



# Activity of chars and activated carbons for removal and decomposition of tar model compounds – A review

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## ABSTRACT

Chars, or carbonized products produced by pyrolysis or gasification, have a porous structure, a high specific surface area and they can be rich in micropores. Such characteristics make them suitable to be used in the cleaning of gasification producer gas. Several authors have been investigating the mechanism of the interaction between tar compounds and char, in order to understand the potential of this application. This review is aimed at summarizing results from reported experimental campaigns, carried out to study the effect of char beds on tar compounds: several research groups have been investigating the subject over the years, using different experimental methods and different chars or activated carbon (AC).

After a first section dedicated to the definition of char and tars, this work reviews a series of studies where model compounds were used to predict the behavior of real tars upon contact with char surface. The review includes research works focused on alkanes decomposition (methane, propane) and more traditional aromatic model tars. The overview of the results shows that the use of biomass char is effective in converting up to 100% of model tars in a gaseous stream, with coke,  $H_2$ , and CO and  $CO_2$  as major products of cracking and reforming reactions. In particular, multi-ring aromatics such as naphthalene showed higher conversion rates. Tar conversion at 700–900 °C is favored by the presence of reforming agents ( $H_2O$ ,  $CO_2$ ), which also contribute in preserving the activity of char over time. Residual char properties that enhance the activity toward tar decomposition include a large surface area and a well-developed microporosity. Both the char properties and the process parameters need to be carefully optimized for the successful application of residual gasification char to producer gas cleaning, and further experiments on real producer gas are needed to implement char-based gas cleaning systems.

## 1. Introduction

In recent years, the increased  $CO_2$  emissions and the related global climatic issues have encouraged research about alternative energy sources to replace fossil fuels. Biomass does not contain fossil carbon, and therefore it has the potential to be a source of renewable energy. Particularly, one of the most promising technologies for biomass-to-energy conversion is gasification. The producer gas can be used for several applications: it can fuel gas turbines or reciprocating engines, or it can be used to produce methane, methanol or Fischer-Tropsch fuels. Gasification has the major drawback of requiring extensive gas cleaning, and the most problematic substance in producer gas is considered to be tar. Tar compounds are generally high molecular weight hydrocarbons that can easily condense, causing several operational problems in downstream processes and components. They are formed during pyrolysis and evolve during gasification in a series of complex

reactions: their nature is strongly dependent on the process conditions.

Many methods for removing tars from producer gas have been investigated, and they can be divided into two main groups: primary and secondary methods [1]. Primary methods act inside the gasifier (in-situ) to prevent tar formation or convert nascent tars, e.g. modification of the gasifier design or optimization of operating conditions, and addition of bed additives or catalysts. Common bed additives are Ni-based catalysts, dolomites and magnesites, zeolites, olivine and iron catalysts: they are effective in reducing the amount of tars, by converting them into stable gases ( $H_2$ , CO and  $CO_2$ ), but they encounter deactivation and cause problems related with the carryover of fines [1]. Secondary methods include various downstream treatments such as hot gas cleaning (thermal or catalytic cracking, oxidative and steam conversion), and mechanical methods such as cyclones and filters. In general, thermal and catalytic methods are considered the most attractive because of their high effectivity. However, they require careful

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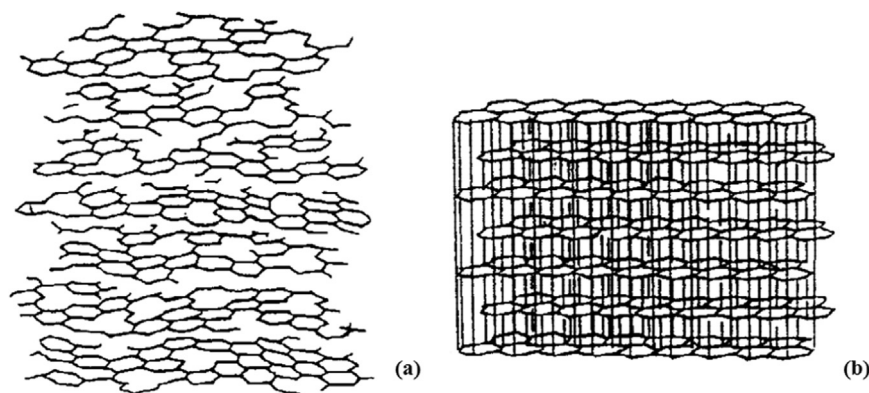


Fig. 1. Schematic difference between turbostratic (a) and graphite (b) structure. (Adapted from [10] with permission from Taylor & Francis Ltd.).

optimization in order to minimize the energy consumption and preserve the overall efficiency of the process. At present, none of these methods has been found to be a breakthrough, in terms of effectivity and economic viability.

A potential solution for downstream tar removal is the use of char. Ideally, after gasification the feedstock is reduced to pure ash, but usually the more stable fraction of carbon is preserved in the residues of the process, especially in gasifiers operating at low temperature (750–800 °C) [2]. Being a by-product of gasification, char is continuously produced and available. If used for gas cleaning it could avoid the problem of deactivation, which is usually limiting for other catalysts: spent char can be continuously recycled in the system and gasified along with fresh feedstock. In addition, residual char is currently considered a waste for disposal, therefore its repurposing would represent an economic benefit for any gasification plant [3].

Understanding and optimizing the interaction between char and tars is not an easy task and it requires bringing together carbon science and tar chemistry. Depending on the composition of the tar mixture, char properties and reaction conditions, different physical and chemical processes can take place on char surface when contacting with tars. The complexity of the problem is given by the heterogeneity of the tar mixture and by the nature of char, which can have manifold characteristics depending on the conditions of carbonization. In order to simplify the matter, model compounds are often used in laboratory-scale experiments to predict the behavior of the real tar mixture. Several research groups have used single tar compounds for investigating reaction paths and quantify the conversion of certain aromatics or alkanes. Adsorption capacity and catalytic activity for model tars conversion were measured for different carbon materials, and often commercial activated carbon was chosen as reference. In some cases, char was impregnated with metal oxides or alkali, or acid washed to remove all inorganics with the aim of investigating separately the effect of different char characteristics.

This work collects results from a series of studies dedicated to tar model compounds interacting with a solid carbon surface. The need for organizing such results is given by the lack of a method for establishing the efficiency of char for tar conversion, and the lack of a systematic evaluation of the main parameters influencing the efficiency of char for tar conversion (char properties and reaction conditions). Researchers have been using a variety of different setups, reaction conditions and char types in the experiments. The aim of this review is to identify the main reaction pathways and to list the most important parameters affecting tar decomposition on the char surface. Such overview provides basis for a more rigorous definition of the interaction mechanisms between tar compounds and solid carbon, paving the way to the design of tar removal systems based on char.

The first section of this review is dedicated to clarifying the terminology to define char and similar carbonaceous materials. Next, the most commonly used model tar compounds are shortly presented. The

following section is dedicated to the effect of char on alkanes, while the last focuses on mono-ring aromatics and Polycyclic Aromatic Hydrocarbons (PAHs).

## 2. Defining carbon materials for gas cleaning applications

Carbon can be found in nature with different shapes and structures: diamond, graphite, graphene, or less ordered forms such as char or activated carbon. To avoid disarray, it is useful to clarify the terminology used for the different carbon materials treated in this review, referring to the definitions given by the International Committee for Characterization and terminology of Carbon [4,5].

### 2.1. Carbonization

The carbonaceous materials treated in this work are the solid products of carbonization, a process which is defined as “the formation of material with increasing carbon content from organic material, usually by pyrolysis” [4]. Carbonization can take place under different conditions (pressure, temperature, oxygen level), thus producing different carbonaceous structures. The process leads to a progressive increase in the crystalline order: during pyrolysis, volatiles are removed from the organic material, and the carbon atoms are arranged in stacks of flat aromatic sheets randomly cross-linked [6]. The sequence of structural changes occurring during biomass carbonization is well described by Keilueit et al. [7]. At temperatures higher than 700 °C, turbostratic carbon (Fig. 1a) is formed: it is still less packed and less ordered in comparison with graphite-like carbon (Fig. 1b), therefore it results in higher porosity and high surface area [8]. High carbonization temperatures (1000 °C) decrease the total porosity because of the formation of graphite with a more closely packed structure [9].

In presence of a limited amount of oxidizing agent (sub-stoichiometric), partial combustion leads to an increase in temperature and char is exposed to the endothermic gasification reactions: some of the carbon will react leaving the residual char structure with a more stable carbon fraction, fewer functional groups and a larger ash fraction.

### 2.2. Char and activated carbon

Two types of carbonization products are of particular interest in this context: char and activated carbon (AC). As defined by the International Committee, char is “a carbonization product of a natural or synthetic organic material, which has not passed through a fluid stage during carbonization” [5]. The parent material for char can be coal or biomass.

