

Full Length Article

Steam reforming of main tar compounds over industrial gasification char

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ABSTRACT

Biomass gasification, including the gasification of waste, is a mature technology where biomass particles are converted mainly into a combustible gas called producer gas. However, cleaning the producer gas remains a significant challenge. This study tests multiple chars produced from an industrial gasifier, a pilot-scale gasifier, and a lab pyrolysis reactor for their efficiency in removing naphthalene, ethylbenzene, and toluene. Moreover, the study evaluates the impact of reforming environment (N_2 and synthetic syngas with/without steam) and temperature (650 °C, 750 °C). At 750 °C and in the absence of a catalyst, switching the carrier gas from N_2 to synthetic syngas enhanced the toluene and naphthalene removal efficiencies significantly. The catalyst impact was more pronounced at 650 °C, with the best-performing char characterized by a high surface area ($1454 \text{ m}^2 \text{ g}^{-1}$) and ash content (10.15 wt%). In absence of steam, the tar content was reduced from 39.9 g Nm^{-3} to 24.3 g Nm^{-3} . Introducing steam further reduced the outlet tar content to 11.7 g Nm^{-3} . Utilizing gasification char for tar reforming not only adds value to waste but also aligns with the circular economy principles. This process enhances the quality of producer gas with the aid of a sustainably sourced catalyst. Remarkably, the char was used in its original form without modification, yet demonstrated exceptional performance in tar reforming.

1. Introduction

Tar formation during biomass gasification remains a challenging issue. Tar contains mainly polycyclic aromatic hydrocarbons (PAH), heterocyclic compounds, and phenolic compounds [1]. When condensed, tar transforms into a black or brown colored liquid or a viscous semi-solid leading to fouling and blockage of downstream equipment. Tar removal from producer gas can be achieved through primary and secondary methods [2]. The primary methods focus on the prevention or reduction of tar inside the gasifier (in situ) through design changes, operating conditions optimization, or the addition of bed additives or catalysts [2]. Secondary methods involve downstream treatments (e.g., hot gas cleaning, and mechanical separation). Hot gas cleaning includes thermal and catalytical cracking, oxidation, and steam conversion [2].

The tar concentration in the producer gas depends on the gasification technology. Downdraft gasifiers are characterized by one of the lowest tar concentrations in the producer gas at $0.01\text{--}6 \text{ g Nm}^{-3}$ followed by fluidized bed gasifiers ($1\text{--}30 \text{ g Nm}^{-3}$), then updraft gasifiers ($10\text{--}150 \text{ g Nm}^{-3}$) [3]. Depending on the final application of the producer gas, these concentrations have to be further reduced. For instance, the upper tar

limit for syngas production and fuel cell application is 0.1 and $< 1.0 \text{ g Nm}^{-3}$, respectively [3]. Generally, thermal and catalytic techniques are deemed most attractive due to their high effectiveness [4]. Catalytic conversion methods are advantageous in the high conversion efficiencies achieved while operating at moderate temperatures ($700\text{--}800 \text{ °C}$) [5].

Recently, char has gained more attention in the field of tar reforming due to the low preparation cost and sustainable sourcing [6–9]. According to a recent literature review, tar reforming is the second most common application of gasification char, following adsorption [10]. The cost-effectiveness and excellent catalytic activity of char make it an ideal candidate for catalytic tar reformation given the frequent need for catalyst regeneration [5]. Gasification char holds key qualities for catalysis and tar reforming, including high surface area and catalytically active inorganic components [11,12]. Additionally, the weak base nature of gasification char makes it highly resistant to deactivation by coke and heavy metals deposition [6]. The development of mesoporous/microporous structures in gasification char arises from the activating agent used (air, CO_2 , and/or steam) during gasification. The proportion of the pore size depends on the char precursor and gasification conditions. The pore size distribution significantly impacts species diffusion

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Table 1

Summary of tar reforming reactions (reproduced from [5] with permission from Elsevier).

Reaction	Name	ΔH_0 (kJ mol ⁻¹)	Reaction Number
$C_nH_m \rightarrow C_nH_j + kH_2$	Thermal Cracking		(1)
$C_nH_m + nCO_2 \rightarrow 2nCO + \frac{m}{2}H_2$	Dry Reforming	297.0	(2)
$C_nH_m + nH_2O \rightarrow (n + \frac{m}{2})H_2 + nCO$	Steam Reforming		(3)
$C_nH_m + 2nH_2O \rightarrow (2n + \frac{m}{2})H_2 + nCO_2$	Steam Reforming		(4)
$C_nH_m + H_2O \rightarrow C_{n-1}H_m + CO + H_2$	Steam Dealkylation		(5)
$C_nH_m + H_2 \rightarrow C_{n-1}H_{m-2} + CH_4$	Hydrodealkylation/ Hydrogenolysis		(6)
$C_nH_m + \frac{4n-m}{2}H_2 \rightarrow nCH_4$	Hydrocracking		(7)
$C_nH_m \rightarrow nC + \frac{m}{2}H_2$	Carbon Formation		(8)
$C_nH_m + H_2O \rightarrow C_nH_j + CO_2 + H_2 + CO$	Partial Oxidation		(9)
$CH_4 + H_2O \rightarrow 3H_2 + CO$	Methane Steam Reforming	206.1	(10)
$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$	Methane Dry Reforming	247.3	(11)
$CO + H_2O \rightarrow H_2 + CO_2$	Water-Gas Shift	-41.2	(12)
$CO + 3H_2 \rightarrow CH_4 + H_2O$	Methanation	-205.8	(13)
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	Methanation	77.2	(14)
$C + H_2O \rightarrow H_2 + CO$	Steam Gasification/ Water Gas	131.1	(15)
$C + 2H_2 \rightarrow CH_4$	Hydrogasification/ Methanation	-74.5	(16)
$C + CO_2 \rightarrow 2CO$	Boudouard	172.5	(17)

within the char matrix which is critical in the catalytic processes [11].

Multiple parallel and consecutive reactions take place during tar reforming and the catalyst deactivation process. The first reactions classification can be based on the absence (dry) or presence of steam. These reactions can be further classified based on the reactants involved and their enthalpies (ΔH_0). For instance, the reaction of tar compounds (C_nH_m), primary gases (CH_4 , CO , CO_2 , H_2), or carbon (C) with steam or primary gases. These reactions are summarized in Table 1.

This study focuses on key tar compounds, including naphthalene ($C_{10}H_8$), ethylbenzene (C_8H_{10}), toluene (C_7H_8), styrene (C_8H_8), and benzene (C_6H_6). Steam and dry reforming reactions of naphthalene primarily lead to the formation of gaseous products such as H_2 and CO (Fig. 1). Additionally, lighter hydrocarbons and soot may also form [13]. There is an elevated tendency towards coke formation as the number of

aromatic rings in hydrocarbon molecules increases [13].

Previous research has demonstrated that the reforming of ethylbenzene using char from waste and commercial catalysts produces benzene (C_6H_6), toluene (C_7H_8), styrene (C_8H_8), and coke [14–16]. Styrene can be generated either through the thermal cracking reaction [17,18] using activated carbon and $CrOx/Al_2O_3$ catalyst or through dehydrogenation reaction [19,20] using wood char. Moreover, ethylbenzene can react with hydrogen and produce toluene and benzene through hydrogenolysis reaction (6) [21].

