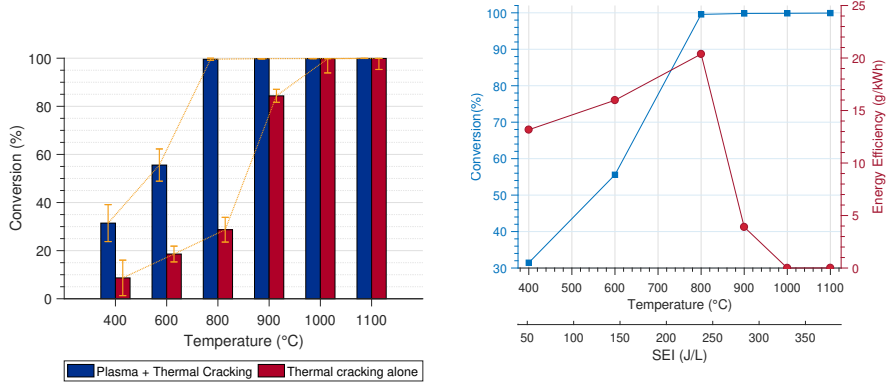
(a) Thermal cracking vs. plasma-enhanced thermal cracking of naphthalene

(b) Energy efficiency and plasma-enhanced thermal conversion vs. Temperature

Figure 6: Evolution of conversion and energy efficiency (EE) with temperature

- Reaction R4 represents the collisions between two radicals that lead to non-reactive radicals ,which do not react with any naphthalene molecule.

$$N_2 + e^- \longrightarrow N_2{}^* + e^- \tag{R1}$$

$$C_{10}H_8 + N_2{}^* \longrightarrow products + N_2 \tag{R2}$$

$$N_2{}^* + N_2 \longrightarrow byproducts \tag{R3}$$

$$N_2{}^* + N_2{}^* \longrightarrow byproducts \tag{R4}$$
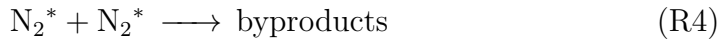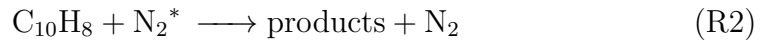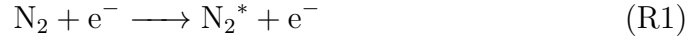
The main radical leading to tar cracking (N_2^*) is the metastable $N_2(A^3\Sigma)$, due to its higher reaction rate [46] and longer lifetime [69, 70]. In addition to this metastable compound, other excited states can help to remove

20

naphthalene such $N_2(a'^1\Sigma_u^-)$, $N_2(a^1\Pi_g)$, $N_2(B^3\Pi_g)$ and $N_2(B^3\Sigma_u^-)$ [51]. Other reactions like excitation of naphthalene due to electron impact are not taken into account in this model due to the small electron cross sections of hydrocarbons together with the small concentration of naphthalene with respect to nitrogen [34].

The plasma naphthalene removal kinetics will depend on the way radicals are consumed. The ideal use of the radicals is the naphthalene removal given by the reaction R2, while reactions R3, R4 lead to inefficiencies.

By making a mass balance over the reactive species N_2^*, the radical termination due to naphthalene removal and the radical termination due to collisions with bulk gas molecules lead to equations 6 and 7 respectively.

$$[C]_f - [C]_o = k_1 * SEI \tag{6}$$

$$\frac{[C]_f}{[C]_o} = exp\left(-\frac{SEI}{\beta}\right) \tag{7}$$

where $[C]_f$ and $[C]_o$ are expressed in mol/L, k_1 in mol/J and SEI and β in J/L.