Biochar is a particular type of char which is mainly intended for soil application, and should meet specific criteria as described in the European Biochar Certificate (EBC) [11] or the International Biochar Initiative (IBI) Standard [12]. Both are voluntary standards and describe biochar as a material produced through oxygen-limited thermal



Fig. 2. Schematic structure of AC. (Reprinted from [14], pag. 2. Copyright 1990 Elsevier).

conversion of biomass, thus including pyrolysis and gasification processes.

On the other hand, AC is “a char, which has been subjected to reaction with gases, sometimes adding chemicals, e.g.  $\text{ZnCl}_2$ , during or after carbonization in order to increase its porosity” [5]. During activation, the irregular structure of char reacts with gases, enhancing the porosity of the material. This gives the ACs a large surface area (up to  $2500 \text{ m}^2/\text{g}$ ), a microporous structure and a high surface reactivity [13]. The structure of activated carbons has been described by Stoeckli [14] as constituted by bent aromatic sheets and strips with gaps of various dimension between them, forming slit-shaped micropores (Fig. 2).

ACs are widely used in adsorption processes. They may assist the capture of organic volatile compounds and adsorb hydrocarbons and PAHs [15–22]. ACs are also commonly used for gas cleaning in combustion plants, to remove metals and dioxins at  $150\text{--}200^\circ\text{C}$  [23].

The structural characteristics of carbon materials are defined by the distribution of micropores (cavities with mouths smaller than  $2 \text{ nm}$ ), mesopores and macropores ( $> 50 \text{ nm}$ ), while the chemical properties are defined by the inorganics dispersed on the surface and by the presence of oxygen-containing functional groups at the edges of the graphite sheets: acidic groups such as lactones, carboxylic acid or phenol and basic groups such as carbonylic, quinonic and pyrone structures. Oxygen sites enhance the adsorption of polar molecules and in general they are known to influence the adsorption capacity and catalytic activity of char [6,18,24].

Biomass-derived char generally has a lower surface area and adsorption capacity in comparison with ACs, but nonetheless shares many of their features. This is particularly true if char undergoes a certain degree of gasification, which is analogue to an activation process. Even if it does not undergo activation, char usually has a porous structure, a high surface area and it is rich in micropores.

The parent material naturally contains minor elements such as Alkali and Alkaline Earth Metals (AAEM), Fe, Al, Si and P that can increase the catalytic properties [25]. Moreover, depending on the carbonization conditions, the surface of char can have oxygen functional groups.

Because of its AC-like characteristics, char has a good potential to be used as adsorbent, catalyst support, and even as a catalyst on its own [6,25–28]. Specifically, it offers a number of favorable features for adsorption and catalytic conversion of aromatics and alkanes. In recent years, the application of non-activated carbonization products to gas treatment has been suggested and studied by several authors. A study by Benedetti et al. [3], considers gasification-derived biochar as a substitute for AC, pointing out that double-stage gasifiers are particularly suitable for producing residual char with characteristics comparable with AC. As a matter of fact, in staged processes the pyrolysis and the gasification steps are carried out separately, thus resembling an AC manufacturing process. Residual char has therefore the potential to be used as AC without any further activation treatment: operating conditions of gasification can be tuned to deliver a residual char with suitable

Table 1  
Common tar model compounds.

Model tar	Tar class	Formula	Structure
Methane	–	$\text{CH}_4$	
Toluene	II	$\text{C}_6\text{H}_5\text{-CH}_3$	
Phenol	II	$\text{C}_6\text{H}_6\text{O}$	
Naphthalene	III	$\text{C}_{10}\text{H}_8$	
Phenanthrene	III	$\text{C}_{14}\text{H}_{10}$	
Anthracene	III	$\text{C}_{14}\text{H}_{10}$	
Pyrene	III	$\text{C}_{16}\text{H}_{10}$	

properties to be directly used for adsorption or gas treatment.

### 3. Tar model compounds

A general classification of the compounds in the tar mixture is based on their order of appearance within the gasification process [29]:

- **Primary tars** are produced during pyrolysis, in the temperature range  $400\text{--}700^\circ\text{C}$ . They are completely converted if the temperature surpasses  $800^\circ\text{C}$ . This class includes oxygenated compounds such as levoglucosan, hydroxyacetaldehyde and furfurals originating from cellulose and hemicellulose, together with methoxyphenols which are derived from lignin.
- **Secondary tars** are formed by gas-phase reactions of primary tars at  $700\text{--}850^\circ\text{C}$  and they include phenolic compounds and alkenes (Table 1). The abundance of this class of tars has a peak around  $750^\circ\text{C}$ .
- **Tertiary tars** include methyl-derivatives of aromatics, such as methyl-acenaphthylene, methylnaphthalene, toluene and indene. They are formed in the temperature range  $650\text{--}1000^\circ\text{C}$ . Polycyclic Aromatic Hydrocarbons (PAH) are also formed such as naphthalene, acenaphthylene, anthracene/phenanthrene and pyrene (Table 1).

Above 1000 °C naphthalene is dominant over other species.

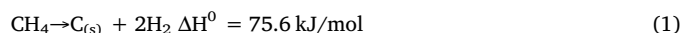
To investigate and predict the behavior of tars, model compounds have been widely used as representatives of different tar classes. Some of the most common model tar molecules are reported in Table 1. Toluene, phenol and naphthalene are frequently used, as these compounds generally make up the most part of total tar. PAHs are also often used as model tars because they are problematic pollutants in the producer gas, and they are highly refractory. In some cases, alkanes such as methane and propane have been used as model tars, even if they lack the aromatic structure or not defined as members of the above tar classes.

Indeed, there may be differences in the behavior of model tars in comparison with real tar mixtures, and results should always be treated considering the differences with actual process conditions. It is here appropriate to consider the works published by Mastral et al., where the adsorption of pure model PAHs on ACs was compared with the behavior of PAHs mixtures [30], PAHs with steam [31], and PAHs-containing flue gases from real combustion [9]. The differences in the adsorption dynamics showed that the process is affected by the presence of molecules different from the pure model compounds. Specifically, a mixture of naphthalene and phenanthrene was adsorbed on AC, and it was observed that the presence of a second PAH in the gas stream reduced the adsorption efficiency, as both molecules compete for adsorption sites [30]. Similarly, adsorption tests of various PAHs in presence of combustion flue gas revealed that other molecules (H<sub>2</sub>O, smaller volatile organic compounds) can compete with PAHs, blocking the narrowest adsorption sites and affecting the overall adsorption capacity [9]. Indeed, the presence of steam in the gas phase (10%) decreased the adsorption capacity of phenanthrene for 13 out of 16 tested ACs [31].

This suggests that results obtained by using model compounds alone should be verified in conditions as similar as possible to reality. Nonetheless, studying the behavior of model compounds can be useful in understanding the adsorption or decomposition dynamic of real tars.

#### 4. High temperature chemistry of alkanes as tar model compounds over char

Studies on heterogeneous reactions of light hydrocarbons have been investigated in order to understand the catalytic properties of a carbonaceous surface within the temperature range 850–1000 °C. An overview of the experimental conditions in the reviewed papers can be found in Table 2. It is worthwhile to include this section in the present review, as many of the processes observed at the surface of char or AC are similar to those encountered for aromatic model tars. Particularly, the decomposition of methane through carbon deposition, often referred to as thermocatalytic decomposition (Reaction (1)), has been object of study because carbon materials offer advantages to be used as catalyst for H<sub>2</sub> production [32].



Muradov [32] tested different types of commercial AC as catalysts for this application: ACs exhibited high initial catalytic activity, but showed deactivation over 1 hour period. A proportional relationship was observed between the catalytic activity and the BET specific surface area of AC. The same author [33] worked also with various carbon materials (AC, carbon black, graphite, glassy carbon, acetylene black), with the aim to determine the structural or chemical factors influencing CH<sub>4</sub> decomposition. The “degree of order” in the carbon structure was found to affect heterogeneous reactions: amorphous or microcrystalline carbons such as ACs appear to be richer in energetic discontinuities (e.g. reactive edges of carbon crystallites), forming active sites for CH<sub>4</sub> decomposition. Furthermore, these results showed that transition metals impurities on the carbon surface play a minor role in catalysis. Oxygen-containing functional groups appeared to have an effect solely in the first stages of the process.

Likewise, Moliner et al. [34] compared the activity of various ACs for CH<sub>4</sub> decomposition. They focused on the effect of surface chemistry and porosity and concluded that the most effective chars were the ones with a BET surface area around 1000 m<sup>2</sup>/g. The concentration of oxygen functional groups on the surface only influenced the initial activity, but did not correlate with longer-term activity of chars, in agreement with [33]. Deactivation was observed and ascribed to micropores blocking by carbon deposition. Prolonged activity (240 min) was ensured by large surface area, together with an appropriate pore size distribution including mesopores and wide microporosity to facilitate diffusion. Suelves et al. [35] further evaluated the effect of different textural characteristics of AC on CH<sub>4</sub> conversion by using thermogravimetric analysis (TGA) to quantify the deposition of solid carbon. The results showed that the higher the total pore volume of fresh char, the higher the amount of deposited carbon, meaning that a larger pore volume implies an increased activity. They also confirmed the relation between the concentration of oxygenated functional groups and the initial reaction rate.