The presence of reforming agents (H_2O , CO_2) appears to induce high tar conversion, while the addition of H_2 and CO inhibits toluene and naphthalene conversions [4,13]. Steam and hydrogen react with the tar compounds to predominantly produce benzene through dealkylation reaction (5) and hydrodealkylation reaction (6) [22].

Furthermore, competitive tar reforming reactions have been previously observed [24–26] though not fully understood [5]. For instance, a study found that the reforming efficiency of a single compound of tar surrogate (toluene only) was significantly higher than a tar mixture (toluene/naphthalene) [24]. Similarly, benzene conversion during the catalytic reforming of a benzene/naphthalene mixture was significantly lower than the conversion of benzene only [26]. Benzene is completely converted at 500 °C, while in the presence of naphthalene and at temperatures above 750 °C, benzene conversion starts [26]. The authors suggest that at a temperature below 900 °C, poorly reformed naphthalene covers the active sites on the catalyst, thus affecting the reforming efficiency of other tar compounds [24]. Notably, naphthalene is considered one of the most stable and difficult-to-reform tar components [27].

This study aims to evaluate the performance of multiple chars produced from an industrial gasifier, a pilot-scale gasifier, and a lab pyrolysis reactor in tar removal efficiency. The effects of reforming environment, and temperature on tar reforming were also evaluated through multiple tests in N_2 synthetic syngas, and steam. The novelty of this work lies in investigating the performance of gasification char from a commercial gasification plant among other chars in dry and steam reforming of a tar mixture instead of a single surrogate. This study is driven by the concepts of biomass cascade use as well as circular economy where waste or by-products are turned into useful materials to improve the overall process.

2. Materials and methods

2.1. Char production

In this study, we investigated three materials. First, pilot-scale gasification char (PGC) was collected from a pilot-scale downdraft gasifier operating under the Bioenergy and Biofuel Lab of the Free

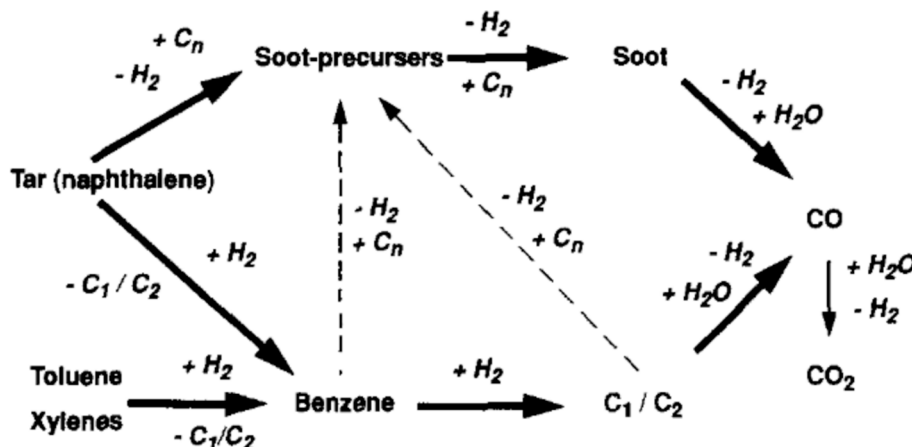


Fig. 1. Naphthalene reaction pathways in the presence of hydrogen and steam (reprinted from [23] with permission from Elsevier).

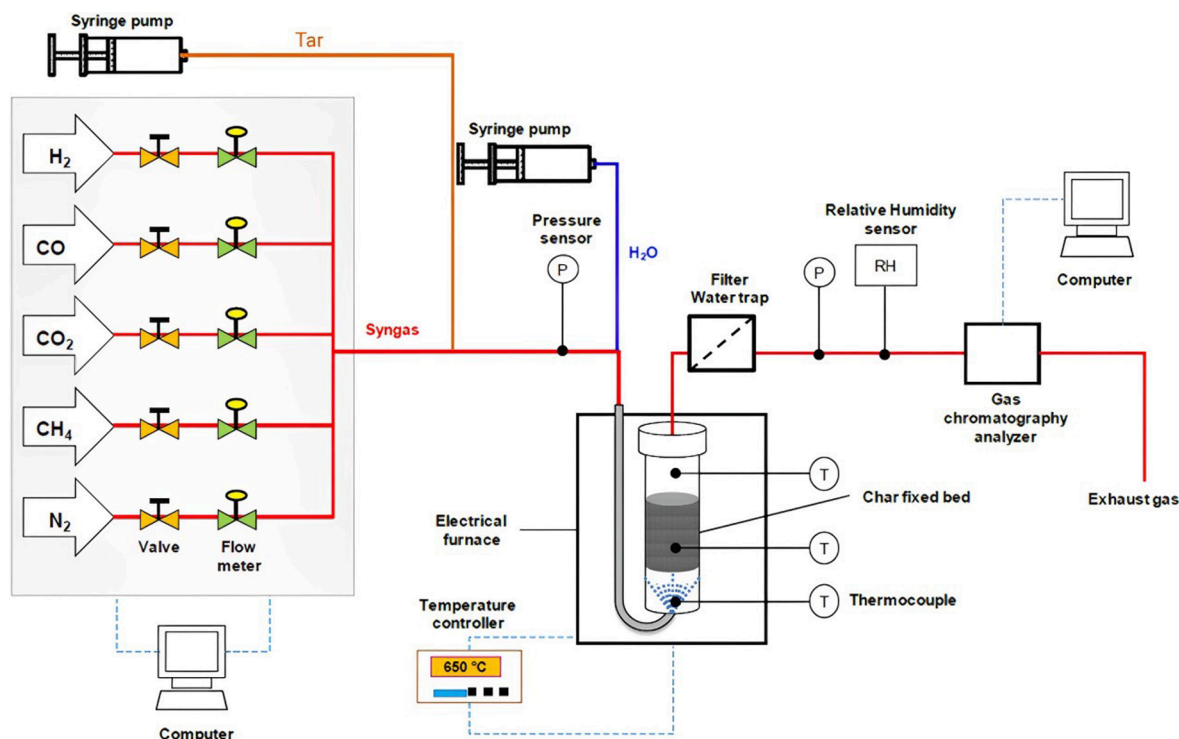


Fig. 2. Schematic diagram of the lab-scale tar reforming setup. (adapted from [29]).

