Seashell waste-derived materials for secondary catalytic tar reduction in municipal solid waste gasification

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Abstract

Catalytic tar removal from producer gas is critical for the economic feasibility of Municipal Solid Waste (MSW) gasification in the waste-to-energy(WtE) approach. Nickel- and noble-metal catalysts have the highest tar cracking activities, but they increase costs, use scarce materials, and generate dangerous byproducts. To overcome these drawbacks, naturally occurring materials should be used for tar cracking. In this paper, two nanomaterials, synthesized from oyster and mussel waste shells respectively, are used to clean syngas from MSW in a secondary tar cracking unit. We observed that they reform class 1 tar (heavy tars that condense at high temperatures at very low concentrations) into class 3 tar (light hydrocarbons that are not important in condensation) and benzene. Although both catalysts' composition and textural properties were identical, crystallite size and especially specific surface area variation was enough to generate a change in product selectivity. A larger crystallite size and SSA shows a soot yield reduction of 95% with respect to the non-catalytic case, simultaneously increasing the H_2/CO at 1000°C.

Keywords: Tar removal, gasification, Municipal Solid Waste, green catalyst, Waste-to-Energy

Abbreviations: SSA, Specific Surface Area; ELFM, Enhanced Landfill Mining; Nm³, Normal cubic meter; MSW, Municipal Solid Waste; WtE, Waste-to-Energy; WtM, Waste-to-Materials; PAH, Polyaromatic Hydrocarbons; GC, Gas Chromatography; BET, Brunauer-Emmett-Teller; BJH, Barret-Joyner-Halenda; XRF, X-Ray Fluorescence; XRD, X-Ray Diffraction; SPA/SPE, Solid-phase adsorption / Solid-phase Extraction; ER, Equivalent Ratio.

1. Introduction

Human sustainability on earth is being menaced by depletion of natural sources, the impact of waste to the environment (water, air, and soil) and the lack of clean, reliable, affordable and modern energy resources [1]. In response to these challenges, strategies like Enhanced Landfill Mining (ELFM) have gained attention for treating the Municipal Solid Waste (MSW) contained in the 150.000 to 500.000 landfill sites across Europe [2] reducing the environmental impact of such waste while recovering energy (WtE) and materials (WtM) from it. Within the ELFM context, gasification has been evaluated as a technology with a higher potential than incineration or pyrolysis for WtE and WtM valorization routes [3].

Although gasification is a mature technology, MSW gasification is still under study and many challenges need to be overcome to arrive at mass market implementation [4]. One of them is the production of tar, a byproduct of gasification that pollutes the producer gas, and that consists of all

hydrocarbons with a molecular weight higher than benzene [5]. Tar is a big issue from the operational point of view, causing clogging in pipes and accessories, and from the environmental point of view, playing a significant role in the gasification environmental impact [6, 7, 8]. The main consequence of tar presence in syngas is unacceptable maintenance times, which makes tar removal so costly, that it has caused the disappearance of many gasification projects [8]. Tar can also increase the toxicity risks for all operators in contact with it, increase the rate of corrosion in metallic pipes and devices and increase the deactivation of active sites in supported metal catalysts.

Catalysts have been used as the most popular technology for tar cracking either in-situ (i.e. inside the gasifier together with the feedstock) or ex-situ (in a secondary unit downstream the gasifier) or in both configurations as suggested by Claude et al. [9] in a temperature range of 400-1000°C. In this temperature range, catalysts convert tar into lighter gases without involving substantial cooling or heating of the producer gas, which makes them ideal for this task, especially when energy valorization is envisaged.

However, the catalysts with the highest catalytic activity, long-term stability, and low carbon deposition during tar cracking contain metals like Ni, Pt, Pd, Rh, or Ru [10, 11, 12] which have a reduced availability in nature and therefore high prices. The use of cheap greener catalysts (especially the ones derived from waste) has attracted attention of recent research studies to reduce the environmental impact with respect to metal supported catalysts in syngas cleaning [13], or to increase the lifetime of such metal-based catalysts by preconditioning the syngas to avoid their deactivation.

Using waste-derived materials for tar cracking can increase the waste

treatment performance of the gasification process, by reducing the amount of waste dumped and by finding a cheap greener precursor for tar removal catalysts. Indeed, many waste-derived materials have demonstrated to be effective in various catalytic processes. For instance, red mud, a residue from the aluminum industry, is used in catalytic bio-oil upgrading [14], in coal and biomass hydrogenation [15] and in naphthalene and SO_x catalytic reduction [15]; and slags from steel industry are used for aqueous pollutant removal [16]. Apart from the examples given above, there is a long list of materials obtained from waste which have shown to be suitable for being used as catalysts in different processes [17] which can be exploited in tar abatement.