The plot of the left side of the above equations with respect to SEI allows to determine which mechanism is followed during the removal process: if there is a linear trend between concentations and SEI, plasma excited species are consumed by naphthalene decomposition while a logaritmic relationship between the ratio of final to initial concentrations and SEI indicates that plasma is consumed by collisions with the bulk gas. The aforementioned graphs are presented in figure 7, where none of the graphs shows a linear trend, however, comparing the two figures we can distinguish two different

21

₃₂₆ regions.
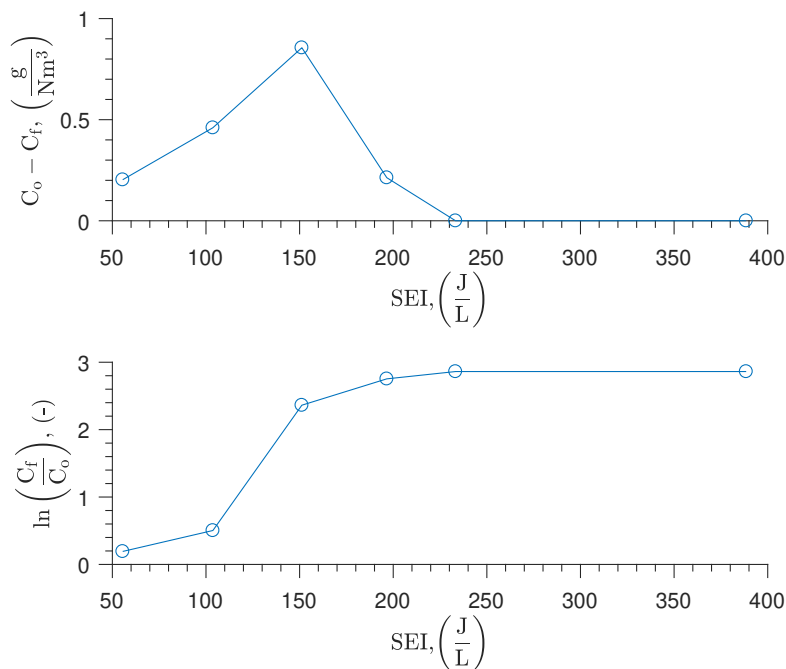
Figure 7: Plasma naphthalene removal with respect to SEI. Upper graph: No linear radical termination kinetics R2. Lower part: Linear radical termination kinetics R3

₃₂₇ The first region, below and up to 800°C (corresponding to an SEI of 150
₃₂₈ J/L) there is a linear proportionality between the concentrations and the SEI
₃₂₉ in the upper graph of figure 7; this describes that in this region the naphtha-
₃₃₀ lene removal is dominated by reactions with plasma reactive species. In the
₃₃₁ second region, above 800°C, where there is a logarithmic proportionality be-
₃₃₂ tween the ratio of concentrations and the SEI in the lower graph of 7; here the
₃₃₃ plasma reactive species are consumed by collisions with bulk gas molecules,
₃₃₄ indicating that the reduction of naphthalene concentration is dominated by
₃₃₅ thermal cracking.

₃₃₆ These results suggest that after a specific threshold, in this case 800°C,

22

thermal tar cracking modeling is sufficient to simulate tar removal. This explains why the simulations of other researchers based on thermal cracking only, are sufficient to describe the concentrations of tar after a thermal plasma cleaning unit [27, 28, 30]. However further experiments need to be performed in order to evaluate how the residence time can affect the threshold where thermal cracking is dominant, since the study of Materazzi et al. [28] evidences that at short residence times($<$2s), the effect of plasma excited species can play a significant role for naphthalene and benzene removal.

4. Conclusion

Gasification of MSW is a promising technology for waste treatment and energy valorization, but it is strongly limited by the presence of tar. MSW gasification experiments showed that the most difficult tar compound to be removed by thermal cracking is naphthalene. Naphthalene cracking was then studied under a nanosecond-pulsed (ns-pulsed) plasma unit in a downstream reactor, where total naphthalene removal was achieved at 800°C a temperature much lower than the one needed in thermal removal alone, which was around 1000°C. A maximum energy efficiency was also reached at 800°C.

A global kinetic model shows that below 800°C, the main mechanism of plasma excited species consumption is naphthalene cracking, while above this temperature,the main consumption mechanism is through collisions with the bulk gas. From these results, we can expect that with real tar, a temperature well below 800°C is needed for complete tar removal using a plasma-aided thermal plasma system since most of the compounds found in tar, with the exception of PAHs heavier than tar, have a cracking temperature much lower

23

than the one of naphthalene. The optimal energy efficiency for real tar removal is expected also to shift towards a lower temperature. An opposite trend should be seen for benzene and heavy PAHs molecules like pyrene, which need higher temperatures to be cracked [65, 71], expecting to have a lower energy efficiency at a given temperature when compared to naphthalene.

Acknowledgement

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