University of Bozen-Bolzano, Italy [12,28]. Additionally, the same wood pellets used in the open-top gasifier were steam activated to produce lab-scale pyrolysis char (SA-LPC). Steam activation was performed by heating the precursor material at $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 (0.75 mL min^{-1}) atmosphere in a rotary furnace until activation temperature was reached. The activation stage was carried out at $850\text{ }^{\circ}\text{C}$ by introducing liquid H_2O at 0.7 mL min^{-1} and N_2 flow of 0.5 mL min^{-1} for 90 min. Finally, industrialized gasification char (IGC) was collected from a commercial dual-stage gasification plant in the region of South Tyrol (IT). The plant operates on softwood (chips) at $850\text{ }^{\circ}\text{C}$ and air as gasifying agent. To facilitate the use of IGC in tar reforming, it was sieved into two primary particle size categories: fine ($<0.5\text{ mm}$, referred to as IGC-F) and coarse ($>0.5\text{ mm}$, referred to as IGC-C). Only the coarse fraction was used to avoid creating a large pressure drop in the reformer. In summary, the three chars used were PGC, SA-LPC, and IGC-C. Our selection aimed to encompass chars from various thermochemical processes, process scales, and particle sizes. PGC and IGC-C were chosen to assess the impact of the char production scale, as well as the effect of different particle sizes (pellets 5–10 mm and coarse powder $>0.5\text{ mm}$). Additionally, those two gasification chars were compared to SA-LPC, which is produced through pyrolysis.

2.2. Char characterization

Various characterization techniques were employed to examine the surface properties and chemical composition of the char prior to and after the tar reforming experiments. Proximate analysis (VM: volatile matter, FC: fixed carbon, and ash) was conducted in triplicate using

thermogravimetric analysis (TGA) according to the modified ASTM D7582-24 standard. In brief, samples were initially dried at $105\text{ }^{\circ}\text{C}$, then heated in a nitrogen atmosphere up to $950\text{ }^{\circ}\text{C}$, and finally combusted in air at $550\text{ }^{\circ}\text{C}$. Elemental composition (CHNS) analysis was conducted in triplicates using an elemental analyzer (Vario MACRO cube, Elementar). Other elements such as Na, K, and Ca were estimated using X-ray fluorescence (XRF, SHIMADZU EDX-800HS). Surface properties were evaluated through nitrogen adsorption–desorption at 77 K . The Brunauer–Emmet–Teller (BET) theory was used to measure the surface area. Mesopore and micropore volumes were determined using Barrett–Joyner–Halenda (BJH), and Horvath–Kawazoe (HK) theories, respectively. Samples were vacuum degassed at $350\text{ }^{\circ}\text{C}$ for 24 h before analysis. The surface area and pore volume analyses were conducted at least in duplicates. The surface morphology of the char was examined through scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) using ZEISS Merlin® FE-SEM instrument.

2.3. Tar reforming

The schematic diagram of the lab-scale tar reforming setup is shown in Fig. 2. The synthetic syngas is mixed with the tar mixture at a heated section of the gas line and fed from the bottom of the reactor. The inlet gas composition for H_2 , CO , CO_2 , CH_4 , and N_2 were 16 ± 1 , 22 ± 3 , 12 ± 1 , 3 ± 0.2 , and 47 ± 4 , vol%, respectively. They closely resemble the gas composition at the pilot-scale gasifier at the Free University of Bozen-Bolzano [28]. The stainless-steel cylindrical reactor has a diameter of 2.1 cm and is placed vertically inside an electrical furnace. Both the reactor and the furnace were equipped with three thermocouples to monitor the temperature gradient. The synthetic tar mixture is composed of naphthalene, toluene, and ethylbenzene with the following concentrations 2.6 , 14.1 , and 23.1 g Nm^{-3} , respectively, and the total inlet flow rate was maintained at 0.68 NL min^{-1} . The gas hourly space velocity (GHSV), residence time, and superficial velocity through the bed column are given in Table 2.

Table 2
Lab-scale reactor performance parameters.

Temperature	GHSV	Residence Time	Superficial Velocity
$^{\circ}\text{C}$	h^{-1}	s	m s^{-1}
650	18,252	0.20	0.10
750	20,229	0.18	0.11

Table 3

Overview of the lab-scale experimental conditions.

Catalyst	Temperature	Gas	Steam	Bed Mass	Bed Height	Test Duration	Inlet Total Tar Concentration
	°C		mL min ⁻¹	g	mm	h	g Nm ⁻³
	650	Synthetic Syngas	0.14 0.28			1	39.9
	750						
	650	N ₂				2	
	750						
PGC	650	Synthetic Syngas		2	2	1	
	750						
		N ₂				2	
SA-LPC	650	Synthetic Syngas		2	2	1	
	750						
IGC-C	650	Synthetic Syngas	0.14 0.28	1	2	1	
	750						

In this study, the impact of multiple factors on tar reforming was investigated. These factors include the catalyst type (PGC, SA-LPC, IGC-C), temperature: (650 °C, 750 °C), and carrier gas (synthetic syngas, N₂). Additionally, we examined the influence of steam flow rate ranging from without steam, 0.14 mL min⁻¹, and 0.28 mL min⁻¹, or alternatively expressed as percentages of 0 vol%, 7 vol%, and 51 vol%, respectively. This investigation would result in a total of 36 experimental runs if all possible combinations were investigated. Instead, an iterative approach was followed to reduce the number of runs. In the first iteration, the impact of carrier gas was investigated by fixing the other factors (catalyst type, temperature, and steam flow rate), while varying the carrier gas. From the results of this experimental campaign, a preliminary conclusion was made and a single carrier gas was chosen. The same approach was followed for the selection of the catalyst type. Finally, all steam flow rates were investigated with the best-performing catalyst at the lowest temperature to reduce the influence of thermal cracking. The tested combinations are listed in Table 3. Thermal cracking experiments (without a catalyst) were also performed to better understand the influence of the catalyst alone.

2.4. Primary gases and tar analysis

The outlet gas composition was analyzed using an online gas chromatograph analyzer (SRA Instruments R 3000). The analyzer was calibrated for ethylbenzene (C₈H₁₀), toluene (C₇H₈), styrene (C₈H₈), and benzene (C₆H₆). A Supelclean™ LC-NH2 solid-phase extraction (SPE) tube, with a bed weight of 500 mg and a volume of 3 mL, was employed for sampling naphthalene. The SPE tube was attached to a 300 mL syringe on one end and a BRAUN Sterican® needle (20 G × 2 3/4") on the other. The needle was inserted into a sampling port downstream of the tar reformer to collect the tar from the producer gas. Based on prior research, a sample volume of 300 mL of producer gas through the SPE bed was deemed sufficient [30], and this volume was used in the current study. Before sampling, the tubes were conditioned by passing 1500 µL (or 5 bed volumes) of dichloromethane through the sorbent material to condition the bed and remove any organic contaminants that could interfere with the tar samples [31]. The tubes were then dried for 5 min at 125 °C [32]. Tar extraction was carried out by passing 1500 µL of dichloromethane through the SPE tube.

The tar concentration measured using the gas analyzer had certain limitations. For instance, the sampling frequency was approximately every 3 min. Additionally, there was a time delay between the injection of tar into the reactor and the gas analyzer's display of the actual tar concentration in the reactor. To account for these variations over time, the chromatogram was integrated over time to estimate the tar concentration over the entire test duration using the following formula:

Table 4

Chars proximate analysis.