In the specific case of tar reduction, most of the catalysts derived from residues have been obtained from the char [18, 19, 20, 21, 22, 23], and the ashes [24, 25] produced from thermochemical treatment of the same feed-stock. In addition to the aforementioned materials, calcined waste shells for tar cracking purposes have been gaining attention. Thanks to their high calcium content they have been used in processes such biodiesel production [26, 27, 28, 29, 30, 31, 32], photocatalytic removal of dyes from water [33], and CO₂ capture in gasification and combustion processes [34, 35, 36, 37].

Other calcium-rich materials have been successfully used for tar removal, like calcined dolomite and olivine for biomass tar removal in-situ [39, 40, 41, 42, 43, 44, 45, 46] and ex-situ [39, 47, 48, 49, 50], however both minerals must be exploited in mines. Using waste shells would avoid the mining activity usually linked to the use of dolomite, olivine and other metal-based catalysts, reducing also the environmental impacts associated with it. So far, among

Basis of classification	Nomenclature	Description	Properties	Representative compounds
Molecular weight	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	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 (≥ 4 rings)	Condense at high temperatures even at low concentrations	Fluoranthene, pyrene, crysene, perylene, coronene

Table 1: Tar compound classification according to ECN [38]. Acronyms: GC = Gas Chromatography, PAH = Polyaromatic Hydrocarbons.

the different seafood shells available, only scallop and egg waste shells have been investigated for in-situ tar reduction in biomass steam gasification as active phase and as catalyst supports [51, 52, 53, 54].

The addition of in-situ catalysts makes no sense for specific feedstocks, like excavated MSW, due to the high ash and soil content (between 34% and 60%) [55], because adding an in-situ catalyst would increase the already enormous amount of ash. Moreover, in the aforementioned studies, only gas composition changes are tracked, but there is no information about the evolution of tar composition and soot generation during the tests, both of which are critical for the design of downstream processes and to evaluate the catalytic tar cracking performance.

There is thus still a need for exploring calcium-rich materials derived from shells as catalyst alone, especially under optimized conditions in a secondary tar cracking unit. Therefore, in this study we explore the catalytic tar reduc-

tion from MSW gasification using catalysts derived from two type of shells, *Crassostrea Gigas* and *Mytilus Edulis*, both of them having a worldwide production of 575.626 and 182.626 tonnes per year respectively [56], generating subsequently significant amounts of waste. The tar catalytic cracking activity is isolated from other catalytic effects by using them in a secondary reactor downstream a MSW gasifier allowing also to find better operating conditions for tar cracking. A detailed tar distribution analysis is done according to the classification made by the Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek TNO (former Energy Center of the Netherlands ECN) presented in table 1, and the tar dew point is determined using the online tool provided by the same institution [57].

2. Experimental

2.1. Municipal Solid Waste preparation

The MSW used in this research was obtained from a ballistic separation of excavated waste from the Mont-Saint-Guibert landfill in Belgium. For the gasification tests, the lightest waste fraction between 200-90mm was selected (also known as a 2D fraction) due to its high calorific value (22.4 MJ/kg) [58] which is comparable to the one of woody biomass (around 20 MJ/kg) [59] and low-rank coals [60] (between 18-24 MJ/kg). The fraction consisted of 0.7% wood, 3.5% paper, 8.4% textile, 42.3% plastics, 10.5% other combustible materials, 1.9% metals, 1.5% inert materials, and 31.2% fine particles as was measured by a hand sorting method by García-Lopez et al. [58]. The samples were dried in a furnace at 105°C before the gasification tests. The MSW's ultimate analysis revealed that the sample contained 40.5% of C,

6.1% of H, 1.1% of N, and 4.3% of O (in Wt% on a dry basis) with the rest of the MSW sample being composed of inorganic minerals and metals. The proximate analysis showed 55.3% of volatile matter and 42.9% of ashes with an undetermined amount of fixed carbon (on a Wt% on a dry basis). The proximate analysis of the MSW sample gives a total composition higher than 100%, which has also been found in other studies dealing with high-ash content samples, due to the high amount of metals and inorganic compounds that oxidize during the proximate analysis making challenging to determine the amount of fixed carbon [61].

