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ON THE OXIDATION OF 2,5-DIMETHYLFURAN IN A JET-STIRRED REACTOR AT 1 BAR

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ABSTRACT

2,5-Dimethylfuran-O₂-N₂ mixtures were oxidized in a fused-silica jet-stirred reactor at atmospheric pressure, over a range of temperatures (740–1280 K) and for equivalence ratios ranging from 0.5 to 4. Samples of the reacting mixtures were collected in Pyrex bulbs using a sonic probe for gas chromatography (GC) analyses, and sent to an FTIR for online quantification. A large number of oxidation products were observed by GC-TCD, GC-FID, and GC-MS. Our previously proposed detailed chemical kinetic reaction mechanism was used to rationalize the experimental results.

Keywords: biofuels, oxidation, pollutants, jet-stirred reactor, 2,5-dimethylfuran

1. INTRODUCTION

2,5-Dimethylfuran (2,5-DMF) is a cyclic ether that has been proposed as a substitute fuel for internal combustion engines. Similarly to ethanol, 2,5-DMF displays distinctive physicochemical characteristics that render it a promising substitute for gasoline. 2,5-DMF displays a greater affinity for gasoline than ethanol. In comparison to ethanol, 2,5-DMF exhibits a higher boiling point, a higher energy density, and a lower solubility in water. The principal characteristics of 2,5-DMF, ethanol, gasoline and diesel [1, 2] are compared in Table 1. In 2007, for the first time, Roman-Leshkov et al. [3] proposed a new route for the production of 2,5-DMF from sugar contained in biomass. This is a catalyzed process that transforms fructose into 5-hydroxymethylfurfural, an intermediate product that can be converted into 2,5-DMF. This discovery has generated enormous interest in this potential fuel over the last decades. The synthesis of 2,5-DMF has been the subject of numerous studies as reviewed in [2, 4]. The application of 2,5-DMF as a fuel in engines requires a good understanding of its pyrolysis and oxidation mechanisms. In this regard, many research studies have been carried out using different experimental devices (flames, reactors, shock tubes, and engines). Grela et al. [5] conducted an experimental study on the thermal decomposition (pyrolysis) of 2,5-DMF. They measured the decomposition products of 2,5-DMF in a very low pressure (1 mTorr) flow reactor at high temperature (1050-1270 K), leading to the proposal of a model for the

pyrolysis of 2,5-DMF. In 1998, Lifshitz et al. [6] studied the pyrolysis of 2,5-DMF in a shock tube (2-3.7 bar; 1070-1370 K). They obtained the distribution of the decomposition products of 2,5-DMF. They deduced the rate constants of several reactions and developed a kinetic scheme comprising 50 species and 181 reactions. More recently, many theoretical and experimental studies have been carried out to better understand the pyrolysis of 2,5-DMF [7, 8]. The first studies on the characterization of 2,5-DMF flames date back to 2009. Wu et al. [9] published a qualitative study on the identification of intermediate species in the combustion of the 2,5-DMF/O₂/Ar mixture at 30 Torr and fuel-rich conditions ($\phi=2$). Taking into account the identified species, they proposed different consumption pathways for furan, 2-methyl furan (2-MF), and 2,5-DMF. Wu et al. completed their studies by measuring the laminar flame speeds of the 2,5-DMF/air mixture as a function of temperature [10] and pressure [11]. In 2010, Tian et al. [12] used a constant volume spherical combustion chamber to measure the laminar flame speeds of 2,5-DMF, ethanol, and gasoline at atmospheric pressure, at several initial temperatures (50, 75, and 100 °C) and equivalence ratios (ϕ) of 0.6 to 2. The first detailed kinetic model of the oxidation and pyrolysis of 2,5-DMF was proposed in 2013 by Sirjean et al. [13]. The first measurements of auto-ignition times of 2,5-DMF/O₂/Ar mixtures were obtained using a shock tube at 1 and 4 bar, 1300-1831 K, and $\phi=0.5, 1, \text{ and } 1.5$. Validation of the model was conducted using both experimental results and pyrolysis data. [6].

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Table 1: Main physicochemical characteristics of ethanol, 2,5-dimethylfuran, gasoline and Diesel.

