



Detailed kinetic study of anisole pyrolysis and oxidation to understand tar formation during biomass combustion and gasification



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ABSTRACT

Anisole was chosen as the simplest surrogate for primary tar from lignin pyrolysis to study the gas-phase chemistry of methoxyphenol conversion. Methoxyphenols are one of the main precursors of PAH and soot in biomass combustion and gasification. These reactions are of paramount importance for the atmospheric environment, to mitigate emissions from wood combustion, and for reducing tar formation during gasification. Anisole pyrolysis and stoichiometric oxidation were studied in a jet-stirred reactor (673–1173 K, residence time 2 s, 800 Torr (106.7 kPa), under dilute conditions) coupled with gas chromatography–flame ionization detector and mass spectrometry. Decomposition of anisole starts at 750 K and a conversion degree of 50% is obtained at about 850 K under both studied conditions. The main products of reaction vary with temperature and are phenol, methane, carbon monoxide, benzene, and hydrogen. A detailed kinetic model (303 species, 1922 reactions) based on a combustion model for light aromatic compounds has been extended to anisole. The model predicts the conversion of anisole and the formation of the main products well. The reaction flux analyses show that anisole decomposes mainly to phenoxy and methyl radicals in both pyrolysis and oxidation conditions. The decomposition of phenoxy radicals is the main source of cyclopentadienyl radicals, which are the main precursor of naphthalene and heavier PAH in these conditions.

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1. Introduction

Environmental concerns such as the control of greenhouse gas emissions have led to an increased interest in the use of renewable energy. Biomass is widely used in combustion but can also be utilized in more advanced applications such as the production of a synthesis gas (syngas, a mixture of CO and H₂), which can be used for the production of liquid fuels such as Fisher–Tropsch or methanol. Lignocellulosic biomass may be a promising feedstock through the gasification processes [1,2], but tar is also formed during gasification [3]. The tar content in the product gas is the major cumbersome and problematic parameter in the gasification processes [4]. Tar represents a complex mixture of over 100 compounds [5,6]. It leads to fouling, coke deposition, and catalyst deactivation. Hence, tar conversion or removal is one of the main challenges for the successful development of commercial gasification technologies and has been extensively studied [7,8].

Evans and Milne [5] defined three main classes of tars: primary tars (low temperature, oxygenated) and secondary and tertiary tars (benzene, polycyclic aromatic hydrocarbons—PAHs, etc.). In combustion and gasification reactors, the heaviest (tertiary) tars are

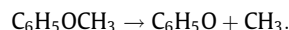
formed by the conversion of primary tars, for instance, in the free-board or emulsion phase of a fluidized bed or in the flame during combustion. A better understanding of the detailed gas-phase chemistry leading from primary tars to secondary and tertiary ones is needed. The aim of this work is to deeply understand these reactions under conditions representative of biomass gasification in air-blown fluidized beds, but also PAH formation in wood combustion furnaces [9]. A significant fraction of aromatic tars and soot originates from lignin pyrolysis products mainly composed of guaiacol-type and syringol-type units [5,10–12]. Carbohydrates from cellulose and hemicellulose can also contribute to aromatic formation through the production of light unsaturated species such as acetylene and propargyl radicals [5,13,14]. The simplest aromatic model compound with a methyl ether unit, which is anisole, has been chosen as a surrogate for lignin primary tar, as a first step toward developing an advanced elementary kinetic model including major primary tar surrogates.

To date, there have been very few works on tar gas-phase conversion coupling well-controlled experiments, tar quantitative analysis, and elementary modeling, especially concerning anisole. Earlier experiments for anisole pyrolysis were performed in a stirred-flow reactor by Mulcahy et al. [15], who reported that reactions between methyl radicals and anisole proceed mainly by H-abstraction on the methoxy group, which is about 12 times faster

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than the attack on the aromatic ring. A mechanism for the formation of the main identified products (benzaldehyde, toluene, and methane) was also proposed. During the 1980s, Schlosberg et al. [16] quantified 10 products of anisole decomposition after a 2-min pyrolysis at 723 K. A shock tube study of the decomposition of anisole between 1000 and 1580 K and at pressures from 0.4 to 0.9 atm permitted an evaluation of the rate constant of the unimolecular decomposition of phenoxy radicals (C_6H_5O) to CO and C_5H_5 and of the reaction of methyl radicals with phenoxy to form cresols [17]. Mackie et al. [18] studied the pyrolysis of anisole in a perfectly stirred reactor over the temperature range 850–1000 K and at low pressure (between 16 and 120×10^{-3} atm). The yields of the main products (CH_4 , C_2H_6 , C_6H_5OH , methylcyclopentadiene, CO, cresols, benzene, and benzaldehyde) as functions of temperature at two residence times (0.14 and 0.95 s) were reported and a rate constant was proposed for the unimolecular decomposition of anisole:



