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Removal of naphthalene by activated carbons from hot gas

F. Di Gregorio [a,*], F. Parrillo [b], E. Salzano [c], F. Cammarota [d], U. Arena [a,b]

[a] *AMRA – Analysis and Monitoring of Environmental Risk, Via Nuova Agnano, 11, 80125 Napoli, Italy*
[b] *Department of Environmental, Biological and Pharmaceutical Science and Technologies, Second University of Naples, Via Vivaldi 43, 81100 Caserta, Italy*
[c] *Department of Civil, Chemical, Environmental, and Materials Engineering, Alma Mater Studiorum – University of Bologna, Via Terracini 28, 40131 Bologna, Italy*
[d] *Institute for Research on Combustion, National Research Council, Via Diocleziano 328, 80124 Napoli, Italy*

HIGHLIGHTS

- Naphthalene was utilized as the reference tar compound.
- Adsorption tests were carried out at 750–900 °C with three activated carbons.
- The effects of temperature, test duration and naphthalene concentration were investigated.
- Complete naphthalene removal was obtained at high temperatures and concentrations.
- A partial reforming of adsorbed naphthalene was observed with release of hydrogen.

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ABSTRACT

The gasification of biomass and waste is a potentially high efficiency process for energy generation. However, the appropriate cleaning of the produced fuel gas is a major issue, in particular for tar removal. This study investigates the performance of three new-generation activated carbons, which are able to adsorb a wide spectrum of tars at high temperature, from 750 °C up to 900 °C. For this purpose, a laboratory-scale hot gas filtration apparatus was designed and set-up. Experimental tests were carried out with naphthalene as the reference tar compound. The selected activated carbons were tested under different conditions of temperature, test duration and naphthalene concentration. The procedure allows evaluating the contributions of adsorption and cracking phenomena on the overall tar removal efficiency. Complete naphthalene removal was obtained with two of the selected activated carbons, at 850 °C and 900 °C respectively. Simultaneously, a partial reforming of adsorbed naphthalene was observed, and molecular hydrogen was detected in the gas phase. Results were correlated to the differences in porosimetry and chemical surface of the selected activated carbons, as well as to those highlighted by Scanning Electronic Microscopy and X-ray analyses. Finally, a procedure for activated carbon regeneration by carbon dioxide is reported, together with results from preliminary tests.

1. Introduction

Biomass and waste for energy recovery are two debated issues on our days, and improvements for their management and utilization are investigated worldwide. Despite increasing attention to waste prevention and recycling, total municipal solid waste (MSW) generation has increased in Europe from about 150 million tonnes in 1980 to more than 213 million tonnes in 2012 [1]. Worldwide it is projected to double by 2030. In order to improve the sustainability of waste management and to divert waste from landfill, thermal treatments are key actors, because they strongly reduce the mass and volume of waste and efficiently recover its energy [2,3]. Based on these observations, the European Union recently adopted a "20-20-20" Renewable Energy Directive, setting climate change, reduction targets for the next decade, based in large part on biomass valorisation. This means to compete with fossil energy sources and their high efficient energy conversion devices. Accordingly, in the last decade great research and development efforts have been dedicated to efficient conversion technologies for biomass and waste [4].

Gasification technologies, in particular those involving fluidized bed reactors, have attracted worldwide attention due to their wide range of applications and benefits [5–7]. The operating experience of the last two decades indicates that gasification plants for energy recovery from waste and biomass need optimal combinations of

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[*] Corresponding author. Tel.: +39 0823 274593.
E-mail address: fabrizio.digregorio@unina2.it (F. Di Gregorio).

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gasification technology, gas cleaning treatment, and final energy conversion, in order to minimize the formation of contaminants in the produced fuel gas (syngas) and to maximize availability and efficiency of the plant [8]. The selection and the proper design and operation of the gas cleaning section is key to efficiently removing the suite of organic and inorganic contaminants present in the syngas. It is crucial to define appropriate measures to minimize the formation of contaminants inside the reactors as well as to evaluate proper syngas cleaning options [9,10].

In this framework, the removal of high-molecular-weight polynuclear hydrocarbons, characterized by high dew point temperatures (generally above 300 °C), and collectively known as tar, is a major issue. Tar removal is the greatest technical challenge to be overcome for wider application of gasification systems, because tar can condense along pipes, heat exchangers and particulate filters, leading to fouling, plugging or choking [11,12], seriously reducing plant availability and increasing operating costs [13].

Different approaches to tar removal, based on mechanical, thermal, catalytic, or chemical treatments have been proposed. However, a technique able to simultaneously provide technical reliability, economic feasibility, and efficient tar removal without decreasing syngas quality is so far unavailable [14–17].