Dufour et al. [36] evaluated the catalytic activity of wood char (non-activated) for CH<sub>4</sub> decomposition investigating the role of inorganics (K, Ca and Mg), pore texture and surface chemistry. Since demineralized samples exerted the same methane conversion as untreated ones, the authors surmise that the effect of inorganics is negligible. Similar remarks were made for the role of oxygen surface groups. As a consequence, active sites for carbon deposition are rather likely to be constituted by unsaturated carbon atoms, forming high energy sites as described also in [33]. CH<sub>4</sub> reacting in a N<sub>2</sub> atmosphere rapidly deactivated the carbon catalyst, probably because of the pores closure due to carbon deposition. In agreement with results from other studies [37–39], the presence of CO<sub>2</sub> or H<sub>2</sub>O was found to prevent the pores blocking and to maintain the char catalytic activity. In a latter work, Dufour et al. [40] examined more closely the mechanism of

**Table 2**  
Overview of experimental conditions for tests on alkanes decomposition.

Author	Tested model compounds	Tested char (carbonization temperature)	Char bed temperature [°C]	Char particle size [μm]	Reaction atmosphere composition
[33] Muradov et al.	Methane	Carbon blackCommercial ACVarious carbon materials (graphite, glassy carbon, acetylene black)	850	n.r.	CH <sub>4</sub>
[34] Moliner et al.	Methane	Commercial ACsCoal char (800 °C)	850–950	< 100	CH <sub>4</sub>
[35] Suelves et al.	Methane	Carbon blackCommercial AC	900	n.r.	CH <sub>4</sub>
[36] Dufour et al.	Methane	Pine wood char (750 °C)	1000	200–400	N <sub>2</sub> , CH <sub>4</sub> , mix of H <sub>2</sub> /CO/ CO <sub>2</sub> (artificial syngas)
[40] Dufour et al.	Methane	Pine wood char (750 °C)Demineralized pine wood char (750 °C)	1000	200–400	N <sub>2</sub> , H <sub>2</sub> O
[41] Klinghoffer et al.	MethanePropane	Poplar char(CO <sub>2</sub> and H <sub>2</sub> O gasified at 550, 750 and 920 °C)	20–900	(Parent) 1000–4000	N <sub>2</sub>
[25] Klinghoffer et al.	Methane	Poplar char(CO <sub>2</sub> and H <sub>2</sub> O gasified at 550, 750 and 920 °C)	700–750–850	(Parent) 1000–4000	N <sub>2</sub>



**Table 3**  
Overview of experimental conditions for adsorption of aromatics on char.

Author	Tested model compounds	Tested char (carbonization temperature)	Char bed temperature [°C]	Char particle size [μm]	Reaction atmosphere composition
[17] Mastral et al.	Phenanthrene(1.5 ppm)	10 carbonaceous materials(various parent materials)	125, 150, 175	100–200	Helium
[48] Mastral et al.	NaphthalenePhenanthrenePyrene(1.5 ppm)	16 carbonaceous materials(various parent materials)	n.r.	100–200	Helium
[31] Mastral et al.	Phenanthrene(1.5 ppm)	16 carbonaceous materials(various parent materials)	150	100–200	Helium Steam (0–20%)
[16] Mastral et al.	Naphthalene Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene	Coke from German Rhenish lignite	150	100–200	Helium
[49] Mastral et al.	NaphthaleneFluorene, Phenanthrene, Fluoranthene, Pyrene	Coke from German Rhenish lignite	150	100–200	Helium
[50] García et al.	Phenanthrene(1.5 ppm)	Commercial AC (with various degrees of surface oxidation)	150	100–200	Helium
[15] Hu et al.	Phenolo-cresolNaphthalene1-methylnaphthalene	Commercial activated carbons	150–250	1000/2000/4000	N <sub>2</sub>
[51] Lillo-Ródenas et al.	BenzeneToluene	Commercial activated carbonsSteam activated charChemical activated chars (NaOH, KOH)	25	PowderGranular (1300–1500) Pellets (2200)	Helium

deactivation and regeneration of wood char, confirming the role of steam gasification for the long-term sustainability of H<sub>2</sub> production. During CH<sub>4</sub> conversion, a thin coating of reactive pyrolytic carbon was formed on the surface. The authors suggest that wood char might represent a cheap and effective catalyst for converting both CH<sub>4</sub> and tars into an H<sub>2</sub>-rich syngas.

The catalytic properties of gasification-derived char for the decomposition of CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> were investigated by Klinghoffer et al. [41]. The properties of wood char produced in a fluid bed gasifier under different conditions (steam, CO<sub>2</sub>, 550, 750 and 920 °C) were investigated alongside with the char activity toward alkanes decomposition. Results showed that char surface area and the micropore structure strongly depends on the gasification conditions: longer residence time and higher temperature favored the development of a large surface area. The use of CO<sub>2</sub> as a gasifying agent, in comparison with steam, enhanced the formation of micropores.

Char catalytic activity on the decomposition of CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>, was measured by TGA. The mass gain of char was used to quantify the deposition on the surface from hydrocarbon decomposition. Exposure to CH<sub>4</sub> induced an increase of the char mass starting at 700 °C. At the same temperature, C<sub>3</sub>H<sub>8</sub> induced a higher mass gain. According to the author, these results demonstrate the ability of char to catalyze hydrocarbon decomposition via cleavage of C–C and C–H bonds, suggesting that char may be a good catalyst for tar decomposition. Post-test characterization of char surface in Environmental Scanning Microscopy and Energy Dispersive X-ray (ESEM/EDX) showed a high carbon concentration on the pores, especially at the iron sites, suggesting that the metal acts as an active site for catalytic reactions.

The same research group [25] further studied the role of inorganics at the char surface and oxygen functional groups as well. The effect of acidic oxygen groups was tested on CH<sub>4</sub> decomposition at 850 °C and was found not to play an important role: this is ascribed to the fact that acidic oxygen groups are desorbed from the char surface at temperatures lower than 850 °C.

Inorganics such as Ca, Na, K, Mg, P, Si, Fe, Al and Mn were present in the char and in general higher concentrations lead to a higher catalytic activity. Furthermore, the activity of char was higher than that of pure ashes, indicating that carbon works as support on which inorganics are dispersed. Indeed, the author refers to gasification char as a “supported metal catalyst” [41] where the carbonaceous structure with a high surface area provides support for the ash elements.

These studies highlight the most important characteristics of a carbon material such as char for its activity in acyclic hydrocarbons decomposition. Textural characteristics such as large surface area and pore volume are considered essential to the activity of char, especially for the longevity of its catalytic effect. The role of inorganic impurities is not yet defined: to some extent, transition metals such as Ni and Fe and AAEMs were found to play a role in CH<sub>4</sub> decomposition. Certainly the presence of heteroatoms in the carbon structure, together with a low degree of crystalline order promoted the abundance of active sites. In general, results obtained on the decomposition of alkanes showed some promising characteristics of AC, as well as non-activated biomass char for the decomposition of hydrocarbons.

## 5. Adsorption and high temperature chemistry of aromatics as tar model compounds over char

Aromatics are usually the main components of the tar mixture, and they are highly refractory as a consequence of their molecular structure. Their stability is given by the delocalization of electrons in the  $\pi$ -bonds between carbon atoms in the cyclic structure. This effect increases with the number of conjugated rings, making larger PAHs more difficult to remove by thermal treatment. Such process leaves the aromatic structure unchanged. The range of temperatures where physical adsorption is applied is in generally below 250 °C because, as temperature is increased, the adsorption capacity is reduced as a result of the exothermic

