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Research article

Microwave plasma treatment of simulated biomass syngas: Interactions between the permanent syngas compounds and their influence on the model tar compound conversion

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ABSTRACT

Plasma techniques are attracting significant attention in the context of tar removal from the biomass-derived syngas. This research investigated the impact of microwave (MW) plasma on a simulated biomass syngas containing benzene as a model tar compound. The high temperature of the plasma and the presence of reactive species resulted in crucial changes of the gas composition. A significant increase in CO and H_2 concentrations at a cost of CH_4 and CO_2 was observed. It was concluded that CO_2 and H_2 were essential in the conversion of both, methane and benzene. This phenomenon was attributed to the presence of O, OH and H radicals generated in the plasma core zone. While the addition of these compounds allowed achieving conversion efficiency at the level of 97–98%, the presence of methane decreased it to c.a. 60% due to the re-formation of benzene. Moreover, the main by-products of benzene conversion, qualified and quantified, showed the same tendency towards syngas compounds as benzene did.

1. Introduction

Biomass gasification is gaining relentless attention in the context of renewable energy and sustainable development [1,2]. This phenomenon comes from the fact that biomass is a renewable source, widely and relatively evenly distributed along the earth thus accessible locally [3]. Additionally, it is considered as neutral in terms of CO_2 emission [2,3]. Most importantly, gasification can be considered as one of the most flexible fuel conversion processes. The producer gas can be utilized in boilers, engines, turbines or even fuel cells. Moreover, it can be converted into syngas or hydrogen, which might be applied in chemical syntheses of many products, including components of liquid fuels, methanol, and fertilizers [4]. However, despite these advantages, biomass gasification is still far from being a mature technology applied at full commercial scale. While there are few reasons that limit the development of biomass gasification [3], one of them is undoubtedly the presence of tars in the producer gas [3,5].

Tars are a complex mixture of organic compounds that are defined in many ways [6]. One of the simplest and broadest definition states:

"The organics produced under thermal or partial-oxidation regimes (gasification) of any organic material are called "tars" and are generally assumed to be largely aromatic" [5]. These compounds tend to condensate at low temperatures and/or elevated pressure and form soot particles [6]. As a consequence, they may cause malfunctions of turbines, engines, and fuel cells as well as fouling and blocking of pipelines and filters [6,7]. While the concentration of tars in a raw syngas can vary from c.a. 1 to over 100 g/Nm^3 depending on the gasifier and process conditions [5], the tolerable amount of tars ranges from 100 mg/Nm^3 for internal combustion engines to c.a. 1 mg/Nm^3 for synthesis purposes [8,9]. These distant values show how important and efficient the tar removal process must be. In fact, many researchers believe that solving the tars problem would significantly expedite the development of biomass gasification technology [2].

Tar removal methods can be categorized into primary and secondary [6]. Primary methods focus on optimization and control of the gasification process and the gasifier design itself. Secondary methods require the introduction of auxiliary devices and usually are a necessity when a high purity syngas is demanded. These methods can be grouped into four subcategories: mechanical, thermal, catalytic, and plasma methods. Mechanical methods involve mainly the application of scrubbers, washing towers, filters, and any other absorbing/adsorbing devices [6,10]. While they allow achieving a sufficiently low tar concentration, their main drawbacks are the efficiency drop that comes from the gas cooling and the required waste treatment [9,11]. Thermal

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methods offer a possibility to directly convert tars into valuable products. However, to provide optimal conditions for almost complete thermal cracking of tars, high temperature and sufficient residence time are required [6,7]. These hard to provide parameters can be significantly reduced by the introduction of a catalyst. Numerous catalysts have been investigated in terms of tar conversion, e.g. calcined rocks, olivine, char, and metal catalysts [7,11,12]. Besides showing a high-efficiency tar conversion, catalytic methods enable obtaining higher yields of valuable H_2 and CO. However, their main limitation is the catalyst lifetime. In the presence of gaseous impurities, e.g. H_2S, SO_x or HCl, which adsorb on the active sites, the catalyst might be permanently poisoned and deactivated [9,11]. Moreover, a similar effect might be caused by the coke deposition formed on the catalyst surface during tars conversion [3,11]. The last group, plasma methods, lacks these limitations. Although plasma methods can be considered to be the most complicated and energy consuming, they provide conditions that allow achieving effective tar conversion and increase in the concentration of valuable products, similarly to catalysts. Many plasma techniques have been investigated in terms of tars conversion, e.g. corona discharge [13,14], dielectric barrier discharge [15,16], arc plasma [17,18], gliding arc plasma [19–22] and microwave (MW) plasma [23–25].

From all the aforementioned the microwave plasma can be distinguished due to its electrodeless character. This property can be valuable, since electrodes erosion may limit the plasma technology application, especially in harsh producer gas conditions [26]. Another advantage is that the magnetrons used in microwave plasma generation are the same as those used in other industrial applications of microwaves, which are considered to be mature technologies, e.g. drying, food processing, and heating in general [27]. Microwave technology elements are relatively cheap and have a simple and compact construction similar to household MW ovens. Moreover, they are produced by many companies and their power can vary from few to hundreds of kW, creating a potential to scale up the technology [27,28]. And maybe most importantly, in microwave plasma, a great amount of energy is distributed into vibrational temperature [28,29]. This physical phenomenon is essential in the chemistry of compounds like CO, CO_2, H_2, and N_2, all of which can be present is syngas [30]. Despite its non-thermal character, microwave plasma can be classified as a warm plasma [19,31], meaning that its gas temperature can reach few thousands K. In fact, typical microwave plasma has a gas temperature (in discharge zone) on a level of 4000–6000 K [23,25,29]. Therefore, both non-thermal (e.g. electronic or vibrational excitation) and thermal processes may influence the in-gas reactions and products composition.