2.2. Catalyst preparation and characterization

For this research, 1kg of *Crassostrea Gigas* (Oysters) and 1kg of *Mytilus Edulis* (Mussels) shells were recovered from a local restaurant in the West-Vlananderen region of Belgium. Both samples were kept in a 10% hypochlorite solution to control the odors and bacterial activity before processing the material. Subsequently, the shells were washed with abundant hot water and dried at 110°C overnight. After that, the shells were submerged in a 5% NaOH solution with ultrasound treatment to remove the remaining organic matter. The shells were then washed with hot water until the pH was neutral and dried in an oven at 110°C overnight. The shells were powdered in a mill and the resulting powders were calcined at 1000°C for 4 hours. The calcined materials were again manually ground and subsequently pelleted and crushed to obtain a particle size between 0.8 and 1.2 mm. The two resulting catalysts were labeled as catalyst #1 for the one derived from mussels and catalyst #2 for the one derived from oysters. Three characterization techniques were used for determining the physicochemical properties of the different materials

as described in the next sections.

2.2.1. N₂ physisorption tests

N₂-physisorption tests were performed on a Micromeritics TriStarII Single-point and micromeritics FlowSorbIII. The specific surface area was determined on approximately 0.3 g of powder of each of the two samples with previous degassing at 150°C under vacuum during 2h. The Brunauer-Emmett-Teller (BET) theory was applied to calculate the specific surface areas. Pore size distributions were obtained at the same time from the isotherms based on the Barret-Joyner-Halenda (BJH) theory. Desorption branches were used to determine Specific Surface Area (SSA), pore size distributions, pore-volume, and average pore diameter.

2.2.2. X-ray Fluorescence (XRF)

The elemental composition of the calcined catalysts was carried out using a wavelength dispersive X-ray fluorescence spectrometer (S2 Ranger Bucker), equipped with a palladium tube. For the analysis 500 mg of each of the two calcined catalysts were placed in a closed vessel covered by a mylar film, a plastic transparent to X-rays.

2.2.3. X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) characterizations were carried out at room temperature on a Bruker AXS D8 advance diffractometer in Bragg-Brentano geometry, with a radiation source of CuK α ($\lambda = 0.154$ nm). The XRD pattern was recorded with a step size of 0.05° in 2θ , at 1 step per second, with a scan range of $20^\circ < 2\theta < 80^\circ$. This study was used to determine the crystalline phases of the materials before and after calcination

by comparison with XRD patterns in the Bruker database and to calculate the apparent average crystallite sizes. The apparent average crystallite sizes were estimated by full pattern matching of the corresponding XRD structures using equation 1.

$$d_{cryst} = \frac{k \times \lambda}{\beta \times \cos\theta} \quad (1)$$

where k is the geometric factor ($k=0.89$), β is the width of the line at half height in radians, λ represents the wavelength used and θ is the angle of Bragg in radians. A LaB₆ standard was used to evaluate the instrument resolution.

2.3. Tar cracking tests

The tar catalytic experiments were performed in the setup sketched in Figure 1. Each experiment starts by placing 5g of MSW sample in a holder in the gasifier cold zone (1) while the hot zone (2) reaches 800°C. Simultaneously the downstream secondary tar cracking reactor (3) is also heated-up. During heating up, a nitrogen flow is passed through the system, and once the final temperature is reached, the flow is switched to air with an Equivalent Ratio (ER) of 0.45, and the MSW sample is moved from the gasifier cold zone to the gasifier hot zone. The ER is the ratio of the fuel-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio. The value of 0.45 was chosen because it is a typical value used in gasifiers working above 800°C [62], also allowing to form tar concentrations that do not saturate the SPA column used for sampling.

Once the sample is placed in the hot zone, gases are released from the sample in the reactor (2), pass through the second reactor (3) and, then,

Figure 1: Catalytic test setup. The dotted lines represent off-line measurements while the solid lines represent online analysis. Parts: 1. *Gasifier cold-zone* 2. *Gasifier hot-zone* 3. *Secondary tar cracking reactor* 4. *SPA/SPE sampling* 5. *Tar scrubbing system*.

through a set of bottles containing acetone at -12°C (5) in order to remove tar, while SPA/SPE sampling (4) is done in parallel by sampling 100 ml of gas during the first 5 min of gasification. After the scrubbing section, the gases passed are directed through a glass wool filter placed before gas collection in a Tedlar-bag, to be later subjected to a micro-GC analysis to determine the gas speciation. The syngas yield was measured by an online gas flow-meter. The SPA/SPE column is processed according to the procedure described in [63] to identify and quantify tar molecules from class 2 to class 5 according to the classification shown in table 1, while the scrubbing liquid contained in the bottles is filtered, evaporated (80°C during 12h) and weighted to determine the gravimetric tar yield, which will be referred to as class 5 tar in the Results section. The soot yield is determined by the amount of solid retained during filtering of the scrubbing liquids.