**Table 4**  
Experimental conditions overview of tar model compounds tests.

Author	Tested model compounds	Tested char (carbonization temperature)	Char bed temperature [°C]	Char particle size [μm]	Reaction atmosphere composition
[52] Eggsgaard et al.	Benzene/Phenol/Naphthalene/Phenanthrene	Pine char (800 °C)	600–800	100–500	N <sub>2</sub> /H <sub>2</sub> O
[53] Abu El-Rub et al.	Phenol/Naphthalene	Calcinated dolomite, Olivine/Fluid catalytic cracking/Nickel catalyst/Commercial biomass char/Pine wood char (500 °C)/Pine wood ash (600 °C)	700–900	1400–1700	N <sub>2</sub> , CO <sub>2</sub> /H <sub>2</sub> O
[37] Hosokai et al.	Benzene/Phenol/Naphthalene/Phenanthrene/Pyrene	Commercial char (800 °C)	700–900	1300–2400	N <sub>2</sub> /H <sub>2</sub> O/N <sub>2</sub> H <sub>2</sub> O/H <sub>2</sub> O/H <sub>2</sub> /N <sub>2</sub>
[38] Fuentes-Cano et al.	Toluene/Naphthalene	Coconut char (commercial)/Coal char (commercial)/Dry sewage sludge char (900 °C)	750, 850, 950	1000–2800	N <sub>2</sub> /H <sub>2</sub> /H <sub>2</sub> O
[54] Nitsch et al.	Phenol	Beech wood char (750 °C)	850	700–1000	N <sub>2</sub> H <sub>2</sub> /H <sub>2</sub> O
[55] Huang et al.	Toluene	Sewage Sludge char (900 °C)/Bottom ashes/Dolomite/NiO/γ-Al <sub>2</sub> O <sub>3</sub>	750, 850, 950	1000–1700	N <sub>2</sub>
[56] Lu et al.	Toluene	Sewage Sludge char (900 °C)	750, 850, 950	1000–1700	N <sub>2</sub> CO <sub>2</sub> /H <sub>2</sub> OCO/H <sub>2</sub> O/HCl
[57] Bhandari et al.	Toluene	Switchgrass char (down draft gasifier)/Activated switchgrass char/Acidic surface activated char	700, 800	150–600	N <sub>2</sub> /Artificial syngas(CH <sub>4</sub> /H <sub>2</sub> /CO/CO <sub>2</sub> )
[58] Mani et al.	Toluene	Pine bark char (950 °C)	600–900	212–420	N <sub>2</sub> /H <sub>2</sub> O
[59] Korus et al.	Toluene	Coal-derived activated carbon	650–850	400–850	N <sub>2</sub>
[39] Zhang et al.	Naphthalene	Rice straw char (500 °C)/Ni(NO <sub>3</sub> ) <sub>2</sub> loaded char/Water-washed char	700–900	(Parent)100–150	Argon/Artificial syngas(CH <sub>4</sub> /H <sub>2</sub> /CO/CO <sub>2</sub> )
[23] Di Gregorio et al.	Naphthalene	Commercial ACs (three types)	750–900	3000 (pellets)	N <sub>2</sub>
[60] Nestler et al.	Naphthalene	Spruce char (500 °C, 800 °C)/CO <sub>2</sub> -activated spruce char/Commercial AC	850, 1050	500–2000	N <sub>2</sub>
[61] Feng et al.	Toluene, Phenol, Naphthalene	Rice husk char (RHC)/Acid washed RHC (H-form)/K-loaded RHC (K-form)/Ca-loaded RHC (800 °C)	800	900–1500 (parent)	H <sub>2</sub> O/CO <sub>2</sub>
[62] Hervy et al.	Ethylbenzene	Wood pallets/Food waste/Sludge char (700 °C)	400, 650	500–1600	N <sub>2</sub> , CO

nature of adsorption processes [42]. On the other hand, at higher temperatures chemical bonding with the surface (chemisorption) can take place. Chemisorption is characterized by large interaction potentials: it is often found to occur at temperatures higher than the critical temperature of the adsorbate [43] (e.g. 748.4 °C for naphthalene, 869 °C for phenanthrene [44]). If aromatics are chemisorbed, their molecular structure is modified, and this can be the first stage of a catalytic process leading to cracking and reforming of heavy aromatics. In the following, a series of papers are reviewed where physisorption or chemisorption were studied. An overview of all the experimental conditions is given in Tables 3, 4.

The conversion of model tars is commonly expressed as X (Eq. (2))

$$X = \frac{C_{in} - C_{out}}{C_{in}} * 100 [\%] \quad (2)$$

Being  $C_{in}$  and  $C_{out}$  the model tar concentrations at the inlet and outlet, respectively.

### 5.1. Physical adsorption

Physical adsorption plays an important role in the interaction between hydrocarbons and the surface of chars, therefore it is useful to understand what parameters control this process. ACs are popular for adsorption of PAHs from aqueous solutions [45]. Such a process has been object of several studies, and some of them also investigated the use of biochars for this application [46,47]. In particular, Li et al. [46] found the adsorption capacity of biochars for phenanthrene, fluorene and pyrene to increase with the carbonization temperature (600–800 °C): Biomass char produced at 800 °C performed comparably with ACs. The adsorption of PAHs in gaseous phase on ACs and chars was investigated in the works gathered in Table 3. Mastral et al. investigated the matter testing many varieties of carbon materials for adsorption of PAHs with 2–4 rings [9,16,17,31,48,49] and found that the adsorption capacity of ACs was mostly dependent on their porous-textural characteristics, especially microporosity (or the ratio between the micropore volume to the total pore volume). Specifically, a large micropore volume enhanced the adsorption of pure multi ring compounds [17,48] and their binary mixtures [49]. The adsorption of larger molecules such as phenanthrene and pyrene was favored by large micropores diameters (> 0.7 nm) and by mesoporosity. Mesopores helped accessing the micropores and promoted multilayer interactions [49]. Each compound appeared to have specific needs in terms of pore size distribution, for being optimally adsorbed: for example, larger PAHs were found to be adsorbed more easily on the surface of tested ACs [48]. The role of surface chemistry of chars was investigated by García et al. [50], by measuring the adsorption of phenanthrene on AC with different degrees of surface oxidation: results showed that adsorption capacity is lower for AC with a higher content of surface oxygen groups, which means that the increased polarity of the surface hinders adsorption [50]. These results were later confirmed by Lillo-Ródenas et al. [51]. They studied the adsorption of benzene and toluene on ACs with different porosities and with a reduced content of surface oxygen groups. Adsorption capacities for the two molecules varied on the same char. Narrow microporosity (< 0.7 nm) was found to govern the adsorption of benzene, while all micropores (< 2 nm) participated in the adsorption of toluene. Oxygen functional groups were removed from the char surface by heating to 900 °C: thermally treated AC always showed an increased adsorption capacity. The negative effect of oxygen surface groups was explained with the interaction between aromatic rings of the adsorbate and electron-rich regions of the graphene layers: the oxygen groups withdraw electrons from such layers, hindering the interaction with the adsorbate.

Hu et al. [15] also compared the adsorption on ACs, focusing on their interaction with phenol, naphthalene, o-cresol and 1-methylnaphthalene. Interestingly, tars containing methyl groups were found to be adsorbed more efficiently in comparison with phenol and

naphthalene. The authors suggest that this may be due to interaction between the methyl groups and the hydrophobic functional groups on the surface of the ACs. In agreement with Mastral et al., naphthalene was adsorbed better on microporous AC. The average pore diameter was found to influence the adsorption capacity, depending on the molecular shape and dimensions of the adsorbate: the two most favorable ACs for model tars adsorption had a specific surface area of about 1100 m<sup>2</sup>/g and an average pore size of 1.2 and 1.9 nm.

In conclusion, to achieve high adsorption of aromatics, chars should have:

- (i) Large specific surface area (BET with N<sub>2</sub> around 1000 m<sup>2</sup>/g).
- (ii) Low content of oxygen-containing surface groups.
- (iii) Large micropore volume (N<sub>2</sub> measured > 0.3 cm<sup>3</sup>/g).
- (iv) Appropriate pore size distribution.

The last parameter varies according to the molecules to be adsorbed: narrow microporosity can induce diffusional problems for large molecules (pyrene), whereas it promotes the adsorption of smaller molecules such as benzene.

## 5.2. Chemical adsorption and catalysis

When reaction temperature is above 500–600 °C, chemisorption of aromatics can take place possibly followed by catalyzed reactions resulting in carbon deposition with release of products as H<sub>2</sub>, CO or CO<sub>2</sub> (depending on the reaction atmosphere). An overview of the conditions of experiments at high temperatures is given in Table 4.

The effect of temperature on the reaction pathways taking place at the char surface were investigated by Egsgaard et al. [52]. They evaluated the irreversible binding of aromatic compounds on wood char up to 800 °C, by using a small char bed (6 g). The breakthrough of the model compounds was observed by stable isotope dilution analysis: binding within the bed was measured by the <sup>13</sup>C content of the char using <sup>13</sup>C<sub>6</sub>-benzene as a tracer. Starting already at 600–650 °C char was able to bind tars, with increasing efficiency at higher temperature (up to 800 °C). It was observed that, at 700–800 °C, aromatics were covalently bound to the char surface by radical reactions, becoming part of the char. Naphthalene and phenanthrene were bound more efficiently than lighter compounds whereas phenol showed a different behavior. None of the introduced phenol could be collected after the char bed, partly because of decarbonylation and conversion to naphthalene. Such results suggest that in presence of a gasifying agent, aromatics could form covalent bonds with the char bed, while carbon could simultaneously be removed by gasification reactions in what the authors call a “living char bed”.

Several studies have focused on the evaluation of the achievable conversion values for tar model compounds over char, depending on the properties of char and on the reaction conditions.

