Effect of process conditions on tar formation from thermal reactions of ethylene

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HIGHLIGHTS

- A mixture of tar compounds can be produced by thermal reactions of ethene.
- The amount of tar increases when pressure is increased from 1 to 3.5 bar.
- Also, the fraction of heavier tar compounds increased with pressure.
- Tar-laden product gas can be used in biomass gasification gas cleaning studies.

ARTICLE INFO

ABSTRACT

Thermal reactions of ethylene were studied to understand better the effect of process conditions on tar formation in biomass gasification. The effects of pressure, residence time and temperature on thermal reactions of ethylene were studied. The analysis of products from methane up to pyrene was performed by the novel online GC method. Ethylene conversion increased linearly as a function of pressure and residence time. Tar formation increased exponentially in the pressure range 1–3.5 bar and linearly with the residence time. The fraction of heavier tar compounds was found to increase with temperature and pressure. The tar composition was compared with different biomass gasification tar compositions, and the compositions were found to resemble each other. The obtained tar-laden product gas could be used as a realistic tar model when the cleaning of biomass gasification gas is studied.

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1. Introduction

Gasification of biomass is an efficient and versatile way to convert biomass into energy, fuels or chemicals. Biomass gasification is thereby one solution to help fulfil the renewable energy requirements set by various countries and reduce the dependency on fossil fuels. In order to be able to use biomass gasification gas in catalytic downstream processes or engines, the gas must be cleaned from impurities such as tar and particulates. Tar formation in the gasifier and purification of gasification gas from tar are a major concern because tar causes problems in downstream units through fouling, and soot and coke formation.

Gasification literature presents various definitions of tar and many ways to classify the tar compounds. One of the definitions is that tar is a biomass gasification product that is condensable downstream of the gasifier, and the compounds in tar are generally assumed to be primarily aromatic [1]. This definition is not very exact, thus, in the tar protocol [2], tar is defined as aromatic compounds that are heavier than benzene. This definition will be used in this study. Tar compounds can be classified by formation temperature into primary, secondary and tertiary tar, as has been done by, for example, Milne [1]. Primary tar consists of decomposition products of biomass, which are mostly oxygenated compounds [3,4]. Secondary and tertiary tars are formed by the reactions of primary tar and combinations of fragments of tar compounds [3]. Secondary tar consists of alkylated aromatic one- and two-ring compounds, including heteroaromatics [4]. Tertiary tar consists of aromatic hydrocarbons, such as benzene, naphthalene, phenanthrene, and other polyaromatic hydrocarbons (PAH) [1]. These compounds cannot be found from the source biomass. In tertiary

tar, the product range is also wide, from benzene to heavy aromatics [1]. Thus, other classifications have been used, such as classification based on the physical properties of tar compounds [5] or on the number of rings in a tar compound [3,6].

Gasification of biomass begins with pyrolysis vapour formation, and during gasification, oxygen in the molecules of woody biomass is released as CO and CO_2, and at the same time, radicals and small molecules are formed, reacting further to form aromatics [7]. Part of the oxygen in biomass is also bound to oxygenates, such as phenols. Few studies have been made of the thermal reactions of the primary tars formed in the pyrolysis phase. Lignin, the only part of the wood containing aromatic structures, has been believed to be responsible for tar formation [8]. However, Norinaga et al. [8] showed that tar can also be formed from cellulose even though cellulose does not contain aromatic structures. They studied secondary thermal reactions of primary pyrolysis products of cellulose in the temperature range 700–800 °C. Ethylene, benzene and toluene were formed, among other products. According to Palma [9], PAH compounds are formed by a direct combination of aromatic rings from lignin decomposition, by hydrogen abstraction acetylene addition (HACA) or by abstraction of CO from phenol forming a cyclopentadienyl radical, which reacts further to form PAH. Ledesma et al. [10] studied pyrolysis of eugenol, which represents primary tar formed from lignin. The major hydrocarbons formed in the pyrolysis of eugenol were ethylene and acetylene, and their yield increased with temperature. In addition, the influence of olefins and C_2–C_5 radicals on the formation of tar compounds in gasification is discussed in literature [1,11].

Reactions of hydrocarbon radicals are also discussed in studies related to combustion. These studies have concentrated on PAH and soot formation in flames [12]. There are also many studies related to chemical vapour deposition of carbon. Most of these studies have concentrated on carbon formation by pyrolysis of light hydrocarbons, and the initial reaction steps up to benzene have been modelled in detail [13–15]. Studies related to chemical vapour deposition of carbon have been conducted in conditions below atmospheric pressure. Fewer studies have concentrated on formation pathways for heavier aromatic compounds [16–18]. Shukla and Koshi [17,18] presented different radical mechanisms explaining radical aromatic growth: HACA (hydrogen abstraction and acetylene addition), HAVA (hydrogen abstraction and vinyl radical addition) mechanism, PAC (phenyl addition and cyclization) and MAC (methyl addition and cyclization).

