



Combustion chemistry and flame structure of furan group biofuels using molecular-beam mass spectrometry and gas chromatography – Part III: 2,5-Dimethylfuran



Casimir Togbé^a, Luc-Sy Tran^b, Dong Liu^a, Daniel Felsmann^a, Patrick Oßwald^{a,1},
Pierre-Alexandre Glaude^b, Baptiste Sirjean^b, René Fournet^b, Frédérique Battin-Leclerc^{b,*},
Katharina Kohse-Höinghaus^{a,*}

^a Department of Chemistry, Bielefeld University, Universitätsstraße 25, D-33615 Bielefeld, Germany

^b Laboratoire Réactions et Génie des Procédés (LRGP), CNRS, Université de Lorraine, ENSIC, 1 rue Grandville, BP 20451, 54001 Nancy Cedex, France

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ABSTRACT

This work is the third part of a study focusing on the combustion chemistry and flame structure of furan and selected alkylated derivatives, i.e. furan in Part I, 2-methylfuran (MF) in Part II, and 2,5-dimethylfuran (DMF) in the present work. Two premixed low-pressure (20 and 40 mbar) flat argon-diluted (50%) flames of DMF were studied with electron-ionization molecular-beam mass spectrometry (EI-MBMS) and gas chromatography (GC) under two equivalence ratios ($\phi = 1.0$ and 1.7). Mole fractions of reactants, products, and stable and radical intermediates were measured as a function of the distance to the burner. Kinetic modeling was performed using a reaction mechanism that was further developed in the present series, including Part I and Part II. A reasonable agreement between the present experimental results and the simulation is observed. The main reaction pathways of DMF consumption were derived from a reaction flow analysis. Also, a comparison of the key features for the three flames is presented, as well as a comparison between these flames of furanic compounds and those of other fuels. An a priori surprising ability of DMF to form soot precursors (e.g. 1,3-cyclopentadiene or benzene) compared to less substituted furans and to other fuels has been experimentally observed and is well explained in the model.

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1. Introduction

Biofuel, as a fuel category, is a renewable resource and, although different classes of fuels belong to this category, biofuel is generally thought to hold a promising future [1,2]. Ethanol, the only renewable liquid fuel currently produced in large quantities, has been the subject of numerous publications [3–9], but it suffers from several limitations, including comparatively low energy density, high volatility, and high energy consumption for its production. The search for alternatives to ethanol has become a primary research target. Recent developments have focused their attention on 2,5-dimethylfuran (DMF) as a possible alternative transportation fuel which can be produced from biological sources [10–13]. Also it can be produced by biotechnological methods [14]. DMF offers

several advantages over the current biofuel ethanol, including its 40% higher energy density which is close to that of gasoline [15].

Combustion of DMF has been investigated in engines [15–17] and its pyrolysis and oxidation have also been studied [18,19]. Wu et al. [20] have analyzed DMF/oxygen/argon flames at low pressure (40 mbar) and an equivalence ratio of 2.0 with tunable vacuum ultraviolet (VUV) synchrotron radiation photoionization and molecular-beam mass spectrometry. Their work reports intermediate species identification in the combustion of DMF, and they showed that furan and 2-methylfuran are stable intermediate species in the low-pressure DMF flames. Based on their identification of species, they also proposed possible reaction pathways for the decomposition of furans. Quantitative species profiles were not provided, however. Tian et al. [21] have investigated the laminar flame speed of DMF in the range of equivalence ratios ϕ from 0.6 to 2.0 and initial temperatures from 323 to 373 K. Their study showed that, for $\phi = 0.9$ –1.1, DMF laminar flame speeds are different from those of gasoline by $\sim 10\%$. Also, Wu and co-workers [22] measured laminar burning velocities and Markstein lengths of DMF-air premixed mixtures at different temperatures.

* Corresponding authors. Fax: +33 383378120 (F. Battin-Leclerc), fax: +49 521 106 6027 (K. Kohse-Höinghaus).

E-mail addresses: Frederique.battin-leclerc@univ-lorraine.fr (F. Battin-Leclerc), kkh@uni-bielefeld.de (K. Kohse-Höinghaus).

¹ Present address: German Aerospace Center (DLR), Institute of Combustion Technology, Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany.

Quantum chemical calculations for the DMF system were recently also reported [23,24]. Simmie and Metcalfe [23] employed *ab initio* methods to calculate energies and kinetic rate coefficients for several unimolecular decomposition pathways and free radical reactions involving DMF. They concluded that hydrogen atom migrations to form singlet carbenes are important in the decomposition of these species. Friese et al. [24] studied the thermal decomposition of DMF to form hydrogen atoms and the corresponding radical as well as the DMF + H reaction behind reflected shock waves; these experiments were performed at 1280–1520 K and 980–1250 K, respectively, at pressures of 1.6 and 4.7 bar. The authors concluded that the principal pathway was an addition–elimination mechanism to yield MF and the methyl radical. Most recently, the reaction of DMF with H-atoms has also been studied by Sirjean and Fournet [25,26] using a potential energy surface calculated at the CBS-QB3 level of theory and master equation/RRKM modeling. The major product channels of this reaction observed in that work are the ipso-substitution DMF + H to form MF and the methyl radical as well as the formation of 1,3-butadiene and the acetyl radical (CH₃CO). Sirjean and Fournet [27] performed similar investigations for the 5-methyl-2-furanylmethyl radical via theoretical calculations and master equation/RRKM modeling. Note that the 5-methyl-2-furanylmethyl radical is the most important primary radical formed during the combustion and thermal decomposition of DMF. In their study, pressure-dependent rate coefficients were proposed for pressures from 0.01 bar to 10 bar and temperatures from 1000 K to 2000 K. Using the results of these theoretical investigations, Sirjean et al. [28] have proposed a detailed kinetic model for the oxidation of DMF validated under shock tube conditions ($T = 1300\text{--}1813\text{ K}$) and using pyrolysis data of Lifshitz et al. [19].