Properties	Fuel			
	Ethanol	2,5-DMF	gasoline	Diesel
Chemical formula	C ₂ H ₆ O	C ₆ H ₈ O	C ₄ -C ₁₄	C ₈ -C ₂₅
Composition O/ C/ H (mass %)	34,8/ 52,2/ 13	16,7/ 75/ 8.3	–	–
Molecular weight (g/mol)	46,07	96.13	102	≈ 200
Density (Kg/L)	0.79	0.89	0.74	≈ 0.84
Boiling point (°C)	77.3	93	27-225	180-317
Lower calorific value (MJ/kg)	26.8	33.7	42.7	43
Energy density (MJ/L)	33,9	37.8	57.7	51.2
Auto-ignition temperature (°C)	434	286	420	246
Research octane number	120	119	95	–
Cetane number	5-8	9	10-15	40-55

Somers et al. [14] published a detailed study on the pyrolysis and oxidation of 2,5-DMF. They provided a large set of data obtained using different experimental devices and techniques: (a) they measured species concentrations during the pyrolysis of 2,5-DMF in a shock tube, (b) they obtained auto-ignition delay times in a shock tube at atmospheric to high-pressure (20 and 80 bar), (c) they determined the species concentration profiles in a jet-stirred reactor, and (d) they determined laminar flame speeds at atmospheric pressure. In addition, they developed a kinetic reaction mechanism for the oxidation of 2,5-DMF. In 2014, three in-depth studies on the oxidation of furan and its derivatives (2-methyl furan and 2,5-dimethyl furan) were published. They reported the evolution of the concentration of species in premixed flame of furan [15], 2-methyl furan [16], and 2,5-DMF [17] under similar conditions (20 and 40 mbar at $\phi = 1$ and 1.7). The concentration profiles of the species (reactants, products, stable intermediate species and radicals) were obtained as a function of the distance from the burner. A kinetic model was developed. An experimental study associated with kinetic modeling of the pyrolysis of 2,5-DMF was also published by Cheng et al. [18]. They proposed a detailed kinetic model (1173 reactions and 285 species) inspired by different mechanisms from the literature. They also provided, for the pyrolysis of 2,5-DMF, new experimental data obtained using a flow reactor at different temperatures (780-1470 K) and pressures (30, 50 and 760 Torr). Alexandrino et al. [19] published in 2015 their experimental and modeling work on the pyrolysis and oxidation of 2,5-DMF. They discussed the influence of temperature (500-1400 K), pressure (1-40 bar), 2,5-DMF concentration (100-4500 ppm), and ϕ on the conversion of 2,5-DMF using different flow reactors. They

used their experimental data to validate their kinetic model (1314 reactions and 255 species) inspired by the mechanism proposed by Sirjean et al. [13]. Tran et al. [20, 21] have also worked on the construction of furans oxidation model (furan, 2-MF and 2,5-DMF). They introduced reactions with C8 aromatic hydrocarbons and a sub-mechanism for the formation of polycyclic aromatic hydrocarbons (PAHs) up to C16 was included. They also determined the temperature and concentration profiles of the species in laminar flames of 2-MF and 2,5-DMF, in fuel-rich conditions ($\phi = 1.7$) and at low pressure (40 kPa). These experimental results were used to validate their model. Eldeeb [22] studied the oxidation of 2,5-DMF and isooctane (model compound for gasoline) in shock tube. Autoignition delay measurements were performed at 5-12 atm, in the temperature range 1009-1392 K, and at $\phi = 0.5-2$. They also developed a kinetic model of oxidation for the isooctane/2,5-DMF mixture. The kinetic mechanism of 2,5-DMF oxidation derives from that of Somers et al. [14]. Their shock tube data were used for model validation. Several studies were also performed in engines and pollutant emissions during the combustion of 2,5-DMF and blends with gasoline were determined [23-30].

In this study, we conducted experiments on the oxidation kinetics of 2,5-DMF in a well-stirred reactor to complement previous research [14] and simulated them using the models proposed by Somers et al. [14] and Tran et al. [20].

2. EXPERIMENTAL AND MODELING

2.1 Oxidation experiments

Experiments were conducted in a 42 mL fused silica jet-stirred-reactor (JSR) [31]. We used a HPLC pump with an online degasser to inject the fuel (99% pure). The fuel was delivered to a vaporiser assembly with a flow of N₂. We used a JSR to separate the fuel and oxygen flows to avoid fuel oxidation. Nitrogen and oxygen flow rates were controlled by mass flow meters. We checked the JSR for thermal homogeneity using a silica-protected thermocouple. We studied the oxidation of 2,5-DMF using initial mole fractions $X_{2,5-DMF,in} = 0.1-0.15\%$, a residence time (RT) = 0.07s and 0.1s. We operated at 1 bar, between 740 and 1280 K, in fuel-lean to fuel-rich conditions ($\phi = 0.5$ to 4).

2.2 Chemical analyses

Here, samples of the reacting mixtures were collected in Pyrex bulbs using a sonic probe for gas chromatography (GC) analyses. GC-TCD, GC-FID, and GC-MS were used. Online FTIR quantification was also performed to measure H₂O, CH₂O, CO, and CO₂.

2.3 Kinetic modeling

Kinetic modeling was performed using the PSR code from the Chemkin II computer code library [32]. The kinetic reaction mechanism proposed by Somers et al. [14] for the oxidation of 2,5-DMF over a wide range of conditions,

including earlier JSR oxidation data at 10 bar, was used here. We also tested the mechanism proposed by Tran et al. [20].

