



## Research article

# The influence of the char internal structure and composition on heterogeneous conversion of naphthalene



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## A B S T R A C T

This work studies the heterogeneous conversion of naphthalene over different chars at 800 °C and 900 °C with gas residence times ranging from 0.05 s to 0.15 s. The aim was to analyse the role of the pore size distribution and surface composition on the catalytic activity of the char during batch experiments with a steady gas flow doped with naphthalene. The char samples were produced by steam activation using the same parent material (a pyrolysed Colombian coal). The activation aimed at generating chars with increasing porosities but similar surface composition. An ash-leached char was also prepared to investigate the role of the ash-forming elements on the char activity. The evolution of the naphthalene conversion in the gas phase and the pore size distribution of the char were measured during the tests. The initial naphthalene conversion and the char deactivation rate were seen to be strongly influenced by the concentration of alkali and alkaline earth metallic (AAEM) elements in the char. In absence of AAEM elements, the char surface was rapidly deactivated due to the depletion of surface oxo-groups produced during the char activation. The steam activation of unleached chars does not influence their inherent surface reactivity but significantly enhances the amount of surface area available for tar conversion. A linear correlation between the reaction rate coefficient and the mesopore surface area was determined for the chars with similar surface composition but different pore size distribution.

## 1. Introduction

The presence of heavy tars in the syngas produced in biomass and waste gasification is the main bottleneck for its use in internal combustion engines for power production. The use of cheap and poisoning resistant catalysts for tar conversion is an interesting alternative to expensive secondary gas treatments, such as regenerative oil scrubbers, for small to medium scale plants [1,2]. During the last decade, several works analysing the use of biomass or coal chars for tar abatement/conversion have been published [3–20]. It has been determined that the activity of char material increases significantly at temperatures above 800 °C, allowing tar conversions over char close to that obtained using expensive Ni-based catalysts [3]. On the other hand, most of the available studies have been carried out at laboratory scale and the development of pilot or demonstration plants is still scarce [2,21–23]. A deeper knowledge of the tar conversion process over char (kinetics, deactivation, etc.) is necessary to select the best operation conditions to develop gas cleaning devices based on char catalysts.

The activity of char for tar decomposition varies with the nature of the tar compound. It has been found that reforming of aromatic molecules such as benzene and naphthalene over char does not produce other aromatic compounds but coke over the char surface [4,20]. In contrast, alkylaromatics and heteroatomic-aromatic compounds may produce lighter compounds by dealkylation and decarboxylation [24].

It has been verified that a char bed deactivates when it is exposed to a tar-loaded gas [4,7,11]. Increasing the char bed temperature and/or the steam concentration above a certain level contribute to minimize or even avoid soot formation/deposition. If the rate of carbon conversion by soot/char steam gasification is higher than that of soot deposition, the char activity is maintained over the time [4,7]. These observations indicate that some active sites distributed in the original char matrix are involved in tar conversion, and that the accumulation of soot (produced by tar conversion over the char surface) is the main reason for char deactivation.

The activity of char (and other porous materials) for tar conversion depends on the amount and the nature of the surface available for tar

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reaction [25]. Some authors [14,25,26] reported that the high activity of chars is due to the presence of oxygenated surface groups and alkali and alkaline earth metallic (AAEM) species distributed over the char surface. In other porous catalysts, such as zeolites and  $\gamma$ -alumina, their acidic nature has been suggested to be the origin of their activity [27]. The char activation process with steam or  $\text{CO}_2$  modifies the composition of the char surface, increasing the presence of oxo-groups linked to the carbonaceous material [14,26,28]. This activation process greatly increases the activity towards heavy tar conversion of the original char [17]. However, during tar conversion the characteristics of the char changes, and thus its activity [4,5,7,25,29]. The evolution of the pore size distribution, either increasing or reducing the total surface area (by the balance between the rate of carbon conversion and soot deposition) together with the change in the surface concentration of active groups explain the modifications of the char activity.

The physicochemical characteristics of the produced activated chars depend on different parameters, such as the composition of the parent material, type of activating agent used and reaction temperature [30]. Physical activation with steam or  $\text{CO}_2$  at temperatures above 700 °C is the most common method to produce activated char [14,31,32]. The steam activation is known to produce activated chars with higher mesopore volume while that produced using  $\text{CO}_2$  have a larger micropore volume [32,33]. The concentration of catalytic elements (K and Ca) on the char surface is enhanced by steam [34]. However, the interaction between char and the volatiles produced during the fuel devolatilisation can promote the release of alkaline metals from the char surface at temperatures above 700 °C [35].