The catalytic effect of wood char in cracking and reforming of phenol and naphthalene was investigated by El-Rub et al. [53]. The activities of pine wood char, commercial biochar and pine wood ashes were compared with common catalysts for tar removal, by measuring the change in concentration between inlet and outlet of a heated reactor. At 700 °C, over commercial biochar, 82 wt% of phenol and 99.6 wt% of naphthalene were converted. For naphthalene, biomass char showed the second highest activity among the tested catalysts, after the nickel catalyst. Pure biomass ash produced at 600 °C showed a lower activity for naphthalene conversion in comparison with biomass char. This suggests that the carbon structure has a role itself in the enhancement of the catalytic activity, acting as a support for the inorganics contained in the parent feedstock (in this case MgO, CaO, K<sub>2</sub>O).

These results validate the hypothesis that char has a catalytic effect on decomposition of tars, but the mechanism of the process is not clarified. Hosokai et al. [37] provided a more detailed description of the

decomposition process. They monitored the decomposition rate of model tars over char and the concurrent formation rate of CO, CO<sub>2</sub> and CH<sub>4</sub> under different atmospheres: N<sub>2</sub>, N<sub>2</sub>/steam, and N<sub>2</sub>/H<sub>2</sub>/steam. Under all conditions, aromatics were found to decompose mainly by deposition on the char surface by coking (Reaction (3)), and not by steam reforming (Reaction (4)).

$$C_m H_n \text{ (aromatics)} = C_m H_x \text{ (coke)} + (n-x)/2 H_2 \text{ (Coking/Cracking)} \quad (3)$$

$$C_m H_n \text{ (aromatics)} + H_2 O = (m + n/2) H_2 + m CO \text{ (Steam Reforming)} \quad (4)$$

Micropores constituted active sites for deposition. Deactivation of char was observed under N<sub>2</sub> atmosphere, whereas catalytic activity of char was maintained in presence of steam: gasification reactions enhanced the formation of micropores, preventing the blockage of active sites by coking. For this reason, it is suggested that the gasification rate should be equivalent or greater than the carbon deposition rate, in order to preserve the catalytic activity of char. On the other hand, the addition of H<sub>2</sub> resulted in a slower, but still extensive, decomposition of aromatics. For benzene and naphthalene, lower inlet concentrations led to increased conversion: the initial concentration appeared to be a factor influencing the decomposition.

It is concluded that, if char has a sufficiently large micropore surface area, naphthalene can decompose completely at 750 °C, with a residence time of 0.2 s. Naphthalene, phenol and phenanthrene can reach almost total conversion at 800–900 °C with a steam concentration of 15.5% v/v. Aromatics with more rings per molecule, hence phenanthrene and pyrene, were found to decompose more rapidly than lighter compounds.

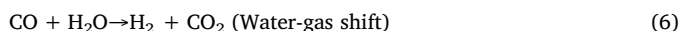
Some of these results were verified by Fuentes-Cano et al. [38]. Using a laboratory fixed bed reactor, they investigated the influence of temperature, steam concentration in the gas on the decomposition rate of toluene and naphthalene, and proposed kinetic expressions to describe the process. Tests were run on three chars originating from various materials and with different surface structure, but the parent material of char did not significantly affect the tar conversion. At 750 °C the conversion rate reached 0.8% for toluene and nearly 100% for naphthalene. Above 850 °C, the decomposition of both compounds was fast and almost complete. However, continuous deactivation of the char activity was observed in both cases. In contrast, at 950 °C, and with a steam concentration of 15% v/v in the gas, the activity of char was maintained. In general, higher temperatures led to a higher conversion and a lower degree of char deactivation with time. The authors propose a two-step conversion mechanism:

- (i) tar deposition on active sites and polymerization, with H<sub>2</sub> and carbon deposition;
- (ii) gasification of deposited carbon.

Such steps retrace the mechanism proposed by Hosokai et al. [37], a mechanism which is also corroborated by Nitsch et al. [54], who further investigated the role of steam in the interaction between tars and the char surface. Phenol degradation was measured over a fixed bed of char in N<sub>2</sub> atmosphere, and with injection of steam and H<sub>2</sub>. In inert atmosphere, a large amount of phenol was observed in the outlet stream, and coking on micropores was evident. Addition of H<sub>2</sub> did not show any major effect on tar reforming. In contrast, in the presence of steam, char showed a strong catalytic activity for phenol removal.

Huang et al. [55] measured the decomposition of toluene over the surface of sewage sludge char (SSC), in N<sub>2</sub> atmosphere. They compared the activity of SSC with bottom ashes from a waste incinerator, dolomite and catalyst NiO/γ-Al<sub>2</sub>O<sub>3</sub>. The latter one produced the highest toluene conversion ratio, followed by dolomite, SSC and bottom ashes. SSC gave a conversion rate as high as 94.5% at 950 °C. The conversion increased significantly when the temperature was raised from 750 °C to 950 °C, and since the H<sub>2</sub> yield followed the same trend in presence of a

catalyst, the authors infer that all tested materials promoted cracking of toluene. In all cases coke deposition occurred, followed by a decrease in BET area. The same phenomenon was also observed in further experiments by the same research group [56], where the effect of the addition of H<sub>2</sub>, CO, CO<sub>2</sub>, steam and HCl was studied on tar cracking and conversion, char pore structure and stability have been examined. The addition of CO<sub>2</sub> and H<sub>2</sub>O favored the further reaction of deposited coke thus limiting the loss of surface area. At 950 °C and in presence of CO<sub>2</sub>, and H<sub>2</sub>O mixed with N<sub>2</sub>, the toluene conversion reached 97.1%. The authors surmise that H<sub>2</sub>O plays a crucial role in the tar cracking process as it takes part in steam reforming as well as in water gas and water-gas shift (Reactions (5) and (6)).



The addition of HCl (which is a common compound produced from municipal solid waste gasification) had a negative effect on the activity of SSC, because it induced the nucleation of chlorides that participated in blocking the pores. In agreement with Fuentes-Cano et al. [38], they observed that presence of CO<sub>2</sub> and H<sub>2</sub>O and higher temperatures prevent deactivation of char.

The decomposition of toluene over char was also investigated by Bhandari et al. [57] at 700 and 800 °C in a fixed bed reactor. The activity of gasification-derived biochar was compared with the activity of the same material after activation and after being coated with citric acid to obtain an acidic carbon surface. The toluene conversion was measured in N<sub>2</sub> atmosphere: the three materials were effective in reducing the toluene concentration with conversion in the range 79–92%. The average conversion was higher for activated carbons than for raw biochar: 86% against 9% at 700 °C. The acidification of the surface improved the conversion of toluene only at 800 °C. In contrast with other studies, the addition of artificial syngas was not beneficial but slightly decreased the conversion rate in the range 69–88%. According to the authors, this effect was due to the adsorption of the gases on the carbon surface. However, the composition of the artificial syngas could have affected the results, particularly because of the abundance of CO. For comparison, the compositions of artificial syngases used in the studies of Bhandari et al. [57] and Lu et al. [56] are reported in Table 5. Activated carbon with acidic surface was less efficient in toluene removal in comparison with the other tested chars; however, the authors suggest that the increased acidity could be useful for removing NH<sub>3</sub> in the producer gas. The significant difference in the performance of raw biochar and activated biochar is ascribed to the low surface area (64 m<sup>2</sup>/g) and pore volume (0.09 cm<sup>3</sup>/g) of the raw material, whereas the tested AC had a pore volume five times higher and a BET surface of 944 m<sup>2</sup>/g.

The effectivity of biochar in enhancing the conversion of toluene was also reported by Mani et al. [58], who measured a conversion ratio of 94% at 900 °C in N<sub>2</sub>/H<sub>2</sub>O atmosphere, with benzene as intermediate product of the cracking reactions. Formation of benzene as a product of toluene decomposition was also observed by Korus et al. [59]. During tests in the temperature range 650–950 °C under inert atmosphere, coke deposition on the surface of AC was measured simultaneously with the benzene production: these two effects resulted to be products of competing pathways of toluene decomposition. The measured conversion of toluene was over 90% when the temperature was 800 °C and higher. Conversion was very efficient only as long as the AC surface was active

(20 min). As soon as the coke deposition became hindered by coking on the AC surface, benzene formation was enhanced. An overview of the toluene conversion ratios obtained over different chars can be found in Table 6.

Naphthalene is a widely used model tar, as it represents one of the most abundant and recalcitrant components of the tar mixture in producer gas. Results on naphthalene conversion efficiencies are gathered in Table 7. Zhang et al. [39] compared the heterogeneous cracking of naphthalene over char with homogeneous decomposition in inert atmosphere. Three different chars were tested: rice straw char, rice straw char loaded with Ni(NO<sub>3</sub>)<sub>2</sub> and water-washed char. Heterogeneous conversion was generally higher than homogeneous conversion, but char showed decreased catalytic activity with time, accompanied by a lower BET surface area. In agreement with previous works, this effect was attributed to the carbon deposition on the active sites of the surface, which is identified as the main decomposition pathway. Nickel-loaded char showed a higher initial activity but a more rapid deactivation, whereas water-washed char induced a generally lower naphthalene conversion in comparison with original rice straw char. Addition of artificial syngas (a mixture of H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub>) resulted in a delayed deactivation of the original rice straw char. Zhang et al. [39] formulated the heterogeneous catalysis for naphthalene decomposition over char in 3 steps:

- (i) adsorption on active sites;
- (ii) dissociation into radicals (naphthyl and hydrogen);
- (iii) desorption of radicals.