3. RESULTS AND DISCUSSION

Many oxidation products were detected during the oxidation of the fuel. They ranged from H_2 to indene. Figure 1 shows an example of the present results.

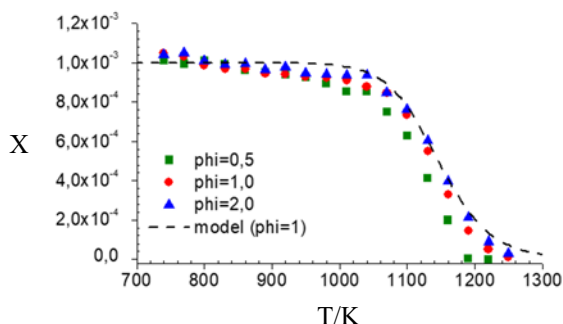


Figure 1: Mole fraction of 2,5-DMF in a JSR ($\phi=0.5, 1.0,$ and 2.0 ; $X_{2,5\text{-DMF},in} = 0.1\%$, $RT = 0.07s$). Data (symbols) are compared to simulations using Somers' model.

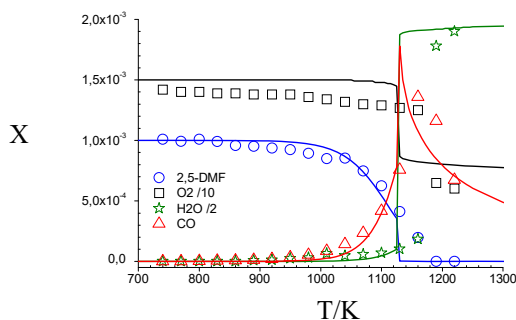


Figure 2: Oxidation of 2,5-DMF in a JSR ($\phi=0.5$; $X_{2,5\text{-DMF},in} = 0.1\%$, $RT = 0.07s$). Model: Somers et al.

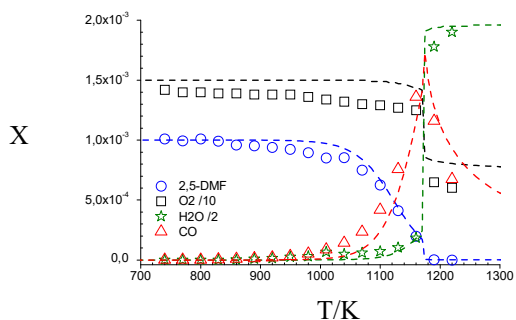


Figure 3: Oxidation of 2,5-DMF in a JSR ($\phi=0.5$; $X_{2,5\text{-DMF},in} = 0.1\%$, $RT = 0.07s$). Model: Tran et al.

From that figure, one can see that the model is in agreement with the data and that the fuel conversion is not very sensitive to the initial oxygen content. Figure 2 shows a comparison of the present data and the results of simulations using the model of Somers. Figure 3 shows the same data compared to simulations using Tran's model. Both models represent the data reasonably well. Reaction pathways were computed using Somers' model (Fig. 4), showing the main oxidation routes of 2,5-DMF. The fuel

reacts mainly (51.2%) via metathesis reactions. The H-atom is removed by reaction with the CH_3 radical (29%), the H atom (15%) and with the OH radical (2.8%). Two different radicals are formed by the metathesis. Another radical is formed by the addition of OH. The fuel is also consumed (13%) by H- addition yielding 1,3-butadiene and 2-MF. The ring opening is a minor pathway.

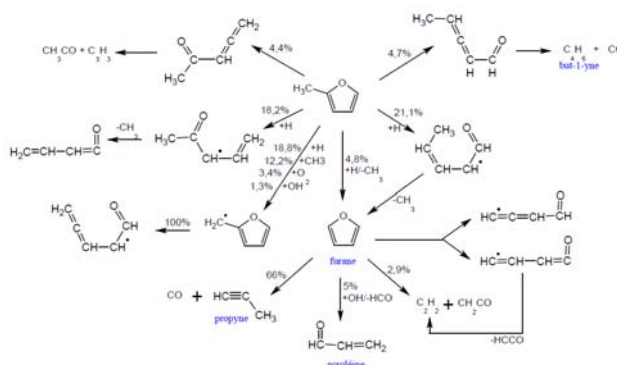


Figure 4: Oxidation of 2,5-DMF in a JSR ($\phi=1$; $X_{2,5\text{-DMF},in} = 0.1\%$, $RT = 0.07s$, $T = 1060 K$ and 15% fuel-conversion).

4. CONCLUSIONS

In this study, we identified a substantial number of oxidation products of 2,5-DMF at atmospheric pressure across a range of fuel-to-air ratios, encompassing fuel-lean to fuel-rich conditions. These findings augment those previously obtained at 10 bar [14]. Two established models from the literature were employed to simulate the experiments, exhibiting a satisfactory degree of alignment with the data.

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