	VM		FC		Ash	
	avg	std	avg	std	avg	std
	wt% (d.b.)					
PGC	4.88	1.42	93.14	0.47	1.97	1.90
SA-LPC	5.70	0.54	92.16	0.59	2.14	0.05
IGC-C	8.63	0.80	81.22	2.02	10.15	1.22

$$C_{out} = \frac{\int_{t_i}^{t_f} C_t dt}{t_{tot}} \quad (18)$$

where C_{out} is the estimated outlet tar concentration over the entire test duration (g Nm⁻³), C_t is the concentration measured every 3 min (g Nm⁻³), t_i is the time at the test initiation (min), t_f is the time at the end of the test (min), and t_{tot} is the test duration (min). This value was compared to the inlet tar concentration C_{in} to evaluate the removal efficiency:

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (19)$$

Another parameter was evaluated that consider the thermal cracking contribution to the removal efficiency as well as the bed mass, which varied for certain catalysts. Tar conversion X_{Tar} was defined as follows:

$$X_{Tar} = \frac{t_{tot} Q ((C_{in} - C_{out,C}) - (C_{in} - C_{out,T}))}{m_{cat}} \quad (20)$$

or

$$X_{Tar} = \frac{t_{tot} Q (C_{out,T} - C_{out,C})}{m_{cat}} \quad (21)$$

where X_{Tar} is the tar conversion (g_{tar} g_{cat}⁻¹), $C_{out,T}$ outlet tar concentration during the thermal cracking (g Nm⁻³), $C_{out,C}$ outlet tar concentration during the catalytical cracking, Q is the volumetric flow rate (Nm³ min⁻¹) and m_{cat} is the catalyst bed mass (g).

3. Results and discussion

3.1. Char characterization

Looking closely at the results of the proximate analysis (Table 4) shows the high variability between the tested materials. Char from the commercial gasification plants had a higher VM content and ash ratio compared to the pilot-scale gasifier and the lab-scale pyrolysis. The high

Table 5

Chars main inorganic minerals (not detected: n.d.).

	PGC	SA-LPC	IGC-C
	wt% ash		
Si	0.7	1.3	1.1
P	3.0	2.6	1.9
S	1.0	n.d.	0.5
K	20.0	16.0	17.1
Ca	60.0	66.3	69.8
Cr	0.7	0.5	n.d.
Mn	9.0	9.4	2.1
Fe	3.0	3.5	1.0
Cu	n.d.	0.3	n.d.

VM and ash ratio content were also associated with a lower FC content.

Analysis of the ash is presented in Table 5. As expected, the ash primarily consists of calcium, potassium, and manganese with a smaller fraction of phosphorus and iron among other elements. Alkali and alkaline earth metals (AAEM) such as potassium and calcium are commonly observed in biomass [33] and are known to play a catalytic role in thermal conversion processes [34].

The CHNS-O composition of the tested chars is outlined in Table 6. Industrialized chars IGC-C exhibited the lowest carbon content (87.08 wt%) among all tested chars. This could be correlated with the high ash content, as discussed earlier. The remaining materials had a carbon content in the range of 91.70 – 94.85 wt%. The highest carbon content was reported for PGC. Oxygen content was also diverse. IGC-C had a moderately high oxygen content. Together with the high ash content, this could be a sign of a high metal oxides content.

The BET surface area of the tested chars varied from 398 to 1454 m² g⁻¹ as presented in Table 7. The BET surface area observed for gasification char is typically higher than unmodified pyrolysis char due to the higher gasification process temperature and the presence of a gasifying agent (air) [35]. Compared to activated carbons, which are generally marked by a surface area ranging from 500 to 1500 m² g⁻¹ [36], two materials from the present study are characterized by a relatively high surface area. The surface area (805 m² g⁻¹) of SA-LPC, which was produced in a single process comprising both pyrolysis and steam activation, was higher than the as-received pilot gasification char. Concerning pore volume distribution, the largest micropore volume percentage was found in SA-LPC (71 %), followed by IGC-C (67 %), and PGC (60 %). IGC-C exhibited a surface area of 1454 m² g⁻¹. To our knowledge, this is one of the highest reported surface areas for unmodified char. A recent literature review reported a gasification char with a similar surface area (1253 m² g⁻¹) that was also from a dual-stage gasifier [10].

Table 6

Chars elemental composition.

	C		H		N		S		O*	H/C	O/C
	avg	std	avg	std	avg	std	avg	std			
PGC	94.85	0.34	0.72	0.04	0.50	0.01	0.18	0.06	1.49	0.09	0.25
SA-LPC	91.70	1.00	1.40	0.30	< LD		< LD		5.20	0.18	0.90
IGC-C	87.08	0.47	0.18	0.09	0.25	0.06	0.33	0.09	4.16	0.02	0.76

*By difference.

LQ: 0.2 %, LD: 0.06 %

Table 7

Textural properties of the investigated chars.

	BET Surface Area	Total Pore Volume	Micropore Volume Horvath-Kawazoe (HK)	Micropore Volume	Mesopore Volume Barrett-Joyner-Halenda (BJH)	Mesopore Volume
	m ² g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	%	cm ³ g ⁻¹	%
PGC	398	0.274	0.164	60	0.110	40
SA-LPC	805	0.459	0.324	71	0.135	29
IGC-C	1454	0.912	0.615	67	0.297	33

SEM images (Fig. 3) of PGC, SA-LPC, and IGC-C reveal a great discrepancy in the surface morphology among the different chars. PGC and SA-LPC which were both in pellet forms are very heterogeneous with low visible porosity. On the other hand, IGC-C has a well-defined surface structure with homogeneous pores and increased porosity. These observations are in line with the surface area discussed earlier. The bright spots on the surface of IGC-C were analyzed with the EDX and the results are shown in Fig. 4. The EDX spectrum indicates the presence of clusters of Ca on the IGC-C surface that could act as catalysts for tar reforming.

3.2. Impact of carrier gas

The literature shows that tar reforming studies are often performed with N₂ as a carrier gas and a single model tar compound to understand the underlying reforming mechanisms. When N₂ is replaced with syngas, the tar reforming performance changes due to the presence of reforming agents such as H₂, and CO₂ which enhances the reforming performance. To mimic real world conditions tar reforming was done in the presence of syngas components. Fig. 5 illustrates the impact of reforming environment on the thermal cracking of three tar components (C₁₀H₈, C₈H₁₀, and C₇H₈). Additionally, cracking by-products (C₈H₈, and C₆H₆) are shown. At 650 °C, the shift in reforming environment from N₂ to synthetic syngas did not impact the cracking performance of toluene and ethylbenzene significantly. On the other hand, naphthalene removal was improved from 0 % to 20 % due to the change in carrier gas at 650 °C. At 750 °C, both toluene and naphthalene removal were enhanced considerably due to the change in carrier gas. On the other hand, ethylbenzene removal improved slightly (92 % in N₂, and 98 % in syngas). Cracking by-product, benzene, showed an upward trend in outlet concentration with the shift from N₂ to synthetic syngas and with the increase in temperature.

Fig. 6 demonstrates the impact of carrier gas on PGC tar reforming performance at 750 °C. The shift from N₂ to synthetic syngas improved the char performance. However, this improvement can be mainly attributed to the increased thermal cracking after switching from N₂ and synthetic syngas. The H₂ and CO₂ in the syngas play a role in the tar reforming reactions as summarized in Table 1.