In an inert atmosphere, radicals react with each other in polymerization and soot formation. If oxidative species are present, they generate mono-ring aromatics, hydrocarbons and gases.

Di Gregorio et al. [23] focused on naphthalene as well and tested the effectivity of three commercial ACs for adsorption and cracking. The characterization of ACs showed that they had different surface areas and pore size distributions and contained varying amount of inorganics on the surface. The comparison between the performances of the ACs showed that Fe, Mg and Al enhance the cracking of tars. The highest and most stable naphthalene conversion in a 4 h test was obtained on AC with larger specific surface area accompanied by a high micropore volume and appropriate pore size distribution (as described by [17,15]). Complete removal of naphthalene from the gas stream was achieved by all ACs at low naphthalene concentration (< 50 g/N m<sup>3</sup>), and for one of the tested ACs, also at higher concentrations (up to 176.7 g/N m<sup>3</sup>). The cracking efficiency decreased with higher concentrations, in agreement with the findings from Hosokai et al. [37].

Likewise Nestler et al. [60] investigated the catalytic activity of biochar towards naphthalene decomposition in inert atmosphere. Spruce wood was carbonized at 500 °C and 800 °C, and part of it was CO<sub>2</sub>-activated. The activities of these chars were compared with that of commercial AC at 850 °C and 1050 °C. CO<sub>2</sub> activation treatment increased the BET surface area (Table 7) and the microporosity (surface and volume) of char, resulting in an improved naphthalene conversion. All chars showed deactivation with time, due to coking and blocking of the active sites. Particularly, non-activated wood chars showed a low conversion rate and a fast deactivation, probably due to low pore volume (~ 0.15 cm<sup>3</sup>/g). In contrast, activated wood chars with a higher surface area and a larger pore volume (~ 0.25 cm<sup>3</sup>/g) performed similarly to the commercial AC.

Feng et al. [61] used K-loaded and Ca-loaded rice straw char to investigate the influence of AAEM on the char catalytic activity towards tar reforming, under H<sub>2</sub>O or CO<sub>2</sub> atmosphere. Toluene, naphthalene and phenol were converted more efficiently in presence of steam, on the surface of K-loaded char. The authors suggest that carbon deposition is promoted by C-O-K clusters on the char surface, which constitute active sites. In contrast, Ca provides fewer active sites, as it bonds to the char with strong double bonds.

**Table 5**  
Artificial syngas compositions from Bhandari et al. [57] and Lu et al. [56].

	H <sub>2</sub> [%]	CH <sub>4</sub>	CO <sub>2</sub>	CO	H <sub>2</sub> O	others
[57] Bhandari et al.	5.2	7.5	16.8	19.3	–	N <sub>2</sub> balance
[56] Lu et al.	–	–	12.5	–	15	N <sub>2</sub> 72.5%
	6	–	–	5	15	N <sub>2</sub> 74%



**Table 6**  
Overview of conversion efficiencies for toluene (n.r. = not reported).

Toluene	Char	BET	Initial concentration $C_{in}$	Atmosphere	Reaction T	Residence time	Conversion ratio $\frac{C_{in} - C_{out}}{C_{in}} \times 100$
		[m <sup>2</sup> /g]	[g/N m <sup>3</sup> ]		[°C]	[s]	[%]
[38] Fuentes-Cano et al.	Coconut char	597	12	N <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub>	750	0.3	80–40
[55] Huang et al.	Sewage sludge char	38	12.9	N <sub>2</sub>	750	0.3	68.8
[56] Lu et al.	Sewage sludge char	74	12.9	N <sub>2</sub> , H <sub>2</sub> O, CO <sub>2</sub>	750	0.3	69.2
				N <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub> , CO	750	0.3	69.0
[57] Bhandari et al.	Switchgrass char	64	2 mL/h	N <sub>2</sub>	700	0.035 [kg h/m <sup>3</sup> ]	78.7
	Activated switchgrass char	944					86.3
[58] Mani et al.	Pine bark char	310–331	9.6 (2500 ppmv)	N <sub>2</sub> , H <sub>2</sub> O	700	1.3	~ 25
[38] Fuentes-Cano et al.	Coconut char	597	12	N <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub>	850	0.3	100–50
[55] Huang et al.	Sewage sludge char	38	12.9	N <sub>2</sub>	850	0.3	81.5
[56] Lu et al.	Sewage sludge char	74	12.9	N <sub>2</sub> , H <sub>2</sub> O, CO <sub>2</sub>	850	0.3	86.5
				N <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub> , CO			86.0
[57] Bhandari et al.	Switchgrass char	64	2 mL/h	N <sub>2</sub>	800	0.035 [kg h/m <sup>3</sup> ]	81
	Activated switchgrass char	944					91.7
[58] Mani et al.	Pine bark char	310–331	9.6 (2500 ppmv)	N <sub>2</sub> , H <sub>2</sub> O	800 900	1.3	~ 45 94
[61] Feng et al.	K-loaded rice husk char	n.r.	0.1 mL/min	CO <sub>2</sub> , H <sub>2</sub> O	800	n.r.	100

**Table 7**  
Overview of conversion efficiencies for naphthalene (n.r. = not reported).

Naphthalene	Char	BET	Initial concentration $C_{in}$	Atmosphere	Reaction T	Residence time	Conversion ratio $X = \frac{C_{in} - C_{out}}{C_{in}} \times 100$
		[m <sup>2</sup> /g]	[g/N m <sup>3</sup> ]		[°C]	[s]	[%]
[37] Hosokai et al.	Commercial char	740	1.5	N <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub>	700	0.2	73
[38] Fuentes-Cano et al.	Coconut char	597	8	N <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub>	750	0.3	90 – 30 (60 min)
[39] Zhang et al.	Rice straw char	262	25.2	Ar	700	20–30 mm bed height; 12 mL/min gas flow	58
[23] Di Gregorio et al.	Activated coal char	740	50–176.7	N <sub>2</sub>	750	50 mm bed height; 20 mL/min gas flow	42
[53] El-Rub et al.	Commercial biomass char	n.r.	90	N <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> O	900	0.3	99.6
[37] Hosokai et al.	Commercial char	740	3	N <sub>2</sub> , H <sub>2</sub> O	850	0.2	> 99.9
				N <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub>	850	0.2	94
[38] Fuentes-Cano et al.	Coconut char	597	8	N <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub>	850	0.3	100–60 (60 min)
[39] Zhang et al.	Rice straw char	262	25.2	Ar	800	20–30 mm bed height; 12 mL/min gas flow	77
[23] Di Gregorio et al.	Activated coal char	740	14.2–176.7	N <sub>2</sub>	850	50 mm bed height; 20 mL/min gas flow	100
[60] Nestler et al.	Activated wood char	600	0.57	N <sub>2</sub>	850	0.19	93–15 (120 min)
	Commercial AC	950	0.57	N <sub>2</sub>			85–65 (120 min)
[61] Feng et al.	K-loaded rice husk char	n.r.	0.1 mL/min	CO <sub>2</sub> , H <sub>2</sub> O	800	n.r.	93.9

Overall, these results indicate that the char activity for tar model compounds decomposition is affected by the volume and size distribution of the pores (especially micropores), but also the inorganics on the surface affect the catalytic activity for tar cracking. Indeed, the effect of the mineral composition of char on tar cracking was also investigated by Hervy et al. [62]. Ethylbenzene was used as a model compound for aromatic hydrocarbons, and its conversion was measured on three different chars produced from waste materials: wood pallets (WP), food waste (FW), sludge (S). The chars were produced with pure WP, and mixing FW/S and WP/FW/S. Chars were thoroughly characterized with various analytical techniques in order to establish their structural and chemical characteristics: significant differences were observed in the composition of the inorganic fraction and in the carbon structure. In comparison with WP char, char produced from a mixture

of FW and S was more effective in removing ethylbenzene from the gas stream, enhancing the cracking onto styrene, benzene, ethylene and toluene. The stronger catalytic activity was partly ascribed to a more disordered carbonaceous structure, but mostly to the higher ash content including Ca, P, Al and K oxides which were well dispersed on the surface.

The overview of these works shows that the effectiveness of biochar in removing tar compounds in gas phase is comparable to that of commercial catalysts: conversion of model compounds can reach 100% under favorable conditions. However, the interaction between tars and char surface implies a complicated synergy of gas-phase and solid-gas reactions, and they can vary significantly depending on the char characteristics and on the reaction conditions: the achievable conversion is difficult to predict. It is evident that temperature plays an important

role, and in order to reach a conversion rate over 90%, a minimum temperature of 800 °C is needed.