In spite of these MW plasma advantages, there is an infinitesimal amount of research on its application in tars conversion. Moreover, these research studies were carried out in the atmosphere of air [25], nitrogen/argon [24] or nitrogen/steam [23] thus showing almost no resemblance to the real syngas composition. At the same time, it was proven that the MW plasma is an effective method of methane conversion by means of dry reforming and steam reforming [32–34]. Additionally, it was demonstrated that CO_2 dissociation and its reduction with hydrogen could be conducted in MW plasma reactors [29,35]. As it has been proven that MW plasma can strongly affect the interaction between CO_2, H_2, CH_4, and H_2O, it seems only logical that the next step should be an investigation of the tar conversion process in simulated syngas. To the authors' knowledge, none of such work has been done to date. Therefore, the goal of this work was to investigate a model tar compound conversion in the simulated syngas MW plasma. Not only the interactions between the major gas components (i.e. CO, CO_2, H_2, CH_4, and N_2) were studied, but also their influence on benzene decomposition.

2. Materials and methods

2.1. Experimental setup

The research was conducted with the use of a 3 kW (c.a. 1.8 kW of microwave power), 2.45 GHz microwave generator. The setup, typical for atmospheric microwave plasma device [32,33], was equipped with a circulator, a reflectometer, a waveguide and a movable plunger. Two tangential inlets allowed for the introduction of plasma agent/process

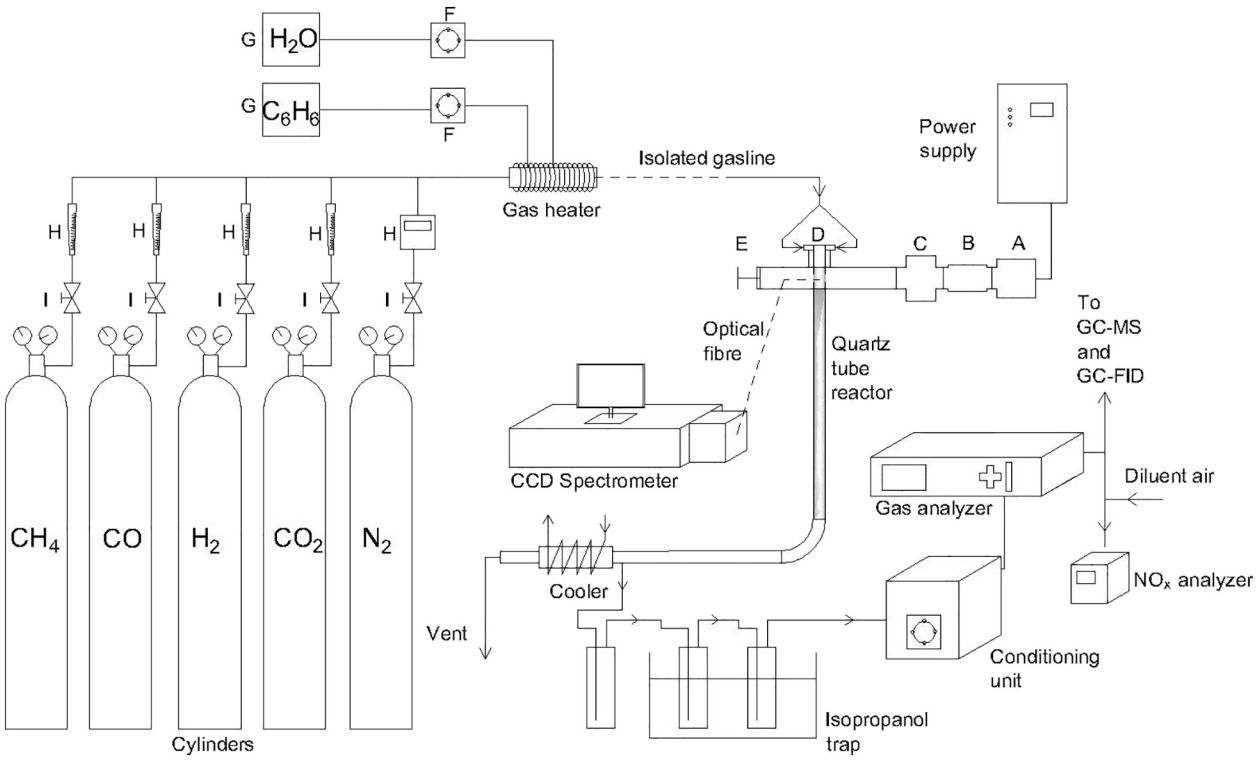

Fig. 1. Length of the microwave plasma discharge: (a) N_2, (b) N_2 and H_2 (c.a. 8.5%), (c) N_2 and CO (c.a. 8.5%), (d) N_2 and CO_2 (c.a. 13%).