While some detailed information on the combustion of DMF is thus available, a quantitative comparison of flame species profiles with a dedicated chemical kinetic mechanism is, to the best of our knowledge, still lacking. In view of the interest in furan and its derivatives as alternative transportation fuels, the present series of experiments of low-pressure furan flames in Part I [29] and 2-methylfuran flames in Part II [30] is now followed by measurements of DMF combustion for two flame stoichiometries under identical conditions as for the other two fuels investigated before. Also, a single model has been developed and tested for all three fuels and six flame conditions. With this consistent approach, it is believed that the knowledge of the combustion of furanic fuels has been considerably advanced, and that further model development including this data may also serve as a basis for transfer of this knowledge to combustion conditions more representative of practical application.

2. Experimental results

The experimental facilities in Bielefeld and Nancy used in this study have been described in detail in [31–33] and in Part I [29]; such details will, therefore, not be reported here again.

Premixed low-pressure (20 mbar and 40 mbar) flat argon-diluted (50%) flames of DMF were investigated for two equivalence

ratios ($\phi = 1.0$ and 1.7). Flame conditions are presented in Table 1. Hydrocarbon and oxygenate species were measured with two methods: Online gas chromatography (GC) was used in Nancy to provide isomer-specific information for stable intermediates, whereas electron-ionization molecular-beam mass spectrometry (EI-MBMS) was performed in Bielefeld to provide stable, radical, and intermediate species. Temperature was derived from the pressure in the first pumping stage by a procedure described in Part I [29] and calibrated at a height of 25 mm above the burner from CO/CO₂ absorption measurements with a quantum cascade laser using tomographic reconstruction [29]. The temperature profile obtained this way traces the fate of a gas sample withdrawn by the probe and is therefore called “perturbed” temperature profile here. When this perturbed temperature profile is used as input for the simulations, no shifts between experimental and modeling profiles have to be applied.

While the study of Wu et al. [20] has been considered as the first analysis of DMF combustion under laminar premixed low-pressure flame conditions, no mole fraction profiles were reported. The present work could then be considered as the first measurement with mole fraction profiles provided.

Figures 1–6 show the mole fraction profiles (EI-MBMS) of reactants, selected intermediates and products for the fuel-rich flame ($\phi = 1.7$). Analogous results for the stoichiometric flame can be found in the Supplemental material (Figs. S1–S5). Exemplary results from GC identification are presented in Figs. 7 and 8. For all important intermediate species, a summary of experimental results is given in Tables 2 and 3. This new set of experimental data from premixed DMF low-pressure flames was used as a basis for detailed chemical kinetic modeling.

For major species presented in Fig. 1, including Ar, O₂, CO, CO₂, H₂O, and fuel, the global combustion behavior is very similar to that found for furan [29] and MF [30]. The measured exhaust gas composition near 43 mm reaches the thermodynamic equilibrium values (open symbols) calculated with Gaseq [34] for the respective flame temperature. The mole fractions of CO and H₂ measured in the fuel-rich flame are larger than those obtained in the stoichiometric flame and remain constant along the post flame region.

For intermediate species (Figs. 2–6 and S1–S5), acetylene (C₂H₂) is the most abundant one with maximum mole fractions of up to 3.1×10^{-2} and 1.4×10^{-2} in the fuel-rich (Fig. 2) and stoichiometric flame (Fig. S1), respectively. An excellent agreement between GC and MBMS measurements can be observed for this species (Table 3). Methane (CH₄), ethene (or ethylene, C₂H₄), and ethane (C₂H₆) are measured with maximum mole fractions of 4.4×10^{-3} , 7.1×10^{-3} , and 3.0×10^{-3} in the fuel-rich flame, respectively (Fig. 2).

Among C₃ hydrocarbon intermediates (Figs. 3 and S2), the mole fraction of C₃H₄ is the largest with maximum values of 3.8×10^{-3} and 2.5×10^{-3} in the fuel-rich and stoichiometric flame, respectively. This trend was also found in the furan [29] and the MF flames [30]. In the stoichiometric flame, the most abundant C₄ species is C₄H₆ (maximum mole fraction of 2.4×10^{-3} , Fig. S2), and it is C₄H₂ in the fuel-rich flame (maximum mole fraction of 4.2×10^{-3} , Fig. 3). While the mole fraction of most C₄ hydrocarbon

Table 1
Flow conditions for dimethylfuran (DMF) flames; SLM: Standard liter per minute.

	ϕ	Burner diameter (mm)	Gas flow (SLM)			Pressure (mbar)	C/O ratio	Dilution (%)	Flow velocity at $T = 333\text{ K}^a$ (cm s ⁻¹)
			DMF	O ₂	Ar				
Bielefeld	1.0	64	0.27	2.01	2.28	20	0.38	50	146
	1.7	64	0.42	1.86	2.28	40	0.61	50	73
Nancy	1.7	60	0.37	1.63	2.00	40	0.61	50	73

^a The flow velocity is referred to the temperature of the burner surface (cooling water).

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