The presence of reforming agents (H<sub>2</sub>O, CO<sub>2</sub>) appears to induce higher conversions, whereas addition of H<sub>2</sub> results slightly detrimental for both toluene [56] and naphthalene [37] conversions. This effect, even if not strong, could be due to the inhibitory effect of H<sub>2</sub> on gasification reactions also observed by Barrio et al. [63].

In general, naphthalene shows higher conversions in comparison to toluene, revealing a preferential interaction of char with heavier aromatics. This is in agreement with the findings of Hosokai et al. [37], who stated that molecules with more fused rings were decomposed faster, and with the preferential adsorption for PAH observed on AC by Mastral et al. [17]. Selectivity towards multi-ring aromatics has also been observed by researchers working with thermal decomposition of pyrolysis-derived tars [64,65].

Such evidence suggests a beneficial effect of partial oxidation of tars before contacting the char: oxidation modifies the tar composition, converting oxygenated compounds into simple PAHs, especially naphthalene [66].

### 5.2.1. Determination of kinetic parameters for Toluene and Naphthalene decomposition

Only a few papers have investigated kinetic parameters for decomposition of model tars, focusing on the kinetics of toluene and naphthalene [38,53,58,67]. For both compounds, the rate equations were found to follow first order kinetics, showing a linear increase in the reaction rate when increasing the inlet concentration.

$$-r_{tar} = k*[C_{tar}] \quad (7)$$

Where  $r_{tar}$  is the tar decomposition rate,  $k$  is the rate constant and  $C_{tar}$  is the model compound concentration in the gas flow. The rate constant was estimated according to Arrhenius' law

$$K = A * e^{\frac{-E_a}{RT}} \quad (8)$$

El-Rub et al. [53] evaluated the kinetic parameters of naphthalene when reacting on commercial biomass char, whereas Mani et al. [58] studied the reaction rate of toluene steam reforming over pine bark biochar. The same research group further investigated the change in the kinetics of toluene steam reforming when the same biochar was impregnated and calcined with iron. Results were published by Kastner et al. [68]. The effect of Fe was to increase the reaction rate and to lower the activation energy. Table 8 reports the kinetics values estimated from experiments on model tar decomposition.

These kinetic expressions only consider the initial activity of char for tar decomposition and they do not take into account any deactivation effect.

Fuentes-Cano et al. [38] proposed an extended kinetic expression describing the effect of deactivation, introducing the activity factor  $a$ : the reaction rate is therefore expressed as in Eq. (9)

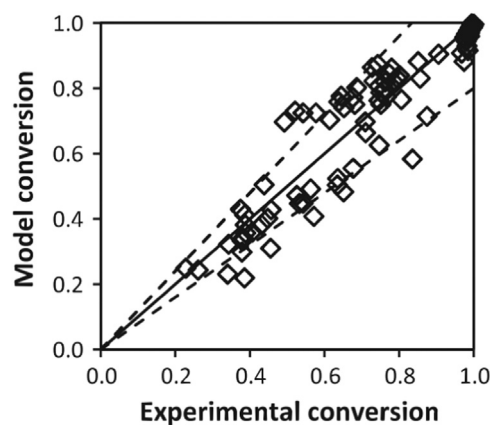
$$-r_{tar} = k*[C_{tar}]*a \quad (9)$$

where  $a = 1$  for fresh char;  $a < 1$  for partially deactivated char. Activity of char is defined as in Eq. (10)

**Table 8**

Kinetics parameters for naphthalene and toluene decomposition over different chars.

Model tar	Catalyst	A [m <sup>3</sup> kg <sup>-1</sup> h <sup>-1</sup> ]	Ea [kJ/mol]
Naphthalene [53]	Commercial biomass char	7.6 * 10 <sup>4</sup>	61
Naphthalene [38]	Coconut biochar	4 * 10 <sup>5</sup>	72
Toluene [38]	Coconut biochar	3.1 * 10 <sup>5</sup>	75
Toluene [58]	Pine bark biochar	2.6 * 10 <sup>5</sup>	90.6
Toluene [68]	18.7% Fe-loaded biochar	5.4 * 10 <sup>3</sup>	48.4



**Fig. 3.** Comparison of kinetic model (heavy line) with experimental results (squares). Dotted lines show  $\pm 20\%$  deviation. (Reprinted from [38], pag.1233. Copyright 2013 Elsevier).

$$a = \frac{-r_{tar,t}}{-r_{tar,0}} \quad (10)$$

where  $r_{tar,t}$  is the reaction rate at time  $t$  and  $r_{tar,0}$  is the initial reaction rate. The activity of char as a function of time was fitted to the empirical expression in Eq. (11).

$$a = \frac{1}{1+k_d t^p} \quad \text{with } p = p_1 + p_2 \left( \frac{T}{1023} \right) \quad (11)$$

Where  $k_d$ ,  $p_1$  and  $p_2$  are empirical parameters, and  $T$  is the char bed temperature, expressed in Kelvin. Comparison of the experimental results with this kinetic model showed a good agreement, being most data within  $\pm 20\%$  of error, as showed in Fig. 3.

Based on these results, the kinetics of tar decomposition on char surfaces should be further investigated with the aim to develop accurate kinetic models and describe the reaction mechanism for different compounds.

### 5.2.2. Carbon deposition and char deactivation

The main reaction pathway for model tars decomposition over char appears to be carbon deposition by polymerization (or coking) on the active sites of the surface. This was observed for both alkanes and aromatics: Fig. 4 shows spent char samples after propane and methane exposure, Figs. 5 and 6 show coke formation after toluene decomposition, whereas the effect of naphthalene exposure on the char structure are captured in Fig. 7.

Coking was often found to cause deactivation of the carbon surface, especially under inert atmosphere. SEM analysis has been widely applied for visualization of deposited carbon [41,57,58,60]: Carbon deposits take up different shapes depending on the reaction conditions. The polymerization is enhanced by specific active sites, as visible in Fig. 4(b) for methane deposition.

Both Hosokai et al. [37] and Nestler et al. [60] observed that on deactivated char, micropore volume was reduced, whereas mesopore volume remained unaltered. This result clearly indicates that micropores are active sites for carbon deposition. This also explains the fact that deactivation is faster on microporous carbons under inert atmosphere, when the deposited carbon quickly blocks the micropore mouths [60]. In contrast, in presence of H<sub>2</sub>O and CO<sub>2</sub>, the activity of char is maintained in time and the yield of stable gases is improved, particularly H<sub>2</sub>, CO, CO<sub>2</sub> and, to a lesser extent, CH<sub>4</sub>.

## 6. Conclusion

The overview of the above summarized studies outlines the state-of-the-art in the understanding of interactions between tar compounds and carbonaceous surface. All in all, it is evident that char has a beneficial

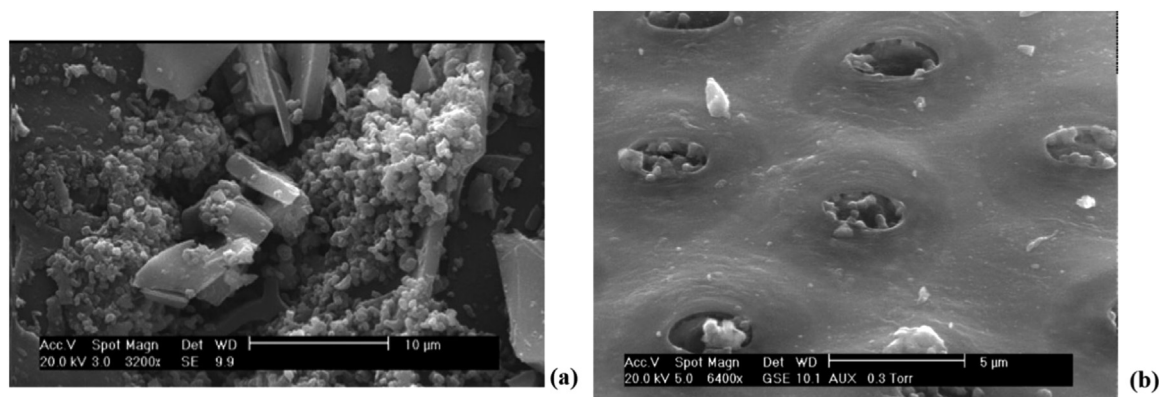


Fig. 4. Carbon deposits on char after propane (a) and methane (b) catalytic decomposition. (Adapted with permission from [41] Copyright 2012 American Chemical Society).

