

# Gas Phase Kinetics of Volatiles from Biomass Pyrolysis. Note II: Furan, 2-methyl-furan, and 2,5-dimethylfuran

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## Abstract

The aim of this work is to develop and discuss a lumped kinetic mechanism of furan, 2-methyl-furan, and 2,5-dimethylfuran to simulate the pyrolysis conditions, experimentally studied in shock tube and flow reactors and in a wide range of temperature and pressure. The comparisons between experimental data and model predictions support the validity of the lumped kinetic model, but also highlight the need of further experimental measurements in order to better understand the chemistry of these components.

## Introduction

The synthesis of new biofuels through second generation methods of production from biomass is one interesting development in recent times, transforming abundant renewable resources, but not crops destined for human consumption, into liquid transportation fuels [1]. These second generation fuels are very promising, but they require a proper knowledge about the formation of toxic intermediates, and more in general about their combustion and ignition behavior. For these reasons there is a growing interest in the successive gas phase reactions not only of furans, but also of all the volatile species released from biomass pyrolysis [2].

A catalytic strategy for the production of 2,5-dimethylfuran (DMF) from biomass was discussed by Román-Leshkov et al. [3]. Compared to ethanol, the advantages of dimethylfuran as a liquid transportation fuel are a higher energy density, a higher boiling point, and a very low water solubility. Furthermore, the interest toward furans lies in their toxic characteristics. As a matter of facts, aromatic heterocycles such as furan are emitted during traditional fuel and biomass combustion and have been identified as air pollutants. Detailed chemical kinetic models exist to describe the combustion of hydrocarbons, but these are less validated and reliable for oxygenated species such as furans and higher alcohols. Thus, furan appears to be an excellent molecule to study the fundamentals of the unimolecular dissociation of large molecules over a wide range of conditions [4].

## Kinetic scheme and numerical methods

A semi-detailed kinetic sub-mechanism for the description of furan, methyl-furan, and dimethylfuran pyrolysis is summarized in Table 1. The successive reactions of

the smaller radicals and molecules involved are already considered in the whole oxidation mechanism for hydrocarbon fuels up to C<sub>16</sub>. The overall kinetic scheme, constituted by ~400 species involved in more than 10000 reactions, is based on a hierarchical modularity [5]. Thermochemical data for most species were obtained from thermodynamic database [6] as well as from the recent work of Sirejan and Fournet [7].

The complete mechanism, including thermo and transport properties, is available online at [www.chem.polimi.it/CRECKModeling/](http://www.chem.polimi.it/CRECKModeling/). All the simulations were performed with the DSMOKE and OpenSMOKE codes [8].

*Table 1. Primary pyrolysis reactions of furan, methyl-furan, and 2,5-dimethylfuran. (Units are mole, l, s, cal)*

<b>Initiation reactions</b>	<b>A</b>	<b>E</b>
Furan = CO + C3H4	1.30E+15	80000
Furan = C2H2 + CH2CO	2.00E+15	86000
Furan = C3H3+HCO	1.00E+15	86500
2MeFuran = CO + C4H6	2.00E+15	81000
2MeFuran > H + CH2CO + C3H3	1.50E+16	85000
2MeFuran > H + HCCO + C3H4	1.50E+16	85000
DMF = CO + C5H8	2.00E+15	81500
DMF > CO + C2H4 + C3H4	2.50E+15	81500
DMF > CO + C4H5P + CH3	2.50E+16	93000
<b>H-abstraction reactions</b>		
R + Furan = RH + RFUR	4 H Vinyl	type
R + 2MeFuran > RH + RMEFUR	3 H Allyl	type
R + DMF > RH + RDMF	6 H Allyl	type
<b>Radical Decomposition reactions</b>		
RFUR > CO + C3H3	3.00E+12	36500
RFUR > CH2CO + C2H	1.00E+13	39000
RMEFUR > CO + C4H5	5.00E+13	30000
RDMF > H2 + C6H5O	3.00E+13	30000
RDMF > H + CyC5H6 + CO	5.00E+13	30000
RDMF > CH3 + CO + C4H4	6.00E+13	30000
RDMF > CH3CO + 2 C2H2	2.00E+13	32000
<b>H addition reactions</b>		
H + Furan > C2H2 + CH3 + CO	1.00E+10	3000
H + Furan > C2H2 + CH2CHO	1.00E+10	2000
H + 2MeFuran > CH3 + C3H4 + CO	2.00E+10	2500
H + 2MeFuran > C4H7 + CO	2.00E+10	2500
H + 2MeFuran > CH3 + Furan	4.00E+09	2500
H + 2MeFuran > C2H2 + CH3 + CH2CO	2.00E+10	2500
H + DMF = CH3CO + C4H6	8.00E+09	2000
H + DMF = CH3 + 2MeFuran	2.50E+10	2000
H + DMF = CH2CO + C4H7	1.00E+10	2000
H + DMF > CO + 1C3H7 + C2H2	1.50E+10	2000