In the different experiments carried out, the conditions in the first reactor

(1) and (2) are kept invariable, while in the secondary tar cracking unit the temperature and the type of catalyst are varied according to the experimental matrix displayed in Table 2. During the non-catalytic test, an empty boat was kept in the secondary tar cracking reactor, while in the other experiments the boat was filled with 5 grams of catalyst.

Tar removal method	Tar removal temperature	
Thermal cracking (No catalyst)	800°C	1000°C
Catalyst #1 (Mussel-derived)	800°C	1000°C
Catalyst #2 (Oyster-derived)	800°C	1000°C

Table 2: Tar cracking experimental matrix.

3. Results

3.1. Characterization of the catalysts

According to XRF tests, both catalysts showed to be rich in calcium with small strontium impurities amounting 99.5 % of calcium and 0.5% strontium after calcination. Although the elemental composition was similar, there appeared small differences when characterizing the porosity of the materials. From the N_2 physisorption tests, presented in figure 2, both catalysts produced before and after calcination a type IV isotherm, with a very small area hysteresis loop, indicating the presence of low mesoporosity. The pore volume, pore size and SSA obtained from the BET analysis of the N_2 isotherms are presented in table 4, where it is clear that catalyst #1 has a lower porosity than catalyst #2, with a SSA of 0.164 and 0.364 $m^2 g^{-1}$ respectively. This SSA is very low compared to other porous catalysts usually used for tar

cracking, though calcium-rich materials obtained from similar sources exhibited also very low SSA values [11], as it can be seen in table 3. The mean pore diameter was 41.5 nm for catalyst #1 and 28.87 nm for catalyst #2.

Type	Catalyst	SSA ($\text{m}^2 \text{g}^{-1}$)	Reference
Biochar	Iron supported on bio- and coal char	400-1400	[64]
	Fly ash supported on char	117	[65]
Zeolite	Ni-MgO over HZSM-5	281-316	[66]
Ca-based materials	Olivine	0.15-1.42	[67]
	Olivine	0.18	[68]
	Dolomite	17.92	[68]
	Dolomite	0.18	[68]
	Dolomite	1-8,8	[48]
	Ni and Fe supported on Olivine	0.81-2.95	[69]
Others	MgO	34	[70]
	γ -Alumina	100	[68]

Table 3: Typical Specific Surface Area (SSA) of different catalysts used for tar cracking

Regarding the crystal structure, the non-calcined materials showed clear differences, while after calcination, both materials were more uniform as is clear from figure 3. Before calcination, catalyst #1 presented two different phases, aragonite, and calcite, while catalyst #2 consisted only of calcite. After calcination at 1000°C, both materials evolved towards CaO, with catalyst #2 showing higher intensity peaks. The only clear difference between both catalysts was the crystallite size estimation, obtained by using equation 1, over the different peaks, which was of $67 \pm 4,4 \text{nm}$ for catalyst #1 and

Figure 2: N₂ adsorption–desorption analysis of mussel and oyster derived materials before and after calcination.

$77 \pm 8, 8 \text{ nm}$ for catalyst #2.

3.2. Syngas yield and composition

The use of both catalysts increased notably the syngas yield at 800°C, when compared to the non-catalytic case, with catalyst #1 showing a higher syngas yield increment. However at 1000°C, the effect of the catalysts on syngas yield is less obvious, and it can be considered as negligible. Syngas composition, on the other hand, exhibited a higher variation at 1000°C for both catalysts when added in the secondary tar cracking unit as can be seen

Catalyst	SSA ($\text{m}^2 \text{ g}^{-1}$)	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Pore size (nm)
#1 non-calcined	0.969	0.005	26.57
#2 non-calcined	1.400	0.010	43.27
#1 calcined	0,164	0.002	63.06
#2 calcined	0,364	0.003	39.87

Table 4: BET analysis of calcined and non-calcined catalysts

Figure 3: XRD patterns of non-calcined (left) and calcined (right) materials.

in figure 4b.

