# Experimental and modeling studies of a biofuel surrogate compound: laminar burning velocities and jet-stirred reactor measurements of anisole☆

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## ABSTRACT

Lignocellulosic biomass is a promising alternative fuel source which can promote energy security, reduce greenhouse gas emissions, and minimize fuel consumption when paired with advanced combustion strategies. Pyrolysis is used to convert lignocellulosic biomass into a complex mixture of phenolic-rich species that can be used in a transportation fuel. Anisole (or methoxybenzene) can be used as a surrogate to represent these phenolic-rich species. Anisole also has attractive properties as a fuel component for use in advanced spark-ignition engines because of its high blending research octane number of 120. Presented in the current work are new measurements of laminar burning velocities, jet-stirred reactor (JSR) speciation of anisole/$O_2$/$N_2$ mixtures, and the development and validation of a detailed chemical kinetic mechanism for anisole. Homogeneous, steady state, fixed gas temperature, perfectly stirred reactor CHEMKIN simulations were used to validate the mechanism against the current JSR measurements and published JSR experiments from CNRS-Nancy. Pyrolysis and oxidation simulations were based on the experimental reactant compositions and thermodynamic state conditions including $P = 1$ bar and $T = 675$–$1275$ K. The oxidation compositions studied in this work span fuel-lean ($\phi = 0.5$), stoichiometric, and fuel rich ($\phi = 2.0$) equivalence ratios. Laminar burning velocities were measured on a heat flux stabilized burner at an unburnt $T = 358$ K, $P = 1$ bar and simulated using the CHEMKIN premixed laminar flame speed module. Ignition delay times of anisole were then simulated at conditions relevant to advanced combustion strategies. Current laminar burning velocity measurements and predicted ignition delay times were compared to gasoline components (e.g., n-heptane, iso-octane, and toluene) and gasoline surrogates to highlight differences and similarities in behavior. Reaction path analysis and sensitivity analysis were used to explain the pathways relevant to the current studies. Under pyrolysis and oxidative conditions, unimolecular decomposition of anisole to phenoxy radicals and methyl radicals was found to be important due to the relatively low bond strength between the oxygen and methyl group, ~65 kcal/mol. Reactions of these abundant phenoxy radicals with $O_2$ were found to be critical to accurately reproduce anisole's reactivity.

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# 1. Introduction

For decades, scientists and engineers have sought to better understand, and possibly return to, one of the earliest techniques for energy conversion – combustion of biomass. Biomass based combustion offers promises of a self-replenishing energy source and domestic energy security for nations, particularly through the development of "second" or even "third" generation biofuels which aim to mitigate environmental and social concerns [1,2]. Further, the properties of biomass derived fuels coupled with advanced combustion strategies may provide greater opportunities to comply with regulations for reduced greenhouse gas emissions and higher fuel economies relative to conventional gasoline and diesel fuels.

Generally, biomass can be broadly categorized as containing three polymers: lignin, hemicellulose, and cellulose. Lignin can compromise on the order of 30% by weight of biomass [3,4] and is a source complementary with agricultural processes generating food. Current and potential future applications of lignin derived compounds include fuels, carbon black substitutes, resins, antioxidants, dispersants, and emulsifiers [5]. A characteristic sub-structure of a lignin polymer is shown in Fig. 1, and contains groups such as phenyl, hydroxyl, propyl, and methoxy. Anisole, or methoxybenzene, is considered to be a potential surrogate compound for lignocellulosic biomass pyrolysis and combustion. Among its features, anisole has favorable combustion properties for gasoline modes of operation including a high blending research octane number (bRON 120 at 10% volume anisole), low blending motored octane number (bMON 98 at 10% volume anisole), density (0.995 kg/L), and moderate net heating value (33.2 MJ/L) [6,7]. A particularly weak bond, approximately 63 kcal mol$^{-1}$, is present in anisole between the oxygen and methyl group which leads to the rapid formation of large quantities of the phenoxy radical [8]. Therefore, studying anisole can also provide valuable insights into the phenoxy radical, which is an important surrogate for intermediates in the oxidation of other aromatics found in conventional gasoline and diesel fuels.

