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Pyrolytic toluene conversion to benzene and coke over activated carbon in a fixed-bed reactor

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HIGHLIGHTS

- Toluene is pyrolysed in the presence of activated carbon.
- Over 90% toluene conversion is maintained for 20 min at 800 °C.
- Coke formation occurs above 800 °C and lasts until carbon surface saturation.
- Benzene and coke formation from toluene are found to be competing reactions.

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ABSTRACT

The catalytic decomposition of tar compounds is an important issue in the cleaning and upgrading of gasification product gases. This work focuses on toluene pyrolysis in a quartz tube reactor with a fixed bed of activated carbon. A toluene to benzene and coke conversion mechanism is also proposed. Liquid decomposition products were analysed with GC-FID. The ash content in the spent carbon was measured, allowing for the determination of coke deposit growth on the carbon surface. Pyrolysis runs were performed at temperatures ranging from 650 to 800 °C and with varying toluene feeding times. It was determined that toluene conversion is maintained above 90% for the first 20 min of pyrolysis at 800 °C. At this initial time, pronounced coking on the carbon surface was observed. Subsequently, toluene conversion decreased, coke deposition was hindered and benzene, a decomposition side product, yield was greatly enhanced. At lower temperatures coking is inhibited and toluene conversions were relatively low. For short, 10 min feeding times and at low temperatures, the benzene share of overall converted toluene is significant. The toluene to benzene conversion model, necessarily based on both experimental results and the literature, shows that coke and benzene creation are competing reactions.

1. Introduction

Biomass gasification is an important and rapidly developing renewable energy technology. One major obstacle is the substantial tar yield from the process. Produced tar causes clogging of pipelines of an installation and prevents the direct use of a producer gas in gas engine or turbines. Tar, created during gasification and removed in a course of syngas cleaning, can also contribute to the diminished efficiency of the process due to a substantial loss of carbon and hydrogen that could otherwise be converted to combustible gaseous species. Therefore various methods for tar cracking are being extensively studied to improve gasification performance [1,2]. Since the overall tar conversion process comprises a vast variety of thermochemical conversion pathways, decomposition of selected tar compounds is often studied experimentally [3,4].

Toluene as a model tar compound has been previously studied [3,5–7], although conversion over catalyst beds was usually performed in a slightly oxidative atmosphere (usually with steam) where reforming reactions of toluene and toluene derived coke might take place. Bhandari et al. [5] studied toluene pyrolysis over activated carbon and biochar in pure N_2 at 700 and 800 °C. Catalyst deactivation with time-on-stream was observed, as well as the creation of some gaseous products, such as CO_2, CO, H_2 and CH_4. They also reported a 25% and 85% decrease of biochar and activated carbon surface area, respectively, after a 4 h run.

Detailed toluene decomposition pathways were examined at higher temperatures and different pressures but with no catalyst

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present, e.g. in shock tubes [8–14]. The initial step of toluene conversion involves the formation of phenyl or benzyl radicals according to the reactions:

$$C_6H_5CH_3 = C_6H_5^{\cdot} + CH_3^{\cdot} \qquad (1)$$

$$C_6H_5CH_3 = C_6H_5CH_2^{\cdot} + H^{\cdot} \qquad (2)$$

Reactions 1 and 2 are reported to occur without catalyst presence at temperatures above 1000 °C [11,14], which are higher than reaction temperatures in the present work. Benzyl radicals are the main product of the decomposition and it was determined that they undergo further conversion to cyclopendadienyl radicals (c-C_5H_5) directly or through a fulvenallene intermediate (C_7H_6) [8,11,15,16]. c-C_5H_5 can consecutively decompose to a propargyl radical (C_3H_3). Acetylene is released as a side product of c-C_5H_5 to C_3H_3 and direct benzyl to c-C_5H_5 decomposition [11]. In these conditions, benzene is reported to be created mainly by hydrogen attack on the toluene molecule [11]:

$$C_6H_5CH_3 + H^{\cdot} = C_6H_6 + CH_3^{\cdot} \qquad (3)$$

Other possible pathways are a termination reaction of phenyl and hydrogen radicals as well as the rearrangement of two propargyl radicals [11]:

$$C_6H_5^{\cdot} + H^{\cdot} = C_6H_6 \qquad (4)$$

$$C_3H_3^{\cdot} + C_3H_3^{\cdot} = C_6H_6 \qquad (5)$$

Since most of the tar decomposition reactions have a radical mechanism, the presence of radical sources strongly affects hydrocarbon conversion. It was reported by Zimmerman and York [17], that in the excess of hydrogen, toluene demethylation to benzene can undergo with efficiency as high as 95%. Moreover, addition of n-heptane to the reaction environment enhanced dealkylation, probably by increasing the amount of free radicals in the gas phase [17]. Lea-Langton et al. [18] studied demethylation of ^{13}C-labeled methyl groups from aromatic hydrocarbons. They reported some methyl groups leaving the studied compounds at mild conditions, while little or no changes to the aromatic ring structures were observed.

