



The influence of temperature and steam on the yields of tar and light hydrocarbon compounds during devolatilization of dried sewage sludge in a fluidized bed

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HIGHLIGHTS

- ▶ Devolatilization tests were conducted between 600 °C and 900 °C.
- ▶ Detailed analysis of tars and light hydrocarbons was performed.
- ▶ Steam concentration (0–30 vol%) hardly influences tar and hydrocarbon yields.
- ▶ Stoichiometric formula of tar was estimated by elemental analysis of tar.
- ▶ Correlations between tar and light hydrocarbon yields were obtained.

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ABSTRACT

The influence of temperature and steam concentration over the yields of tar and light hydrocarbon compounds generated during devolatilization of batches of dried sewage sludge in a laboratory fluidized bed reactor was investigated. Tests were conducted in the temperature range of 600–900 °C with gas residence time of 1.5 s. Thirty-six aromatic tar compounds (from benzene to perylene) were analyzed by GC/MS and light hydrocarbons (CH₄, C₂H₆, C₂H₄, C₂H₂, C₃H₈ and C₃H₆) by GC/thermal conductivity. The content of C, H, N and S in the gravimetric residue of the tar sample (that obtained after vacuum distillation of the original sample) was also analyzed. It was found that increasing the steam concentration (up to 30% molar) did neither modify the aromatic tar composition nor the yield of light hydrocarbons, only slightly affecting the yield of gravimetric tar. Detailed analyses of tar composition and light hydrocarbons enabled us to relate the yields of these compounds at different temperatures, shedding light on the mechanisms of tar conversion into light hydrocarbon species. It also provides shortcut methods for the estimation of tar mixture properties, such as the yields of heavy aromatic compounds and the aromaticity of the tar mixture, from light hydrocarbon measurements at different temperatures.

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1. Introduction

Gasification of biomass and wastes enables the production of a gas useful for chemicals and power production. During the first stage of conversion in a fluidized bed gasifier (FBG), the fuel is decomposed into three main fractions: light gas (non-condensable), solid carbonaceous material containing ash and fixed carbon (char) and a heterogeneous mixture of organic components (tars)

Abbreviations: AAEM, alkali and alkaline-earth metallic species; ANVT, aromatic non volatile tars; daf, dry and ash free fuel; DSS, dried sewage sludge; FBG, fluidized bed gasification/gasifier; GC/MS, gas chromatography/mass spectrometry; HACA, hydrogen abstraction carbon addition; PAH, poly-aromatic hydrocarbons.

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[1]. The risk of bed agglomeration and sintering due to the presence of alkali and alkaline earth metallic (AAEM) species limits the bed temperature to a maximum of 800–900 °C. This temperature is not high enough to completely convert the tar compounds generated during devolatilization, leading to significant concentration of tars in the exit gas. The tar compounds remain as gas above 300–400 °C at atmospheric pressure, but condensation of the gas starts below this temperature. For applications where the gas produced is cooled, condensation of tars may cause major drawbacks, making extensive secondary cleaning necessary. Therefore, conversion and removal of tar compounds is a key issue to be addressed for the optimization of FBG processing biomass and waste species.

Tar can be defined as all organic compounds, produced during the thermochemical conversion of solid fuels, with a molecular mass larger than benzene (excluding soot and char) [2]. This

Table 1
Tar classifications. (a) Extracted from [2] and (b) extracted from [11].

Family	Description
<i>(a)</i>	
Primary	Products derived from the fuel thermal cleavage; levoglucosan, furfurals, guaiacols
Secondary	Phenols and olefins
Tertiary	Alkyl-aromatics
Condensed-tertiary	Poly-aromatic hydrocarbons (PAH)
<i>(b)</i>	
Class 1	GC-undetectable tars; high polarity tars
Class 2	Heterocyclic compounds
Class 3	Mono-aromatic compounds
Class 4	Light aromatics; 2–3 rings PAH compounds
Class 5	Heavy aromatics; 4–7 rings PAH compounds

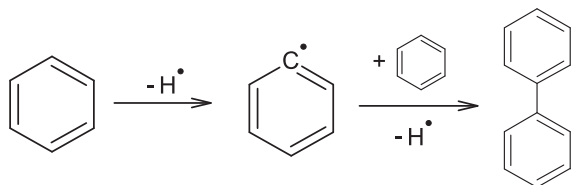
definition includes a complex mixture of organic compounds with a wide range of molecular mass whose composition and reactivity changes during the conversion process [3]. Secondary conversion of tars depends on many factors such as the time–temperature history, the presence of gaseous species like O_2 or H_2O and the presence of catalysts [4]. The thermal treatment of tar mixtures causes not only a decrease in the tar yield but also a change in the molecular structure of the species [5–7]. Tars produced during devolatilization at temperatures between 400 °C and 600 °C comprise mainly complex structures, linked to the parent fuel structure, having high proportion of heteroatoms [7,8]. These tar mixtures are

usually called “primary tars” [3]. At temperatures above 600 °C primary compounds are thermally unstable, decomposing into gas and other tars [5,6]. These secondary tars are mainly composed by aromatic molecules, from mono-aromatics to poly-aromatics, being less reactive than primary tars and difficult to convert below 900 °C. Above this temperature aromatic tars are mainly converted into soot by polymerization reactions [6–10].

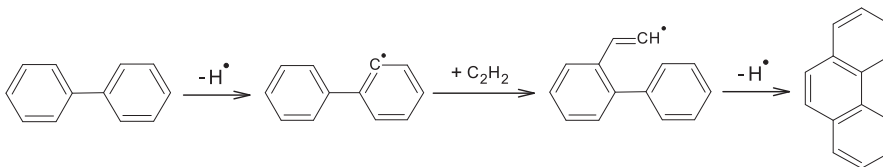
Tar definition was ambiguous until the adoption of standards for tar sampling and analysis [11]. Comparison between different works was difficult because researchers defined tars in a variety of ways, according to their own sampling and analysis methods. Classifications of tar compounds have been proposed aiming at making the characterization of tar samples simpler, enabling the study of tar conversion and mechanisms. The first classification [3], presented in Table 1a, divides the tar compounds in three families on the basis of the so-called severity conditions (temperature and residence time) under which the tars are formed and subsequently converted. The second classification, presented in Table 1b, was oriented to distinguish tars on the basis of their condensing behavior [2].

Tar formation and conversion have been widely studied in the last decades [7–9,12–20]. Two different kinds of experiments have been carried out. In the first type a model tar is converted under controlled atmosphere, allowing for tracking the decomposition process and the determination of the conversion kinetics [9,12–15]. In the second type of tests the production and conversion of tar compounds generated from fuel decomposition are studied. This method is complex but enables determination of a more realistic tar formation–conversion reactivity. Due to the large

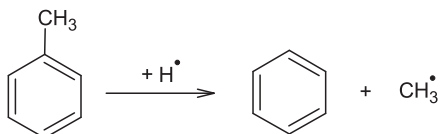
1-Dimerization



2-Light unsaturated hydrocarbon addition to aromatic structures



3-Dealkylation



4-Decarboxylation of phenolic compounds

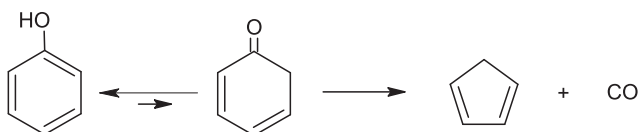


Fig. 1. Mechanisms involved during thermal conversion of aromatic tars.

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