Previous studies include results from engines, shock tubes, reactors, theoretical calculations, and other devices [6–28] with an emphasis on the pyrolysis pathways of anisole. Notably, ignition delay time measurements are limited to a recent ignition quality tester study [28] and there has been one previous laminar burning velocity study [29] to the authors' knowledge. However, there have been several efforts to understand the initial decomposition step during the pyrolysis of anisole. Lin and Lin [14] measured carbon monoxide formation by laser absorption in a shock tube over high temperature (1000–1580 K) and low pressure (0.4–0.9 atm) conditions to determine the unimolecular decomposition rate, R1, of anisole.

$$C_6H_5OCH_3 \rightarrow C_6H_5O + CH_3 \qquad (R1)$$

In their evaluation of the rate, Mackie et al. [13] measured intermediate compounds from a stirred reactor with gas chromatography–mass spectrometry (GS–MS) techniques over complementary t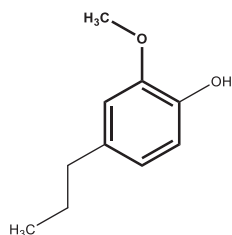emperatures (850–1000 K) and very low pressures (0.02–0.12 atm). The outlet gas of a quartz flow cell at very low pressure ($< 2 \times 10^{-3}$ atm) was analyzed by mass spectrometry in the work of Suryan et al. [15] to measure apparent rate constants for the unimolecular decomposition of anisole and coupled with a Rice–Ramsperger–Kassel–Marcus (RRKM) simulation tool to compute high-pressure limit rate constants. Arends et al. [16] operated two flow reactors to determine a rate for R1, relying on analysis of pyrolysis product measurements by flame ionization (GC-FID) and GS-MS. These works and others significantly aided in the studies to follow on the oxidation of anisole by highlighting the weak bond between the phenoxy and methyl group that dominates pyrolysis and the resulting pathways that lead to the major intermediates methane, phenoxy, phenol, and cresols [8].

Steps toward understanding anisole oxidation kinetics have been slower, with important experimental and kinetic modeling work by Nowakowska et al [8], Hemings et al. [12], and Pecullan et al. [17] among others. Using an atmospheric flow reactor, Pecullan et al. [17] pyrolyzed and oxidized anisole while measuring the stable intermediates up to 10 carbon atoms with GC–MS and GC-FID. A kinetic mechanism was developed by Hemings et al. [12] and validated against literature experimental studies of anisole pyrolysis and oxidation. Recently, Nowakowska et al. developed a kinetic mechanism from their dilute pyrolysis and stoichiometric oxidation jet-stirred reactor experiments at near atmospheric pressure through analysis of stable intermediates quantified by GC-FID, GC-MS, and gas chromatography coupled thermal conductivity detectors (TCD) [8]. These oxidation studies of anisole have shown that the decomposition of anisole to phenoxy and methyl radicals remains a nearly first-order process leading to many stable intermediates concentrations that vary minimally with equivalence ratio [8,12,17].

These previous studies laid the foundation for the current work. This study provides new atmospheric laminar burning velocity measurements in air over a range of stoichiometries, new stable intermediate species measurements from a jet-stirred reactor over several equivalence ratios at atmospheric pressure, and a new detailed chemical kinetic mechanism for the pyrolysis and oxidation of anisole.

# 2. Experimental methods

## 2.1. CNRS-Orleans jet-stirred reactor

The oxidation of anisole (CAS n° 100-66-3, provided by Sigma-Aldrich, purity: 99.7%) was studied in a fused silica jet-stirred reactor at atmospheric pressure and temperatures ranging from 770 to 1250 K for 3 different mixtures (fuel-lean, stoichiometric, and fuel-rich). The residence time and fuel mole fraction were held constant at respectively 70 ms and 1000 ppm while $O_2$ was used as oxidizer and $N_2$ as diluent. A HPLC pump was used to bring the liquid fuel to an in-house vaporizing system: the fuel was first atomized passing through a thin hole and the resulting spray was vaporized by heated grids. The flow was then brought to the reactor through a quartz capillary while the oxidizing mixture flowed separately to avoid premature reactions before the reactor. The two flows were then introduced inside the reactor by four nozzles that generated high turbulence, resulting in a fast and perfect mixing. The reactor was heated by two furnaces and the temperature was continuously monitored by a Pt/Pt-Rh thermocouple located inside the reactor. This thermocouple was inserted into a thin wall fused silica tube to avoid catalytic reactions on the metallic wires. Samples were taken from the reactor by a low pressure sonic probe to freeze any chemical reactions. Samples then flowed through heated lines to an online Fourier Transform InfraRed spectrometer (FTIR) for the analysis of $H_2O$, $CO_2$, CO and $CH_2O$, or to low pressure Pyrex bulbs for further off-line analysis by GC/FID, TCD or MS. These later analyses



**Fig. 1.** A characteristic sub-structure of lignin polymers found in biomass. The atoms and bonds forming anisole (methoxybenzene) are bolded.