3.3. Impact of catalyst

Figs. 7 and 8 compare the performance of the three investigated catalysts. The impact of the catalyst on reforming performance is more pronounced at 650 °C than at 750 °C. This is likely due to the predominance of thermal cracking at 750 °C. The order of improvement in

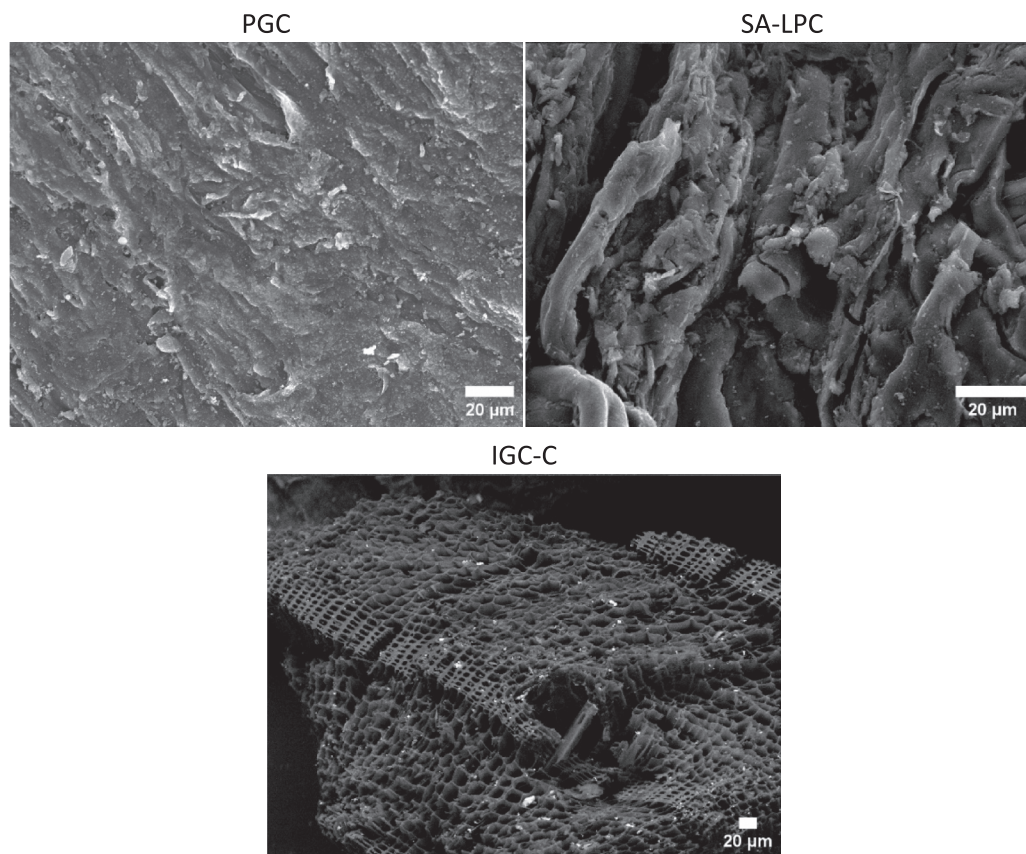


Fig. 3. SEM images of PGC, SA-LPC, and IGC-C chars.

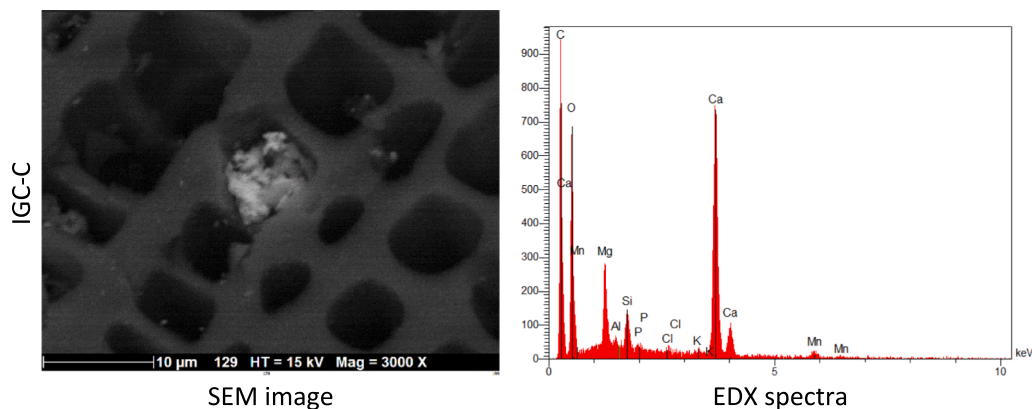


Fig. 4. SEM image with EDX spectrum of IGC-C.

tar removal efficiency is as follows: PGC < SA-LPC < IGC-C. Notably, the toluene outlet concentration remained stable at both temperatures, regardless of the catalyst used. This can be attributed to the formation of toluene as a secondary product of naphthalene and ethylbenzene reforming reactions, as previously explained. At both 650 °C and 750 °C, PGC showed a comparable or lower performance to the thermal cracking case. Similar findings were reported for the cracking of naphthalene [37] and benzene [38], where pyrolysis char demonstrated lower tar conversion rates than thermal cracking. In terms of the generation of by-products at different temperatures, it was observed that at 650 °C more styrene was generated as the removal efficiency of inlet tars increased with better catalysts while benzene remained stable. Conversely, at 750 °C more benzene was generated while styrene remained at a consistently low level.

Regarding the physiochemical properties of the three chars, significant variability is observed. Particularly, ash content, oxygen content, surface area, and pore volume show the greatest variations, as discussed earlier. Char activity correlates with surface area and the presence of metallic species [11]. Studies on char with high ash content (> 25 wt%) showed that bonds are formed between the tars and inorganic species which improves the tar adsorption and heterogeneous reforming [39]. Additionally, the presence of heteroatoms (e.g., O, N, and S) in the carbon matrix increases the catalytic activity [4,40]. IGC-C was characterized by the highest ash content followed by SA-LPC and PGC, while the oxygen content of IGC-C and SA-LPC was comparable. The micropores distribution was similar for all materials, accounting for approximately 60–71 %. Steam activation enhances the catalytic activity by increasing porosity, specific surface area, and polarity (evident through