Even without a catalyst present, some coke formation has been observed in high temperature experiments in shock tubes as well as in acetylene flames [9,11,19]. It is ascribed to the three most plausible mechanisms, namely: hydrogen abstraction – C_2H_2 addition (HACA) [20], cyclopentadienyl radical recombination (CPDR) and phenyl addition/cyclisation (PAC) [13]. PAHs and consequently soot formation through acetylene addition is the most common mechanism in acetylene flames at high temperatures [19]. During aromatic hydrocarbons conversion it might take place as well due to the C_2H_2 being created as a side-product [12]. However, the PAC mechanism was reported to be a dominant one in toluene/benzene pyrolysis, because of the observed increase in PAH molecules with increments of 74 mass units (resulting from phenyl addition, H atom elimination and cyclisation) as well as the rate of soot formation being too large to be ascribed solely to the HACA mechanism [13]. Cyclopentadienyl radical rearrangement is also believed to take place, during the later steps of PAH growth [13].

Coke deposition on catalysts during hydrocarbon thermal processing, like cracking or alkylation, is a common issue in the chemical industry [21–27]. Aluminosilicate materials like zeolites are common catalysts in hydrocarbon chemistry, due to their well-defined pore structure and versatile acidity. Properties of the coke retained in zeolite pores are proved to be highly dependent on the reaction temperature and catalyst structure [22,28–31]. Coking properties of different hydrocarbons were studied extensively over different zeolite types [28,32,33]. Generally, at lower temperatures (~150 °C) coke is comprised of derivatives of the hydrocarbon feedstock and is retained in the zeolite pores partially because of the large coke molecule sizes but mainly due to the low volatility of the coke compounds [28]. At higher temperatures (above 350 °C), the boiling point of coke species is lower than the reaction temperature, therefore compounds are retained within the zeolite mostly because their growth is fast enough for them to reach molecule sizes larger than the zeolite pores and therefore they become trapped within the zeolite structure [28,29]. The initial hydrocarbon decomposition starts over acidic sites or metals on the surface of the catalyst. For acid catalysts, the coking process starts with hydrogen transfer, while for bifunctional catalysts it is initialised, most likely, through a dehydrogenation step on surface metals. Since activated carbons have both functional groups and AAEM species on their surfaces [3,34–36], it is expected that either of the initialisation pathways can occur. Further reactions in the activated carbon pores involve condensation and rearrangement of the molecules. In reported experiments, the coking mechanism involves ion creation, such as in the case of toluene, where a benzenium ion is created [28,29]. The tests performed in this study were carried out at much higher temperatures, therefore it is expected that toluene decomposition and coke creation are radical reactions [37].

The nature of the coke derived at temperatures higher than 350 °C is reported to be independent of the native feedstock molecule and highly correlated to zeolite pore structure and size. Coke molecule size increases with time-on-stream or retention time as a result of further rearrangement reactions [24,28,29]. Therefore, the coke derived from toluene pyrolysis at temperatures above 800 °C is expected to consist mainly of heavy particles insoluble in organic solvents with sizes and shapes corresponding to the activated carbon pores. Since activated carbon pore sizes are larger than that of zeolites [5,22,38–40], limitations of coke molecule growth in this case might be less significant.

So far, detailed toluene decomposition mechanisms have been extensively studied in the presence of zeolites at relatively low temperatures as well as in an empty reactor at temperatures higher than the values typical for a fixed-bed gasifier. This paper is dedicated to addressing this gap in the literature by studying toluene decomposition pathways at moderate temperatures in the range of 600–800 °C with a presence of an activated carbon catalyst. Time-on-stream impact on carbon deactivation, coke deposition and benzene creation are also examined. All runs are performed in an inert nitrogen atmosphere. A toluene to benzene and coke conversion mechanism is also proposed.

2. Experimental

Experiments with toluene conversion over activated carbon (AC) were performed in a laboratory quartz tube reactor. Different feeding times and temperatures were applied to study the performance of AC in an inert atmosphere, where no steam or CO_2 reforming occurs. Unreacted toluene, as well as any liquid conversion products, were analysed by GC-FID. The ash content in spent AC samples was analysed allowing for the detection of any toluene that may have coked on the carbon surface.

2.1. Materials

The catalytic material utilised in this work was a coal-derived activated carbon AC (BG 09 from CBF Vendor AB, Sweden) with particle sizes in a ranging from 0.4 to 0.85 mm and a surface area of 1000–1100 m^2/g. Elemental and ash compositions are reported in Tables 1 and 2, respectively.

As a representative of tar compounds, 99.5% toluene from POCH S.A (Avantor Performance Materials) was used. For GC calibration