The pore size distribution in char catalysts ranges from narrow micropores (internal diameter below 2 nm) up to large macropore cavities. A tar molecule has to move from the gas phase to the external surface of the char particle and then, diffuse into the char pores to be catalytically converted over the char surface. Diffusion of large tar molecules in micropores is constrained, making the amount of surface available for tar conversion lower than the total specific surface area of the char. However, the only literature work correlating internal structure and conversion rates establishes a kinetic equation where the conversion rate is proportional to the micropore (pore diameter below 2 nm) surface area [4]. On the other hand, it has been highlighted [11,25,27,29,36] the role of diffusion limitation and pore mouth blocking of micropores during the conversion of methane (mean diameter 0.38 nm; [36]) and naphthalene (kinetic diameter 0.74 nm; [11]). These diffusional limitations imply that mesoporous chars with high surface area present better long-term stability than microporous chars [25].

Kinetic models taking into account the physicochemical characteristics of the char are necessary to scale up laboratory results obtained with different chars and operating conditions to industrial devices. A deeper understanding of the conversion process over char would enable establishing proper pretreatments of chars (or activated carbons), improving its physicochemical characteristics, as well as the selection of the best experimental conditions to minimize char deactivation. In this work, the catalytic conversion of naphthalene over different char samples has been investigated. The aim is to provide reliable data, necessary for the development of new tar conversion devices, correlating the char characteristics (internal structure and surface composition) with its performance as a catalyst for tar conversion. The chars tested have been prepared using the same parent material (pyrolysed Colombian coal) to produce char samples with different porosities but similar char matrix composition. The influence of the inorganic elements over the naphthalene conversion was studied by leaching the ashes of the parent coal before the activation procedure. Special attention was eventually paid to the evolution of the pore size distribution and the surface composition of the char samples during the conversion of naphthalene.

## 2. Experimental

### 2.1. Char catalysts preparation: Char generation and activation

The different char catalysts were prepared from the same original material, granulates of a Colombian coal, having a size range of 3–6 mm. The first step in the preparation of the char catalysts was the coal devolatilisation under nitrogen flow at 900 °C in a bubbling fluidized bed (BFB) reactor (140 mm ID). The coal char produced, called “C0” in what follows, was further processed to produce two types of samples: activated chars and a leached-activated char. The latter was prepared by leaching a portion of the char C0 by using an acid solution of HCl (0.01 M) to maintain pH = 2 for 1 h at 60 °C [37,38]. After this, the char was rinsed with ultra-pure water, and dried for 12 h at 105 °C before its activation. The leaching process reduced significantly the amount of ashes in the char but a complete removal of inorganic elements was not possible.

The activation process was carried out at 900 °C in a lab-scale BFB reactor (26 mm ID) made of quartz. The activation agent selected was steam diluted with nitrogen (steam partial pressure of 100 mm Hg) being the total pressure equal to 1 atm. One activated sample was produced using the leached C0 char and three activated samples were produced using the non-leached C0 char. In all the activations, a fixed amount of 30 g of char (size 1–3 mm) was loaded in the reactor and heated up to 900 °C in a nitrogen atmosphere. Once the reactor reached the desired temperature, steam was fed to the reactor using a steam saturator. The activation was maintained for different times (50, 100 and 150 min for the non-leached chars and 100 min for the leached char) in order to obtain materials with different porosities. The chars produced were finally cooled down to room temperature by means of a nitrogen stream. The samples produced were named “C50”, “C100”, “C150” and “leached” respectively.

### 2.2. Laboratory apparatus for tar conversion tests

The apparatus used to perform the naphthalene conversion tests over char has three main sections: the feeding system, the reactor and the exit line. The main components are sketched in Fig. 1.

The feeding system contains a rotameter for controlling the nitrogen flowrate and a naphthalene saturator to produce the tar-doped stream. A K type thermocouple, inserted at the saturator exit, was used to measure the temperature of the gas. The pipes between the saturator and the reactor were kept above 150 °C to avoid naphthalene condensation (the naphthalene dew point of the inlet gas was 65 °C).

The reactor used to study the naphthalene conversion over char was a vertical tubular quartz reactor with an internal diameter of 14 mm and a total height of 600 mm. The char bed was placed above a glass frit inside the reactor, located at 430 mm from the top. The mass of char used depends on the gas residence time selected for the test, ranging from 0.75 g for gas residence time of 0.05 s to 2.25 g for gas residence time of 0.15 s. The bed temperature was measured in the centre of the char bed by a K type thermocouple inserted from the top of the reactor. The temperature profile along the reactor above the glass frit, measured modifying the height of the thermocouple, for tests at 800 °C and 900 °C is shown in Fig. 2. The temperature along the char bed was within  $\pm 3$  °C the set temperature in all the tests performed.

The gas at the exit of the reactor can be directed to the sampling device (only during tar samplings) or to the cleaning device (the rest of the test time) by switching a three-way valve. The sampling device consists of three impingers filled with isopropanol at 0 °C. Dedicated experiments showed a capture efficiency of the sampling device above 99% for the conditions analysed in this study. All the lines between the reactor and the sampling/cleaning devices were heated (150 °C) to avoid naphthalene condensation.

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