The H_2 volume fraction was 3 times higher at 1000°C than at 800°C for the catalytic and non-catalytic cases, which agrees with what is expected from a temperature increment [71, 72, 73]. The use of catalyst #1 however, resulted in a slightly higher volume fraction of H_2 when compared to the non-catalytic case, while the use of catalyst #2 decreased the H_2 volume fraction. The CO_2 fraction followed an opposite trend, but with volume

Figure 4: Syngas yield (4a) and syngas composition (4b) in a N₂ free basis.

fractions much lower than the ones of H₂.

CO and CH₄ fractions followed different trends at both temperatures studied. At 800°C, the use of both catalysts did not seem to affect the volume fraction of either of these two gases. On the other hand, at 1000°C, CO fraction was reduced by both catalysts while the CH₄ fraction increased, with catalyst #2 displaying the most notable variation of these two gases compared to the non-catalytic case.

The C₂-gases (which comprise ethylene and acetylene) also showed a different behavior with the two catalysts at the two temperatures studied. While at 800°C catalyst #1 reduced their fraction and catalyst #2 did not, at 1000°C catalyst #2 increased the C₂-gases fraction by 4 while catalyst #1 kept it almost invariable in comparison to the non-catalytic case.

With respect to the H₂:CO ratio the use of both catalysts had a negligible effect at 800°C but they both presented a beneficial effect at 1000°C, passing from 0.9 in the non-catalytic case, to 1.4 and 2.8 for catalyst #1 and #2

respectively.

In summary, catalyst #1 increased more the syngas yield, hydrogen, and methane fraction while catalyst #2 increased more moderately (or even decreased) the syngas yield and the hydrogen fraction at both temperatures. At 800°C the syngas yield variation was more evident in comparison to the non-catalytic case, while at 1000°C syngas composition was more affected than the syngas yield. Even when catalyst #2 reduced the H₂ yield, the H₂:CO ratio was highly improved by using this catalyst, reaching a maximum value of 2.8 but with a simultaneous higher production of C₂- and C₃-gases(which comprise propene and propane).

Figure 5: Tar yield and tar dew point (left, where bars are read on the left and lines on the right) and soot yield (right). Tar dew point is estimated by using tar composition shown in table 5 in the tar dew point calculator provided by ECN [57]

3.3. Tar yield, tar composition and soot yield.

The use of both catalysts reached gravimetric tar (class 5 tar) conversions with respect to the non-catalytic case of 53% and 65 % at 800°C and 70% and 81% at 1000°C for catalyst #1 and #2 respectively, as can be calculated from the tar yields presented in figure 5a. These conversions are not that high compared to the conversion obtained by using supported metal catalysts (which are above 90% at similar temperature ranges) [74]. However, the production of soot, a byproduct of tar cracking, which tends to be more problematic than tar itself, decreased at high temperatures as it can be seen in figure 5b. The soot reduction was especially significant when using catalyst #2. The results at 800°C show that, although tar yield was reduced, soot yield is increased by both catalysts, with catalyst #1 yielding the highest amount of soot.

Apart from soot reduction, catalyst #2 changed the tar distribution (class 2 to 5) such that it decreased the estimated tar dew point from 123 to 109°C (calculated by using concentrations presented in table 5 in the tar dew point calculator given by the ECN [57]) when tar cracking was performed at 1000°C, while with catalyst #1 tar dew point remained invariable, as can be seen in figure 5a. Catalyst #2 exhibited the highest reduction of heavy PAHs (acenaphthylene, phenanthrene, fluoranthene and pyrene), between 38 to 60% with respect to the non-catalytic case at 1000°C, increasing at the same time the amounts of toluene and benzene. Catalyst #1 on the other hand yielded PAHs levels similar to the non-catalytic case at 1000°C, as it can be seen in table 5. The reduction of these PAHs levels is also directly linked to the low soot yield since PAHs are known as precursors of the macroaromatic