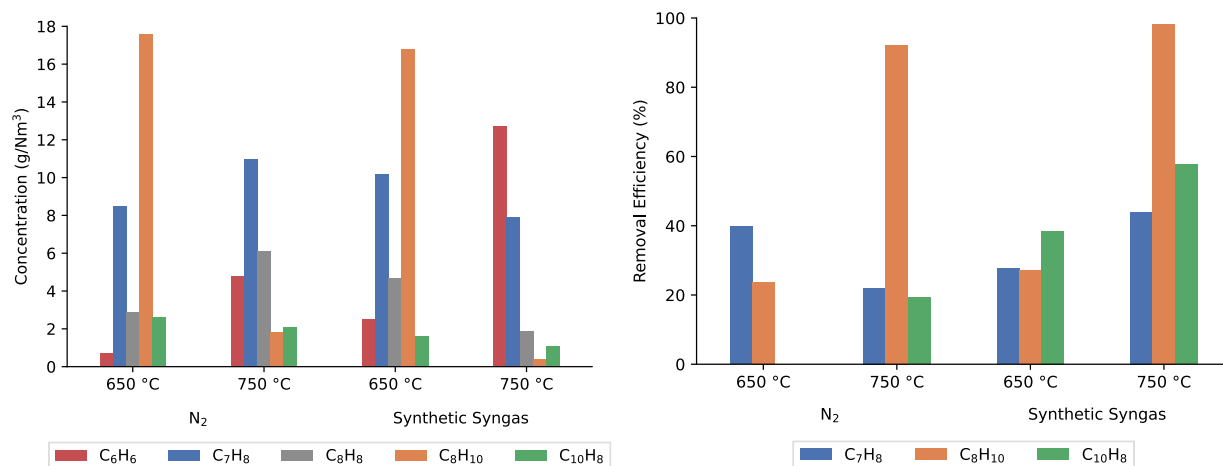


Fig. 5. Thermal cracking performance in terms of concentration (left) and removal efficiency (right) at different temperatures and carrier gases.

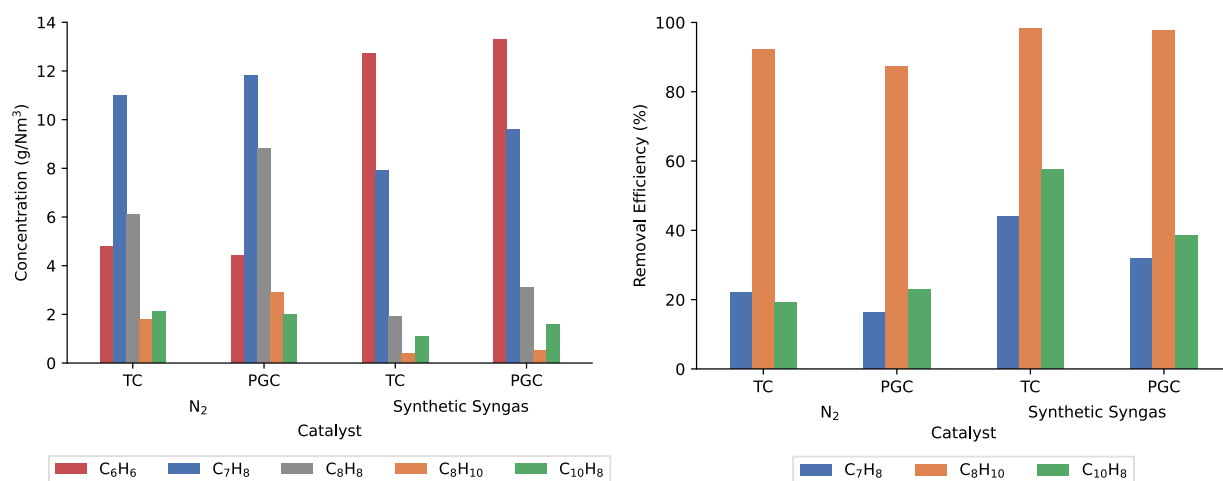


Fig. 6. Impact of carrier gas on PGC performance in terms of concentration (left) and removal efficiency (right) at 750 °C without steam.

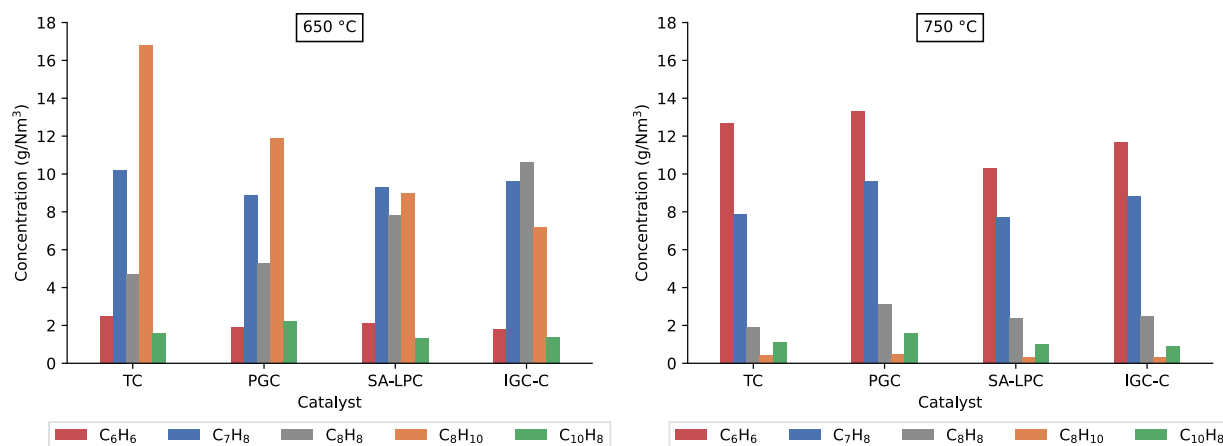


Fig. 7. Outlet tar concentration at 650 °C (left) and 750 °C (right) without steam.

increased O wt% and O-containing functional groups) [41,42]. Activated carbons also exhibit higher energetic discontinuities, such as reactive edges of carbon crystallites, promoting the abundance of active sites [4]. This can explain the similarity between SA-LPC and IGC-C chars' performance and their enhanced performance over PGC. Another major variation between the different catalysts is the difference

in surface area. IGC-C, even with a smaller bed mass than other catalysts, was able to match SA-LPC performance due to the high surface area (1454 m² g⁻¹). Previous work have shown a correlation between the increased tar conversion and char surface area [19].

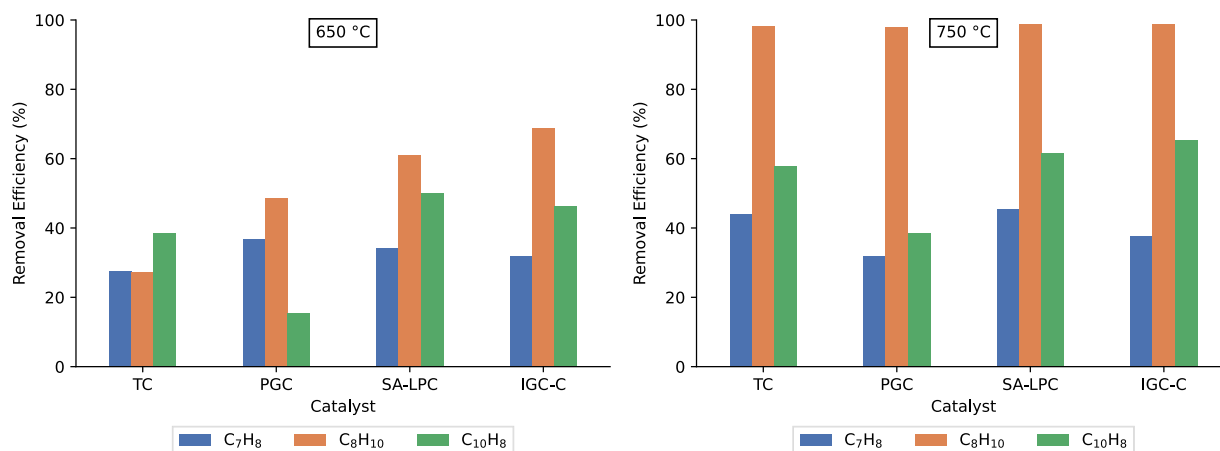


Fig. 8. Tar removal efficiency at 650 °C (left) and 750 °C (right) without steam.