High temperature zones do exist in gasification processes, for example the air/oxygen feed inlet areas in tar reformers (900–1100 °C), downdraft gasifier combustion zones (approx. 1200 °C), fluid bed gasifier freeboards (800–900 °C), etc. Reactor design and development for gasification applications therefore require deep understanding of tar and soot formation in these conditions as well as expertise in the effects of temperature and pressure. Considering tar and other hydrocarbons present in gasification, ethylene is the most abundant compound after methane, usually detected in the range 0.2–4 vol-% in dry gas [19–21]. Ethylene may form soot and tar compounds during hot gas cleaning steps, filtration and reforming.

Syntheses, such as Fischer–Tropsch and methanation, are usually pressurized, thus, pressurizing the gasification process would improve the economics of the whole concept. In biomass gasification literature, pressurised gasifier studies are available, although the effect of pressure on tar formation has not been studied systematically and the results are somewhat contradictory [4,22–25]. In addition, light hydrocarbon pyrolysis studies have been limited to atmospheric or below atmospheric pressure [15–18].

Consequently, the motivations of this study are twofold: (1) What role do the light hydrocarbons play in gasification conditions; can, for example, the residual PAH present in certain conditions in catalytic reforming be explained as being reaction products of the light hydrocarbons? (2) Can we produce proper model tar by thermal reactions of ethylene so that the product can be used as feed in, for example, filter-clogging studies?

2. Materials and methods

2.1. Experimental set-up

The experiments were conducted in a pressurised plug flow reactor system with a quartz reactor. The experimental set-up is illustrated in Fig. 1. The quartz reactor was sealed in a steel reactor that was in a three-zone furnace. The inner diameter of the quartz reactor was 1 or 1.5 cm, depending on the experimental conditions, with a thermocouple pocket of 0.4 cm in diameter in the centre of the reactor. The total length of the reactor was 45 cm. The thermocouple pocket was made of quartz and spanned from the top of the reactor to the bottom and covered the thermocouple completely. The temperature profile of the reactor was measured with a K-type thermocouple under nitrogen flow with an oven temperature of 950 °C. During the experiments, the temperature was measured from a single point, which was the maximum temperature point in the temperature profile measured under N_2.

The residence time was calculated according to the inlet volumetric flow rate at the measured reaction temperature for each experimental condition. The residence time was calculated for the length of the reactor where the temperature was over 900 °C in the temperature profile measured under N_2 flow. The length of the reactor used in the residence time calculation was 27 cm. This was chosen because at 900 °C the conversion of ethylene started to be significant also with short residence times. The temperature used in the result and residence time calculations is the measured reactor temperature.

During the experiments, the H_2 and CH_4 concentrations were followed with a continuous gas analyser. After the concentrations were stabilized, at least two samples with an online gas chromatograph were taken from each experimental condition. For some of the conditions, five samples were taken to check the stability of the system and the repeatability of the analysis. Typically, each experimental condition was maintained for 2–3 h. From time to time, the reactor and the lines were cleaned with a mixture of isopropanol and toluene, after any carbon formed on the quartz reactor walls was burned by air at 850 °C.

The gases were fed to the reactor by mass flow controllers. In all the experiments, the feed gas contained 5 vol-% of ethylene (Aga, 99.95%) in N_2 (Aga, 99.999%). According to Norinaga and Deutschmann [14], small amounts of impurities are important in the initiation of reactions. The impurities in ethylene were analysed to be 1 ppm of methane and 9 ppm of ethane.

2.2. Analysis of products

An online analysis of hydrocarbons from methane up to pyrene was made using an Agilent 7890A gas chromatograph equipped with one injector, two flame ionization detectors (FID) and three columns. The columns were Agilent GS – GASPRO (30 m × 0.32 mm ID, 0 μm film), HP – 5 (30 m × 0.32 mm ID, 0.25 μm film) and a restrictor column (3 m × 0.18 mm). The GS-GASPRO column was used to separate the hydrocarbons that elute before benzene, whereas the HP-5 was used for benzene and other aromatics. The gas was led to a sample loop of 0.25 ml in a six-port valve. From there, it was led to the HP-5 column and after that to the GS-GASPRO column and a FID. Just before benzene and heavier hydrocarbons were eluted from the HP-5 column, the direction of the gas flow was switched into the restrictor column instead of the