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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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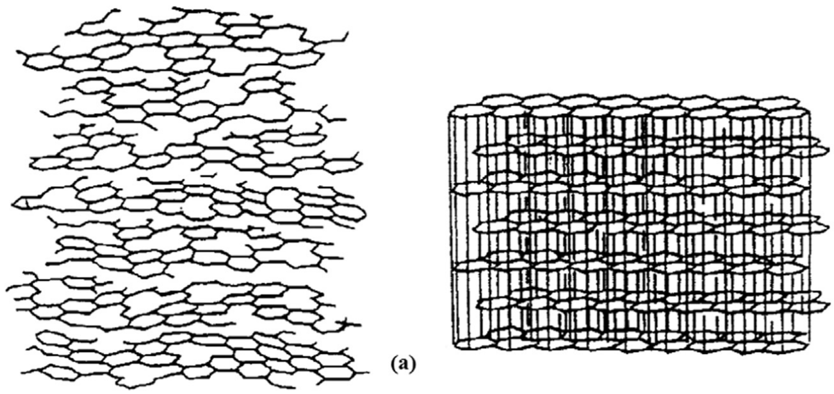

Fig. 1. Schematic difference between turbostratic (a) and graphite (b) structure. (Adapted from [10] with permission from Taylor & Francis Ltd.).

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 Keiluweit 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