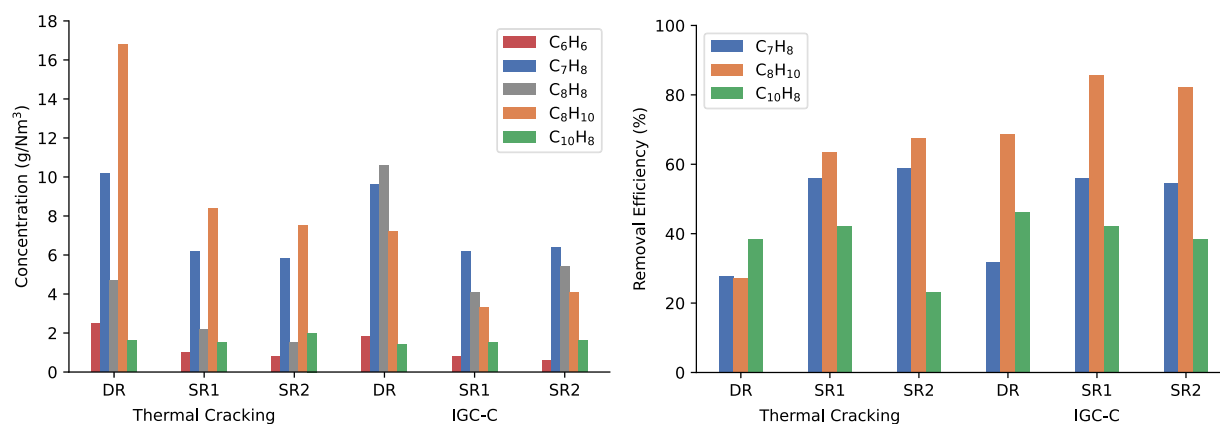


Fig. 9. Outlet tar concentration (left) and tar removal efficiency (right) at 650 °C with steam. DR: dry reforming, SR: steam reforming.

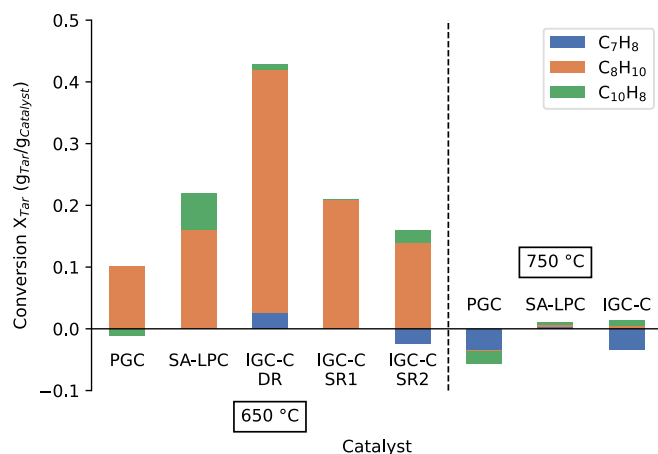


Fig. 10. Tar conversion of different catalysts and test conditions, excluding thermal cracking, and considering bed mass variations. (DR: dry reforming, SR: steam reforming).

3.4. Impact of steam

Tar reforming temperatures of 700–800 °C typically yield significant tar conversion rates, however, there is room for further improvement at even lower temperatures through steam or CO₂ reforming [5]. The influence of steam was investigated with IGC-C at the lowest temperature (650 °C) to minimize the influence of thermal cracking (Fig. 9). The

Table 8

Change in bed mass for test performed in synthetic syngas.

Catalyst	Temperature	Mass Loss	Total Measured Outlet Tars*
	°C	%	g Nm ⁻³
PGC	650	4.3	30.6
SA-LPC		6.2	29.5
IGC-C		6.1	24.3
IGC-C (SR1)		13.0	15.9
IGC-C (SR2)		15.0	11.7
PGC	750	5.3	28.1
SA-LPC		2.3	21.7
IGC-C		7.1	24.2

Naphthalene, ethylbenzene, toluene, styrene, and benzene.

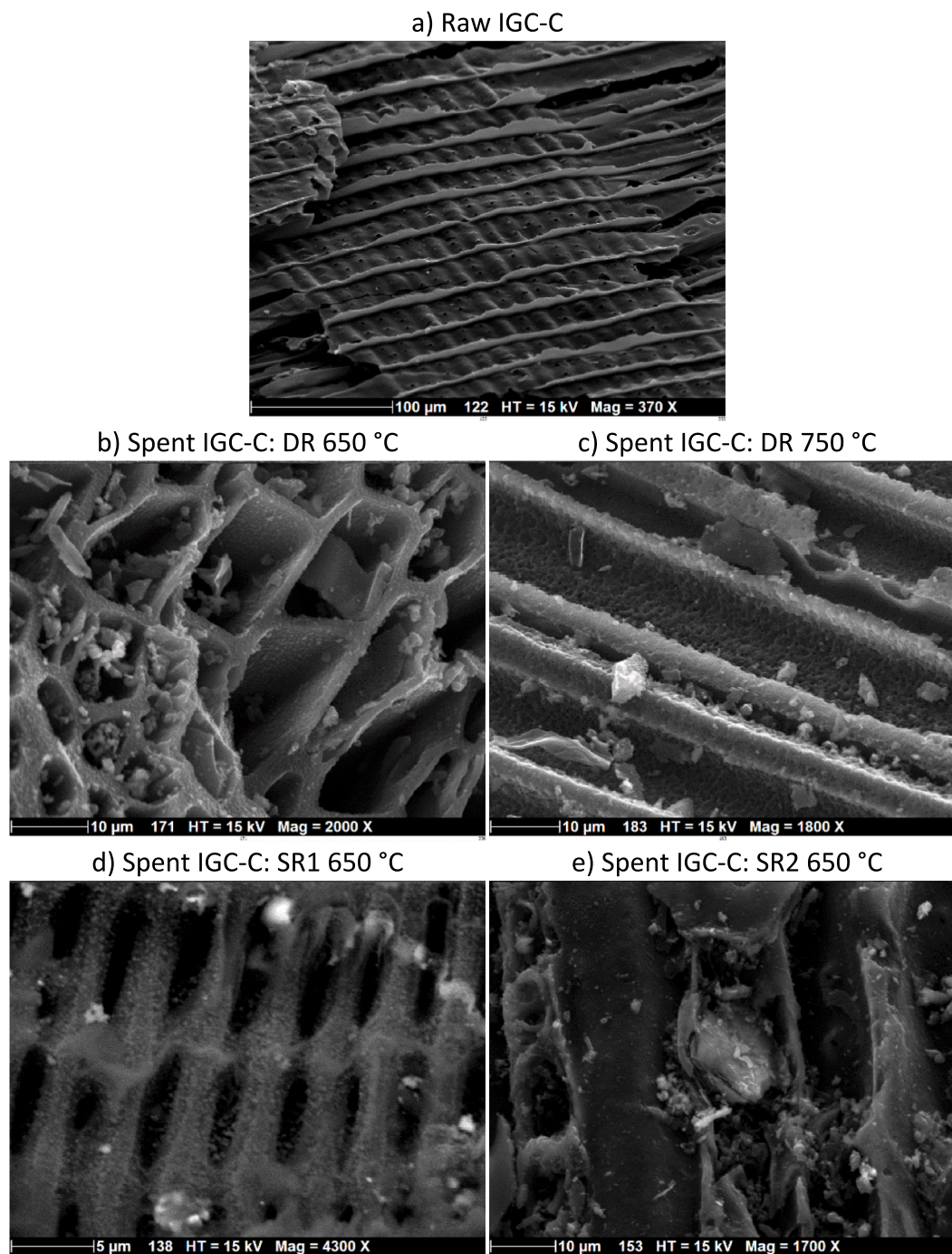
results showed that the addition of steam enhanced both the thermal and catalytic cracking performance. However, the largest improvement in catalytic cracking over the thermal cracking case was observed for dry reforming (without steam). This is shown in Fig. 10. Nonetheless, the overall removal efficiencies of the steam tests were higher than those of the dry reforming tests. The steam can react directly with the tar compounds (Eqs. (3)–(5), and (9)) or through soot gasification (Eq. (15)), as shown in Table 1. Soot is a common by-product of thermal cracking [43], and is gasified in the presence of steam (Eq. (15)) to produce H₂ and CO [23]. Steam gasification of the char bed was also possible. This resulted in the largest bed mass loss (Table 8) among all tests performed.