Rate parameters were $A = (2.9 \pm 1.0) \times 10^{15} s^{-1}$ and $E_a = 64.0 \pm 0.6$ kcal/mol. Arends et al. [19] studied the thermal decomposition of anisole in an excess of hydrogen in a flow reactor over the temperature range 793–1020 K and at atmospheric pressure. The main identified products were similar to those found in previous studies. A first kinetic model for anisole decomposition was proposed, which was composed of 37 reactions involving 23 species. However, some assumptions on the rate constant were made to obtain good agreement with experimental results. Pecullan et al. [20] presented the first study on anisole oxidation. Experiments near 1000 K were performed in the Princeton flow reactor and made it possible to observe that anisole undergoes first-order decay under both pyrolysis and oxidation conditions. It was proved also that under the studied conditions, the distribution of reaction products such as phenol, cresols, methane, and ethane was independent of the equivalence ratio. A new kinetic model was proposed, consisting of 66 reversible reactions involving 31 species. A good prediction of experimental data was reached for anisole, carbon monoxide, methylcyclopentadiene, and total phenolic compounds. More recently, Platonov et al. [21] showed the formation of various decomposition products, including PAHs, during the pyrolysis of anisole at high temperature (1023–1173 K). Friderichsen et al. [22] used a hyperthermal nozzle and a flow tube reactor followed by analysis by mass spectrometry and FTIR spectroscopy. Phenoxy and cyclopentadienyl radicals were found to be important intermediates in the decomposition of anisole. In addition, the identification of 9,10-dihydrofulvalene suggested that this molecule can be considered as a naphthalene precursor ($2 C_5H_5 \rightarrow 9,10$ -dihydrofulvalene \rightarrow naphthalene). To observe radical intermediates, Scheer et al. [23,24] used a hyperthermal tubular flow reactor with about 65 μs residence time. Their results confirm that the first step in the decomposition of anisole is the loss of the methyl group to form a phenoxy radical, followed by the ejection of CO to yield a cyclopentadienyl radical. They showed also that C_5H_5 decomposes to the propargyl radical (CH_2CCH) and acetylene only at high temperature (>1373 K). Afterward, propargyl radical recombination is a significant benzene formation channel. At lower temperatures, most of benzene comes from a ring expansion reaction of methylcyclopentadiene (MCPD), resulting from methyl radicals combining with cyclopentadienyl radicals. Naphthalene formation was attributed also to cyclopentadienyl radical combination. The most recent paper dealing with anisole [25] proposed a new kinetic mechanism validated against experimental data from Pecullan et al. [20] and Platonov et al. [21]. The literature review shows that anisole is a fragile compound, which reacts easily by unimolecular O–CH₃ bond breaking, which leads to methyl and phenoxy radicals. This is consistent with the bond dissociation energies [26,27] involved in anisole and presented in Fig. 1.

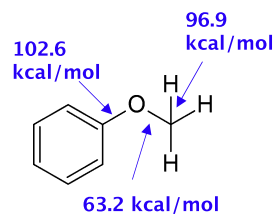


Fig. 1. Structure of anisole and bond dissociation energies.

To the best of our knowledge and despite all these extensive works, there is not yet a detailed kinetic mechanism for anisole pyrolysis and oxidation validated against well-controlled thermal conditions with quantitative analysis of products. Moreover, while the very low value of the C–O bond dissociation energy allows easy decomposition, most studies have been performed at temperatures higher than 1000 K, i.e., higher than that involved in biomass pyrolysis/gasification where primary tars are formed. The present work aims at investigating experimentally and theoretically the kinetics of anisole pyrolysis and oxidation at intermediate temperatures (673–1173 K) and to predict the formation of intermediates leading to secondary and tertiary tars, such as PAHs.

2. Experimental methods

The experimental study was performed in a jet-stirred reactor operated at constant temperature and pressure. The experimental apparatus has already been used for numerous pyrolysis and oxidation gas phase studies. Its description can be found in previous papers [28,29]. The main features of the experimental and analytical methods are described below. It has been shown that under the present conditions, this reactor can be considered as a zero-dimensional ideal perfectly stirred reactor with homogenous temperature and composition. The jet-stirred reactor (Fig. 2) is made of fused silica and consists of an annular preheater and of a sphere in which the reaction takes place, with an injection cross located at the center. The reactor (volume 88 cm³) and the injection cross were designed to obtain four turbulent jets, providing good mixing of the gas phase [30]. The heating of the preheater and of the reactor is achieved by the mean of Thermocoax resistances rolled around the different parts and controlled by Eurotherm 3216 controllers and type K thermocouples (temperature precision better than 1%). The heating of the preheater is divided into two zones, the first one heated at a temperature 150 K lower than the reaction temperature and the second one being heated at the same temperature as the reactor. The reaction temperature was measured by another type K thermocouple located in the intra-annular part of the preheater, with its extremity at the level of the injection cross in the center of the reactor.

The feed of liquid anisole (Sigma Aldrich, purity 99.7%) was controlled by a Coriolis mass flow controller (Bronkhorst). This device was associated with an evaporator in which anisole was mixed with the carrier gas (helium IC or argon 5.0, Messer) and heated to 473 K. The carrier gas flow rate was controlled by a gas mass flow controller (Bronkhorst). The precision of the mass flow controllers is 0.5%. The carrier gas for experiments was helium. A set of experiments was also performed with argon to enable the quantification of hydrogen. The pressure in the reactor was kept constant at 800 Torr (106.7 kPa) using a valve located downstream of the reactor. The residence time of anisole was 2 s for both pyrolysis and oxidation studies.

Unconverted reactant and products were analyzed by means of several gas chromatographs (GC). For pyrolysis studies, the analysis was performed in two steps, as light and heavy species could not be analyzed at the same time. Heavy species (including more

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