Sample Number	A	F	C	B	E	D
Secondary tar cracking temperature (°C)	800	800	800	1000	1000	1000
Catalyst	No catalyst	Catalyst #1	Catalyst #2	No catalyst	Catalyst #1	Catalyst #2
Benzene	40	13890	570	3540	14910	12190
Toluene (Class 3)	1250	17350	4780	110	230	230
m/p-Xylene (Class 2)	1980	1140	2140	60	90	70
o-Xylene (Class 2)	22300	15420	24630	N.D.	40	N.D.
Indan (Class 3)	860	390	710	N.D.	N.D.	N.D.
Indene (Class 4)	9250	5260	8700	N.D.	N.D.	N.D.
Naphthalene (Class 4)	39670	34360	34720	1930	2750	1870
2-Methylnaphthalene (Class 4)	4720	2930	4490	N.D.	N.D.	N.D.
1-Methylnaphthalene (Class 4)	2820	1610	2700	N.D.	N.D.	N.D.
Biphenyl (Class 4)	3510	3130	3560	60	70	40
Acenaphthylene (Class 4)	8580	7330	7740	560	540	240
Acenaphthene (Class 4)	820	560	870	N.D.	N.D.	N.D.
Fluorene (Class 4)	2560	1810	2140	N.D.	N.D.	N.D.
Phenanthrene (Class 4)	7780	6930	7280	370	350	230
Anthracene (Class 4)	2640	1810	2030	N.D.	30	N.D.
Fluorantene (Class 5)	1860	1680	1370	280	290	110
Pyrene (Class 5)	3450	2720	2370	300	310	120
Sum Aromatics	114090	118310	110810	7220	19600	15100
Tar dew point(°C)	172	167	166	122	123	109

Table 5: Tabulated tar distribution of tar class 2 to class 5 under non-catalytic and catalytic tar cracking. (N.D.) stands for not detected. All the concentrations are expressed in mg Nm^{-3} .

structure of soot [75]. On the other hand, at 800°C the PAHs levels were equally reduced by both catalysts, demonstrating that at this temperature the different characteristic of the catalysts (crystallite size and porosity) do not affect greatly tar yield but strongly affect soot selectivity, since catalyst #1 yields almost 3 times more soot than catalyst #2.

The mechanism of catalytic cracking of tar using CaO has been described

by [76], on which many pathways are examined over three model molecules thermodynamically. The most viable mechanism found consists of a dehydrogenation followed by adsorption of the radical over an oxygen atom instead of a calcium one. Chen et al. [76] results also indicate that it is possible that pure aromatic molecules, can be more easily cracked using CaO than certain aromatic molecules with heterocyclic components, like toluene, which may explain the higher conversion of PAHs in favor of a production of monosubstituted aromatics such as toluene.

4. Conclusions

In this study, producer gas obtained from MSW gasification is cleaned by tar cracking using mussels and oyster shells-derived materials. Both materials demonstrated improved syngas yields at low temperatures with a simultaneous tar yield reduction despite their low specific surface areas (SSA). At high temperatures however, the oyster-derived catalyst demonstrated to be more promising for tar removal because, although it barely affects syngas yield, it increased the quality of the syngas by reducing the soot yield, reducing the PAHs concentrations and by simultaneously rising the H_2/CO ratio to a value close to 2.8, which is above the requirement set for Fischer-Tropsch synthesis using cobalt [77, 78] and iron catalysts. This high H_2/CO ratio is however accompanied by higher CH_4 and C_2 -gases volume fractions.

The primary reason for the better performance of the oyster shells-based catalyst seems to be related to the crystallite size and especially the SSA, which is almost twice as large as the one found in mussel shells-based catalyst. The reason why this higher SSA derives in a higher reactivity is that a higher

SSA is connected to more reactive sites in the oyster-derived catalyst than in the mussel-derived catalyst. On the other hand, a bigger crystallite size favors specific catalytic processes [79, 80], due to an increased diffusion time through the crystal, which affects, therefore, the product distribution.

Nevertheless, this crystallite size and porosity difference did not influence strongly tar and syngas yield. The oyster shells-based catalyst also shows better thermal stability, by keeping its pore size after the calcination process.

The oyster-derived catalyst exhibited to be a promising material to be used for tar abatement in gasification in tandem with Ni- and noble metals-supported catalysts (or serving as plausible support) due to three main reasons. The first one is that gravimetric tar levels fell below 2 g Nm^{-3} (which was also obtained with mussel-derived catalysts), which has been suggested as a threshold to avoid coking in Ni-supported catalysts [81]. The second reason is that the oyster-based catalyst reduced PAHs by simultaneously increasing light aromatics, which can reduce coking in Ni- and Rh-based catalysts as demonstrated by Laprune et al. [82] where the poisoning effect of light hydrocarbons is minor compared to the one of PAHs. And because the CaO content in the oyster-derived catalyst can protect the metal-supported catalysts from deactivation by H_2S , which is considered critical because is hardly reversible [83]. This resistance to H_2S deactivation has been already demonstrated by Hernandez et al. [84] with other materials containing CaO.

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