The catalytic tar reforming performance was not significantly affected by the increase in steam levels (SR1 and SR2). A higher steam content was previously found to fill the char pores on the surface,

Table 9

Inlet and outlet gas composition of IGC-C dry and steam reforming tests at 650 °C.

	N ₂	H ₂	CH ₄	CO	CO ₂	N ₂	H ₂	CH ₄	CO	CO ₂
	Inlet vol%					Outlet				
Dry reforming	47	16	3	22	12	51	16	3	18	12
Steam reforming 1						48	19	3	17	13
Steam reforming 2						54	18	2	14	12

**Fig. 11.** Raw and spent IGC-C for dry reforming (DR) tests at 650 °C and 750 °C, and steam reforming (SR) tests at 650 °C.

blocking the catalytically active sites [44,45]. Moreover, increasing the partial pressure of water led to an increase in the selectivity for H₂ and CO₂, while decreasing the selectivity for C₂–C₇ hydrocarbons [13]. A

high steam concentration can maintain the catalyst activity for a longer period and improve the hydrogen yield as shown in Table 9. Steam reforming had fewer by-products than dry reforming.

Fig. 10 presents a comprehensive summary of the tar conversion ratio, considering both the variation in bed mass and thermal cracking baseline. The thermal cracking performance was influenced by both the test temperature and steam level. The lower bed density of IGC-C also resulted in a variation in bed mass (1 g) compared to PGC and SA-LPC (2 g). Accounting for these variations through the tar conversion ratio provides a better understanding of catalysts' performance. Starting with the highest test temperature (750 °C), thermal cracking accounted for almost all the removal performance (X_{Tar} value close to zero). The negative X_{Tar} value at 750 °C primarily stems from toluene, a reforming intermediate product, that seems to be more favored at higher temperatures.

At 650 °C without steam, the conversion ratio aligned well with the removal efficiencies reported in Fig. 8. However, the conversion ratio of the steam tests seemed to decrease in comparison to the dry reforming case. Similar to 750 °C tests, the toluene outlet concentration was higher than the inlet concentration for the IGC-C SR2 test. The reduced conversion ratio, which was comparable to the dry reforming of SA-LPC can be explained by the increased thermal cracking performance with steam.

Finally, the tar conversion (X_{Tar}) should not be mistaken for the maximum adsorption capacity (q), despite sharing the same units (g/g). The current conversion values reported herein are provided to enable comparisons between tests with varying bed mass and thermal cracking performance. Additionally, the tar conversion was calculated based on a 60-minute test duration, which was not enough to fully saturate the bed. Therefore, it is likely that the bed's adsorption capacity exceeds the tar conversion value.

From the SEM images, it seems that soot is formed during the cracking of tar as presented in Fig. 11 b-d. The soot appears as spherical sub-particles (spherules) nucleating on the pore walls of the spent char. Increasing the steam percentage during the SR2 test resulted in a reduced soot formation as shown in Fig. 11 e where the pore walls appear smoother.

4. Conclusions

An initial assessment of tar reforming performance was conducted on three chars (PGC, SA-LPC, and IGC-C) at a lab scale. Tests were conducted at two temperatures (650 °C and 750 °C) under different reforming conditions (N_2 and synthetic syngas), both with and without steam. A tar mixture, consisting of naphthalene, ethylbenzene, and toluene, was used in the assessments. At 650 °C and in the absence of a catalyst, the carrier gas primarily impacted naphthalene removal efficiency and, to a lesser extent, toluene. However, at 750 °C, the carrier gas significantly affected the removal efficiency of both toluene and naphthalene. On the other hand, ethylbenzene seemed unimpacted by the carrier gas. Comparing the performance of the three investigative catalysts in synthetic syngas showed that the impact of the catalyst was more pronounced at 650 °C than at 750 °C. The best-performing char was IGC-C followed by SA-LPC and PGC. IGC-C was characterized by the highest surface area and ash content followed by SA-LPC and PGC, while the oxygen content of IGC-C and SA-LPC was comparable. Such properties correlate with a higher catalytic activity. Introducing steam improved the removal efficiency of IGC-C further. However, this improvement was mostly attributed to the increased thermal cracking with steam as indicated in the tar conversion (X_{Tar}) analysis.

From a global perspective, utilizing gasification char for tar reforming not only adds value to waste but also promotes circular economy principles. This process enhances the quality of producer gas with the aid of a sustainably sourced catalyst. Notably, the char was employed in its original form without any modification, yet it demonstrated exceptional performance in tar reforming. Future research should prioritize the application of gasification char produced at commercial scale, which is often in fine powder form. The use of powder in a fixed bed reactor poses a challenge due to the significant pressure drop or unintended bed fluidization. Therefore, efforts should be directed

towards putting this char into an appropriate form for tar reforming applications. Moreover, gasification char has shown potential in various other applications, such as wastewater treatment, that could also benefit from a pelletized char.

CRedit authorship contribution statement

Ali Abdelaal: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Audrey Villot:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Francesco Patuzzi:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Conceptualization. **Marco Baratieri:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization. **Claire Gerente:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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