This paper describes a hot gas filtration system for tar removal from syngas, based on a combination of adsorption and cracking, operated by a fixed bed of new-generation activated carbons (ACs). These carbons are able to operate at temperatures typical for fluidized bed gasifiers, i.e. between 750 °C and 900 °C [18,19], well above the tar dew point. The proposed method could be potentially utilized inside the fluidized bed reactor or, with greater chance of success, immediately downstream of it [20]. A laboratory-scale hot gas filtration apparatus was designed and set-up to evaluate the performances of this kind of activated carbons. The tests utilized naphthalene as the reference substance for tar [10,21]. Three activated carbons were selected, characterized and utilized under different operating conditions, aiming at evaluating their tar removal performance and estimating the contributions of adsorption and reforming.

2. Experimental

2.1. Tar model compound

Tar removal is a highly debated problem for biomass and waste gasification [22]. Its concentration is strongly affected by the gasification technology and the feedstock used. Tar (identified as C_xH_y) can be reformed into smaller-chain hydrocarbons (C_nH_m), with the simultaneous release of molecular hydrogen, as described by the following "cracking" reaction:

$$aC_xH_y \rightarrow bC_nH_m + cH_2 \qquad (1)$$

This reaction can be promoted by catalysts and/or high temperature [23–25]. In order to simplify the complex tar mixture and to understand in details the adsorption and cracking mechanisms on the activated carbon surfaces, the investigation was specifically designed for naphthalene ($C_{10}H_8$, MW = 128 g/mol; boiling point = 218 °C) supplied by Sigma Aldrich. It is widely used as a reference substance representing the tar mixtures in gasification processes because, whatever the applied technology and the utilized feedstock, it represents the main and most stable tar component [21,26–27].

2.2. Characterization of the activated carbons

Activated carbons are widely utilized in industrial processes for pollutant adsorption at temperatures up to 300 °C, due to their diffused porosity and large surface area. In particular, in waste or biomass-to-energy plants, they are widely applied in the flue gas cleaning section at temperatures of about 150–200 °C, with the main aim of removing mercury, cadmium, heavy metals and dioxins before the stack [28]. For the purpose of this investigation, three commercially available new-generation ACs were selected, based on their ability to adsorb aromatic substances at temperatures up to 900 °C. The ACs, which were all steam-activated, were produced by utilizing Chinese (for AC1 and AC2) and Korean coals (for AC3) as parent material. They have the same pellet size and shape: mechanically extruded, cylindrical shaped, with a diameter of 3 mm. Table 1 reports proximate and ultimate analyses, as well as densities. The values of moisture and ash were measured by placing samples of each activated carbon in a muffle furnace at 105 °C for 12 h and at 950 °C for 2 h, respectively. The element compositions were determined by means of a CHNS LECO analyser, and the proximate analysis used a Perkin Elmer thermogravimetrical balance. Particle and bulk densities were measured following standard procedures, filling a 500 ml graduated cylinder with activated carbon pellets. In particular, the particle density was evaluated by the bulk density after that the void fraction between activated carbon pellets was measured introducing a certain volume of water in the graduated cylinder. The physical and chemical characteristics of the three selected ACs are listed in Table 2.

The specific surface areas were determined by means of a Sorptometer 1042. BET, Langmuir and the *t*-plot equations were evaluated in order to better fit the results based on the different nature of the AC surfaces. Indeed, strong differences in the pore size distri-

Table 1
Proximate and ultimate analyses, and densities for the tested activated carbons.

	AC1	AC2	AC3
Proximate analysis, % as received			
Ash	11.20	8.74	9.09
Fixed carbon	79.32	82.12	74.00
Volatile matter	6.48	6.15	10.06
Moisture	3.00	3.00	6.85
Ultimate analysis, % as received			
C	77.19	82.42	75.54
H	0.40	0.20	0.27
N	0.44	0.55	0.35
S	0.52	1.04	0.44
O (by difference)	7.25	4.05	7.46
Density, kg/m^3			
Bulk density	490	530	480
Particle density	866	1168	868

Table 2
Chemical and physical properties for the tested activated carbons.

	AC1	AC2	AC3
Surface area, m^2/g			
BET	740.2	434.1	947.9
Langmuir	990.2	552.3	N.A.
t-Plot (microporous area)	320.3	550.3	N.A.
t-Plot (non-microporous area)	420.0	2.06	N.A.
Hg porosimetry			
Total pores volume, mm^3/g	494.7	274.6	553.6
Micropores volume, mm^3/g	112.9	193.9	47.7
Mean pore diameter, nm	66.9	146.2	569.3
EDS analysis, %			
Aluminum	1.56	1.10	1.91
Calcium	0.48	2.21	2.51
Iron	0.89	1.28	3.06
Magnesium	0.21	0.28	0.56
Potassium	0.15	0.08	–
Silicon	2.56	1.53	2.71
Sulfur	0.55	2.73	–