



Comparative experimental and modeling study of the low- to moderate-temperature oxidation chemistry of 2,5-dimethylfuran, 2-methylfuran, and furan



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ABSTRACT

The reaction chemistry of furanic fuels, proposed as next-generation bio-derived fuels, has been a target of recent studies. However, quantitative intermediate species profiles at low- to moderate-temperature (LMT) conditions remain scarce. The present paper reports the first systematic full speciation dataset in the temperature range 730–1170 K for three furanic fuels, 2,5-dimethylfuran (DMF), 2-methylfuran (MF), and furan, measured for different equivalence ratios under near-identical LMT conditions in a flow reactor at 1 bar. More than 35 species including reactants, intermediate species, and products were analyzed using electron ionization (EI) molecular-beam mass spectrometry (MBMS). These experimental results provided motivation to extend a previous single joint mechanism for the three furanic fuels, developed for the high-temperature regime in low-pressure premixed flames, to include the LMT oxidation chemistry. A decisive difference of the present mechanism *versus* all previously reported models is a more complete description of fuel radical reactions for LMT oxidation, obtained from theoretical calculations of thermodynamic properties and rate constants.

The experimentally observed differences in fuel conversion behavior and species distribution between the three fuels have been compared to model predictions using the newly extended mechanism. The dependence of fuel conversion on equivalence ratio decreases significantly from DMF to furan, a behavior consistent with the different number of lateral methyl groups in the fuel structure. All three furanic fuels, especially DMF, produce several highly toxic oxygenated species including acrolein, methyl vinyl ketone, furfural, and phenol. These toxic species were found to be products of the primary reactions of these fuels, and these undesirable trends could be explained satisfactorily by the present model, pointing to some caution with regard to the potential emission spectra under LMT conditions.

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1. Introduction

Saturated and unsaturated cyclic ethers such as the derivatives of tetrahydrofuran (THF) and furan, respectively, are being proposed as alternative fuels [1–6]. They are potentially accessible from cellulosic biomass [7–9]. Their properties, including high octane numbers, make them desirable for spark-ignition applications [2–4,6]. Also, these fuels have recently been used as additives for diesel engines [1,5,10,11]. 2-Methyl-THF in blending

with *n*-dibutylether (70%/30% by volume) was found to almost entirely reduce particle emissions from a diesel engine [1]. Furan derivatives showed a superior soot reduction potential compared to *n*-butanol, *n*-heptane, cetanes, and gasoline in blends with diesel fuel [5,10,11]. Because of the presence of double bonds, unsaturated cyclic ethers exhibit a very different oxidation behavior from saturated cyclic ethers [6,12–14]. Furthermore, while some THF derivatives show a negative-temperature-coefficient (NTC) behavior, the latter has not been observed for furans [14–17]. The present paper focusses on the oxidation chemistry of the three *unsaturated cyclic ethers* of the furan family, *i.e.* 2,5-dimethylfuran (DMF), 2-methylfuran (MF), and furan, here called "furanic". Therefore, the following discussions will address only these fuels.

Considerable interest has been devoted to the high-temperature (HT) oxidation chemistry of furanic fuels, *e.g.*, reporting premixed

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Table 1
Main experimental studies of the LMT oxidation chemistry of DMF, MF, and furan.

Fuel	Reactor	T (K)	P (bar)	ϕ	Year & Ref.
DMF	Jet-stirred reactor (species profiles)	530–1190	10	0.5–2	2013 [17]
	Flow reactor (species profiles)	500–1400	1, 20, 40	0.03–3.33	2014 [32], 2015 [33]
	Shock tube (ignition delay times)	820–1210	20, 80	1	2013 [17]
	Rapid compression machine (ignition delay times)	737–1143	16, 30	0.5–2	2016 [30]
MF	Flow reactor (species profiles)	800–1400	1	0.02–3.33	2016 [34]
	Rapid compression machine (ignition delay times)	737–1143	16, 30	1	2016 [30]
	Shock tube (ignition delay times)	820–1215	40	1	2014 [14]
Furan	Jet-stirred reactor (species profiles)	1000–1300	1	–	1988 [31]

