Modelling of tar formation and evolution for biomass gasification: A review

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HIGHLIGHTS

- Review of mechanisms for tar formation and evolution during biomass gasification.
- Identification of pyrolysis products from cellulose, hemicellulose and lignin.
- Identification of common use tar model compounds and their experimental and modelling study.

ARTICLE INFO

ABSTRACT

Many by-products are generated during gasification, such as tar, NO_x, SO_2, and fly ash. In particular, tar elimination from the product gas is necessary to make gasification an attractive option. The presence of tar can cause operational problems to further equipment; heavy tars may condense on cooler surfaces downstream which can lead to blockage of particle filters and fuel lines. With the aim of establishing a mechanism for tar formation, tar precursors were identified based on biomass main components – lignin, cellulose and hemicellulose. This review describes the fundamentals of the possible mechanisms for tar formation and evolution, as well as the background for the development of a model for the simulation of a biomass fluidised bed gasifier.

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1. Introduction

Increasing interest to substitute fossil fuels and reduce greenhouse gas emissions has promoted research on the use of biomass and agricultural waste in energy conversion processes. A technological option that has the potential to become one answer for renewable energy generation is biomass gasification. Even though coal gasification is a well-established technology, its adaptation to biomass gasification poses challenges in the designing of the process. The main reason is the chemical and physical differences between biomass and coal [1]. That is, biomass is characterised by lower fixed carbon, and higher moisture and volatile matter contents than coal.

During gasification many by-products are generated such as NO_x, SO_2, fly ash and tar. In particular, tar formation is one of the major issues to be solved when implementing this technology. The higher volatile matter makes biomass more susceptible to tar formation. Tar is a complex mixture of condensable hydrocarbons comprising single-ring to 5-ring aromatic compounds plus other oxygen-containing hydrocarbons and complex polyaromatic hydrocarbons (PAHs) [2].

The success of biomass gasification requires a reliable system that delivers a quality product. The presence of tar can cause operational problems because of the possible formation of aerosols, soot formation due to repolymerisation, and interaction of tar with other contaminants on fine particles. In addition, heavy tars may condense on cooler surfaces downstream which can lead to blockage of particle filters and fuel lines. Therefore, tar elimination from the product gas is the ultimate goal to make gasification an attractive option.

Methods to reduce and control tar formation during biomass gasification have been divided in primary methods – when the tar is removed inside the gasifier-, and secondary methods – when tar is removed in a separate step after gasification [2]. Primary methods include the appropriate selection of operating parameters, the proper design of the gasifier and the use of suitable bed additives or catalysts during gasification. In contrast, secondary methods comprise tar cracking either thermally or catalytically, or mechanical methods such as the use of cyclones and electrostatic filters. Tar reduction methods have also been categorised in five groups: mechanism methods, self-modification, thermal cracking, catalyst cracking, and plasma methods [3].

Mechanical methods are classified into two types: dry and wet gas cleaning. Dry gas cleaning methods include cyclones, rotating particle separators (RPS), fabric filters, ceramic filters, activated carbon based adsorbers, and sand bed filters which can be used to capture tar from product gas. Wet gas cleaning methods are used after gas cooling at about 20–60 °C; some examples are wet electrostatic precipitators, wet scrubbers, and wet cyclones. However, disadvantages of wet gas cleaning are that synthesis gas has to be cooled down and waste water treatment is required [4].

Self-modification methods comprise the best selection of type of gasifier and operating parameters, such as temperature, equivalence ratio (ER), the type of biomass, pressure, gasifying medium and residence time. Increases of operating temperature have shown to reduce the total number of detectable tars but favoured

the formation of aromatics without substituent groups (such as benzene and naphthalene) [5]. Tar yield and tar oxygen-containing compounds decreased drastically with increases of ER. Experimental work in a fluidised bed gasifier with tree chips showed that raising the pressure from 8 to 21 bars reduced oxygenated components, and particularly phenols were almost completely eliminated, conversely, the PAH fraction increased [6].

Thermal cracking involves conversion or cracking of tar into lighter gases using high temperatures for certain residence time. It was reported for biomass tars, that the maximum quantity of tar was reached at about 773 K and then dropped with increasing temperature. At temperatures >873 K, secondary reactions (i.e. tar cracking) occurred, increasing the amount of non-condensable gases, which improved the energetic content of the product gas [7]. In addition, at least a temperature of 1523 K and residence time of 0.5 s were identified as needed to achieve high tar cracking efficiencies [3]. For catalytic cracking techniques, catalysts commonly employed are classified into six groups: nickel-based catalysts, non-nickel metal catalysts, alkali metal catalysts, basic catalysts, acid catalysts, and activated carbon catalysts [4]. Lastly, the plasma method has been used to simultaneously remove tars and particles; 50% removal of naphthalene was achieved with a corona discharge using an energy density of 40 J/L at 400 °C in about 3 min [8]. Devi et al. [2] and Han and Kim [3] have comprehensively reviewed tar reduction methods, interested readers should refer to those reports.

Tar is often classified according to its appearance as primary, secondary and tertiary tars. Primary tars have been identified as consisting of mainly oxygenated compounds produced at 673–973 K. Secondary tars are produced at around 973–1123 K and comprise phenolics and olefins; whilst tertiary tars are formed at temperatures around 1123–1273 K and consist of complex aromatic compounds [9]. As part of the tertiary tars, aromatics such as PAHs are found. Other tar classification is based on the molecular weight of tar compounds, which are divided by classes: class 1 refers to GC-undetectable tars, like heaviest tars that condense at high temperatures even at low concentrations; class 2 refers to heterocyclic compounds that generally have high water solubility, such as phenol and cresol; class 3 includes 1-ring aromatic compounds, e.g. xylene and toluene; class 4 refers to 2–3 ring PAH compounds, such as naphthalene and phenanthrene; and, class 5 includes higher PAH compounds, that is, 4–7 ring aromatic compounds from fluoranthene to coronene [3]. Another description for tar, based on tar sampling and analysis, is gravimetric tar. It refers to numerous individual tar compounds quantified in the liquid tar sample from gasifier systems, which will exclude compounds evaporated during the determination of gravimetric tar. Thus, total tar refers to the sum of gravimetric tar and the tar in the evaporation residue [9].

Due to the complexity of tar, most reports are mainly concerned with the identification and quantification of PAH from pyrolysis or combustion. In the case of kinetic studies, attention has been given to the determination of either kinetic parameters for the overall weight loss of the fuel or kinetic parameters for the evolution of light gases (such as CO, CH_4 and H_2). As a result, kinetic data and theoretical comprehension of the tar reaction processes during bio-