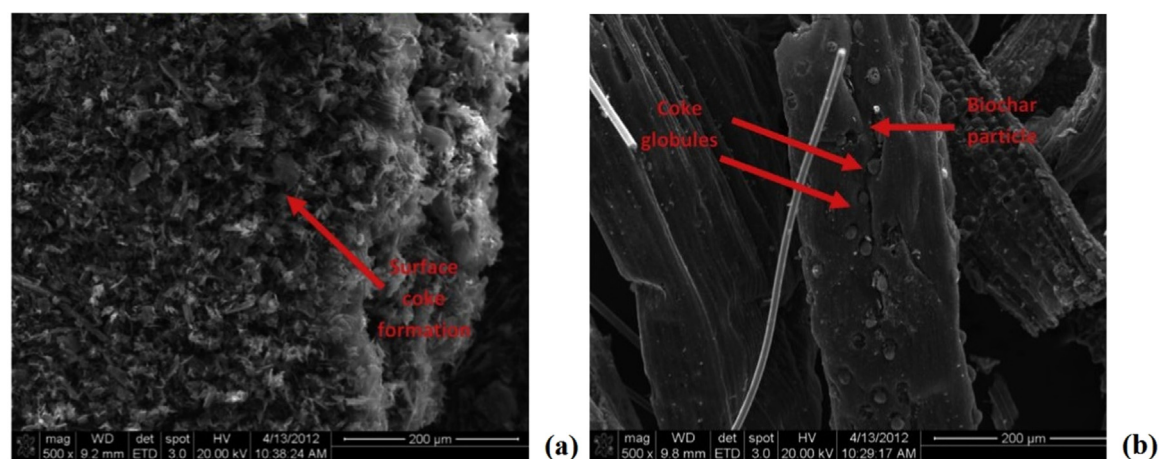


Fig. 5. Carbon deposits on AC (a) and biochar (b) from toluene decomposition in producer gas atmosphere at 700 °C. (Adapted from [45] pag 351. Copyright 2014 Elsevier).

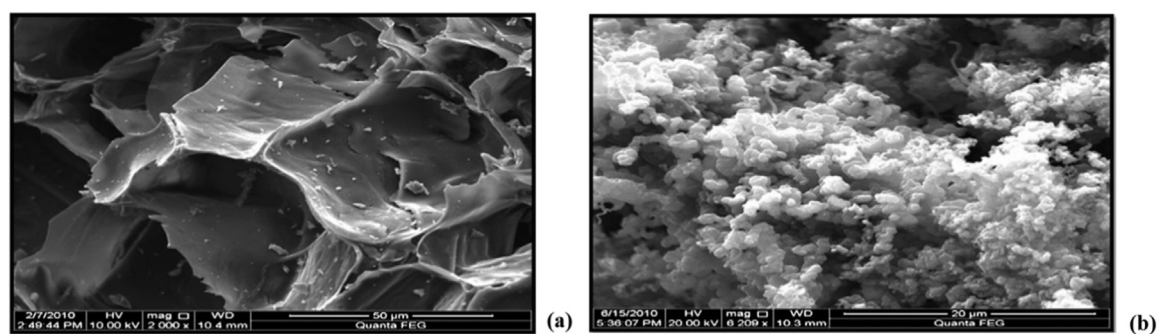


Fig. 6. Fresh pine bark char (a) and spent char (b) after 6 days of toluene exposure at 800 °C. (Reprinted from [46], pag 124. Copyright 2013 Elsevier).

effect on the removal or conversion of tar model compounds from a gaseous flow, and could be used as adsorbent or catalyst for gas cleaning. Chars produced with gasification and pyrolysis can be comparable to activated carbons in terms of effectivity for decomposition of model tars. The processes taking place at the surface strongly depend on the reaction conditions: adsorption is predominant at lower temperatures, whereas reforming reactions require higher temperatures and presence of  $\text{CO}_2$  or  $\text{H}_2\text{O}$  in the gas phase. Biomass char can catalyze the decomposition of  $\text{CH}_4$  and  $\text{C}_3\text{H}_8$  producing  $\text{H}_2$ . The induced conversion of toluene and phenol can be higher than 80% at 800°, whereas naphthalene can reach 100% conversion upon contact with the char surface.

Biomass char can be suitable to be used as a catalyst in producer gas

treatment for removing tars, especially multi-ring aromatics: indeed, biochar appears to catalyze tars cracking and reforming due to a synergy of surface chemistry and morphology. However, the properties of the char surface and the reaction conditions must be optimized in order to achieve complete conversion

In general, the abundance of active sites is favored by defects in the carbon structure (microcrystallinity, turbostratic carbon), and in presence of inorganic impurities. In particular, AAEM and metals (e.g. Fe, Al) appear to be effective in forming active sites, when they are well dispersed at accessible sites (micropores) on the surface. As a matter of fact, pure biomass ash always showed a lower activity in comparison with biomass char [25,53,55], indicating that the presence of carbon improves the catalytic activity acting as support.



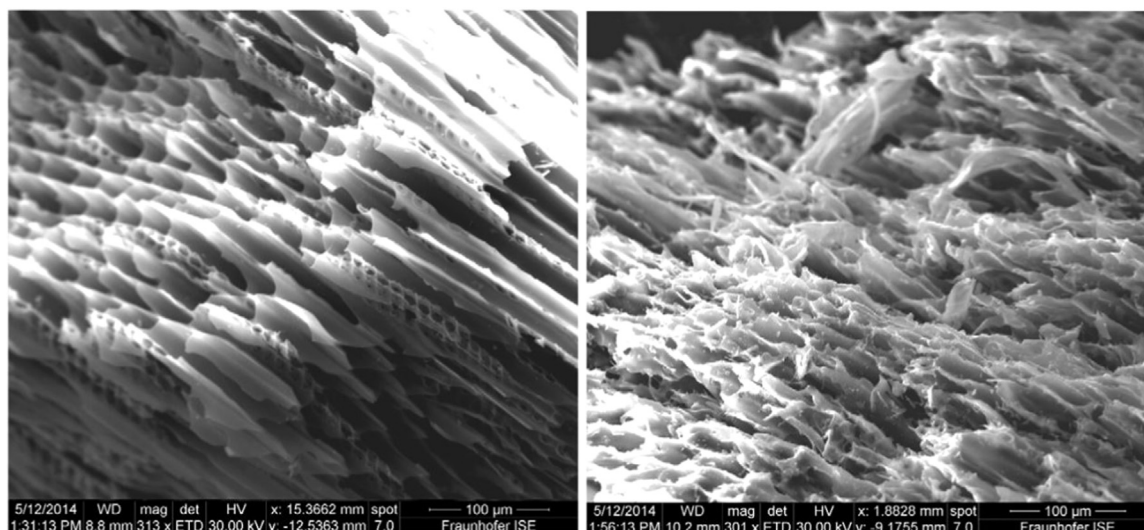


Fig. 7. Structural changes in activated biochar after 5 h of naphthalene exposure at 850 °C. The tracheids fracturing is due to cracking reactions, including carbon deposition. (Adapted from [60], pag 38. Copyright 2016 Elsevier).

It is difficult to quantify the effect of oxygen-containing functional groups, because at high temperature they are disrupted and simultaneously created by carbon deposition. For  $\text{CH}_4$  decomposition they were found to have an effect only in the initial activity of char [34] or no effect at all [25], and to have a negative effect on PAHs adsorption [51] and toluene decomposition [57]. In general, their effect on the decomposition of both alkanes and aromatics appears as secondary.

In contrast, the surface area (generally quantified with BET values) emerges as an important factor, together with the pore volume and the pore size distribution: the ratio between the micropore volume and the total pore volume should be high, as active sites appear to be housed in the micropores. A good pore structure enhances the long term activity of biochar as a catalyst, especially in presence of a reforming agent. In inert atmosphere, coking on the char surface leads to blocking of the active sites. Therefore, to prevent deactivation, the following points should be considered:

- (i) The char should have a high micropore volume, but the pore size distribution should include mesopores, so that diffusion is not hindered.
- (ii)  $\text{H}_2\text{O}$  or  $\text{CO}_2$  should be present, together with a temperature high enough to allow the gasification of deposited carbon.

Steam or dry reforming can be useful to create a dynamic equilibrium of coke deposition and gasification in the catalytic bed: the rate of gasification should be equal or higher to the rate of coke deposition, but not so high to quickly consume the solid bed.

An optimal solution for gas cleaning in biomass gasification would be the use of residual char as catalyst, possibly without further treatments. For the practical implementation of such solution, it would be useful to define correlations between the rate of tar decomposition, or the tar reactivity, and the char characteristics and reaction conditions, for representative model tars.

The reaction conditions to be considered should be:

- Temperature and pressure.
- Gas phase composition ( $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ).
- Tar species concentration.
- Residence time.

Determinant char properties that should be regarded are:

- Specific surface area (BET).

- Total pore volume.
- Pore size distribution: micropores volume to total volume ratio, or average pore diameter.
- Concentration of inorganic elements on the char surface.

All of these parameters are interdependent, and together they influence the effectivity of model tar conversion. With this in mind, it would be beneficial to dedicate future research activities to testing of char beds for the cleaning of real producer gas, with the aim to optimize and balance tar conversion and char gasification for an effective and stable gas cleaning.

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