flame speciation [18–23], shock tube ignition [17,24–27], and flame speed [17,27] experiments as well as model developments [17–19,24,28]. Xu et al. [29] have recently presented an overview of such studies. Only limited work has addressed, however, the low- to moderate-temperature (LMT) oxidation of these fuels, as summarized in Table 1. Global properties such as LMT ignition delay times for DMF and MF were recently obtained in shock tubes and a rapid compression machine (RCM) [14,17,30]. These studies reported a complicated dependence of the relative reactivity on the fuel's molecular structure and on operating conditions [30]. More detailed information on the combustion chemistry including species profiles is quite scarce. Somers et al. [17] measured oxidation species profiles for DMF in a high-pressure jet-stirred reactor (JSR) at 530–1190 K. The early work of Thorton et al. [31] provided JSR data for furan at 1000–1300 K but did not include the mole fraction profile of acrolein, a crucial intermediate of furan oxidation. Limited species data have been reported from flow reactor experiments for DMF [32,33] and MF [34] that focused on soot formation or on interaction with nitric oxide; fuel-specific intermediates were not provided. Similar to the sparse experimental investigations, the modeling effort for LMT oxidation of the furanics has also been quite limited. Davis and Sarathy [35] have studied OH-addition to the furan ring and Waddington-type reactions; they noted a dominant role of the ring opening reaction of the radical produced from OH-addition to the furan ring. Somers et al. [17] proposed a DMF mechanism that includes a treatment of some important reactions under LMT conditions. Some of these reactions such as OH-addition on DMF and H-abstractions from DMF by HO₂ were investigated using theoretical calculation methods, whereas rate constants of other important reactions such as H-abstractions from DMF by O₂ and reactions of the fuel radical with O₂, HO₂, and CH₃O₂ were still estimated at the high-pressure limit under omission of details. Xu et al. [30] suggested some modifications to the latest release of the Somers et al. model [28] by simply increasing or decreasing rate constants of some reactions to reach a reasonable agreement between model predictions and their RCM ignition delay time data of MF and DMF, an approach that cannot provide further fundamental insight.

To the best of our knowledge, no experiment to date has addressed the quantification of species for the three unsaturated cyclic ethers furan, MF, and DMF, under identical LMT oxidation conditions. Such quantitative data is known to be very useful to analyze and understand details of the reaction mechanism in this technically relevant temperature regime. For an improved insight into the LMT chemistry of these three furanic fuels, we have thus experimentally and numerically studied their oxidation systematically under near-identical conditions at different stoichiometries.

The paper structure is organized as follows. First, the methodologies will be described in Section 2. This section includes a description of the experimental setup (Section 2.1), the methods used in the kinetic model development (Section 2.2), as well as theoretical calculation (Section 2.3) and simulation methods (Section 2.4). Next, the results will be presented and discussed in Section 3. This section includes firstly results from the theoretical

calculations and the model construction (Section 3.1), and secondly experimental results presented and discussed intertwined with the model predictions (Section 3.2). In the latter section, the fuel conversion will be described in Section 3.2.1, fuel-specific intermediate species in Section 3.2.2, and then comparisons of the formation of potential pollutants between three furanic fuels, and between flow reactor and flame in Section 3.2.3. Finally, a summary of the main results obtained in the present work and perspectives will be presented in Section 4.

2. Methodologies

2.1. Experiment

The oxidation of the three fuels was investigated in a laminar flow reactor at 1 bar for 9 fuel/O₂/Ar mixtures with a total flow rate of ~1.0 standard liters per minute (SLM) for three equivalence ratios ($\phi \sim 0.5$, ~ 1.0 , ~ 2.0). Experimental conditions are summarized in Table 2. The experimental setup including both, reactor and mass spectrometer has been described in detail in [36–38]. The flow reactor is a fused silica tube (8 mm inner diameter, 830 mm length) that can be heated to a set temperature; it features three independent heating sections of approximately 300, 200, and 200 mm length, each monitored by a Ni–Cr/Ni thermocouple. Temperature profiles along the reactor's centerline were determined in a flow of 1 SLM pure argon for different set temperatures using a Ni–Cr/Ni thermocouple. The error in the maximum value of each temperature profile was estimated to be within 5%. However, this uncertainty for a given temperature is identical for all measured mixtures and therefore, a relative comparison of trends between the mixtures can be performed with significantly higher precision.

The flow reactor was coupled to an electron ionization molecular-beam mass spectrometer (EI-MBMS). The gases were sampled at the reactor outlet via a quartz nozzle (~50 μ m orifice diameter) and expanded into the 1st pumping stage, pumped to 10⁻⁴ mbar by a turbo-molecular pump. The formed molecular beam was further sampled by a copper skimmer at the 2nd pumping stage, and then extracted to the ionization chamber (<10⁻⁶ mbar). Chemical species were ionized with an electron beam of 20 eV generated by a hot-wire ionizer and accelerated into the reflectron time-of-flight (TOF) mass spectrometer (Kaesdorf) [37] with a mass resolution of $m/\Delta m \sim 2300$ to separate the ions by their different masses. A multichannel plate was used for detection.

The premixed gas mixtures of different equivalence ratios contained 84–96% Ar to limit self-sustaining combustion. Liquid fuels (>99%) were supplied using a syringe pump and evaporated at 393 K. Gas flow rates were metered by calibrated mass flow controllers. The gas composition was determined as a function of the reactor temperature with temperature steps of 5–6 K. The mole fraction evaluation from the obtained EI-MBMS data was then performed according to the procedures in [37,38]. The cross section of the expected dominant isomer was used for the mole

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