## Comparisons with experimental data

As a first step towards a complete kinetic analysis, this kinetic work is simply related to the pyrolysis of furan, methyl-furan, and dimethylfuran.

### Furan

Lifshitz et al. [9] and Organ and Mackie [10] studied furan pyrolysis and suggested that the initial and rate-determining step of furan dissociation is a ring-opening process, a cleavage of the C-O bond, and the formation of a very unstable intermediate biradical. Two parallel processes, initiated by a 1,2-H transfer, result in the formation of cyclic carbene intermediates. They lead to the prevailing formation of CO and propyne, together with  $C_2H_2$  and ketene. These are the dominant pathways and allow the modeling of furan pyrolysis with the formation of the major products. Direct ring scission in furan, either on a singlet or triplet surface, is found to be too energetic to appreciably contribute [11]. Thus, only a minor chain radical reaction path is supported by propargyl ( $C_3H_3$ ) and acyl (HCO) radicals. H atoms and  $C_3H_3$  radicals arise essentially from propyne, while H abstraction from furan by methyl radicals is the main source of methane. The overall rate constant of furan decomposition can be treated as an unimolecular reaction rate, as also confirmed by Tian et al. [12]. The branching ratio amongst the different product channels depends on the energy and structure of multiple transition states.

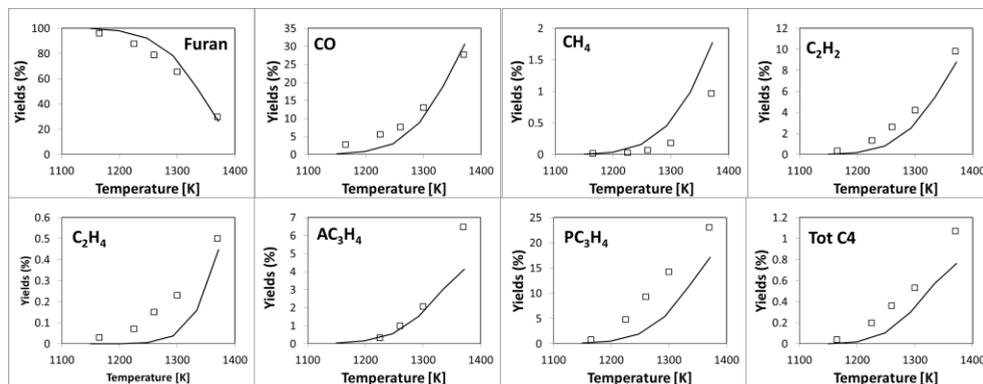


Figure 1. Furan pyrolysis diluted with 99% Ar at  $\sim 3$  atm. Comparison of experimental (symbols) and predicted molar yields (lines with small symbols). [9]

Lifshitz et al. [9] studied the thermal decomposition of furan behind reflected shocks in a single shock tube, over the temperature range 1050-1460 K, at total gas densities of  $\sim 3 \times 10^{-5}$  mol/cm<sup>3</sup>. Similarly, Organ and Mackie [10] studied the kinetics of pyrolysis of furan diluted in argon behind reflected shock waves in a shock tube over the temperature range 1100-1700 K, at pressures of  $\sim 20$  atm and at uniform residence times of  $\sim 0.3$  ms. In agreement with Lifshitz et al. [9], Organ and Mackie [10] found a rate constant for the first order overall decomposition rate

of furan  $k=10^{15.3\pm 0.3} \exp[-78600(\pm 2)/RT]$  [s<sup>-1</sup>]. Principal products are carbon monoxide and C<sub>3</sub>H<sub>4</sub> together with acetylene and ketene. Figure 1 and 2 show detailed comparisons with both these experimental data.

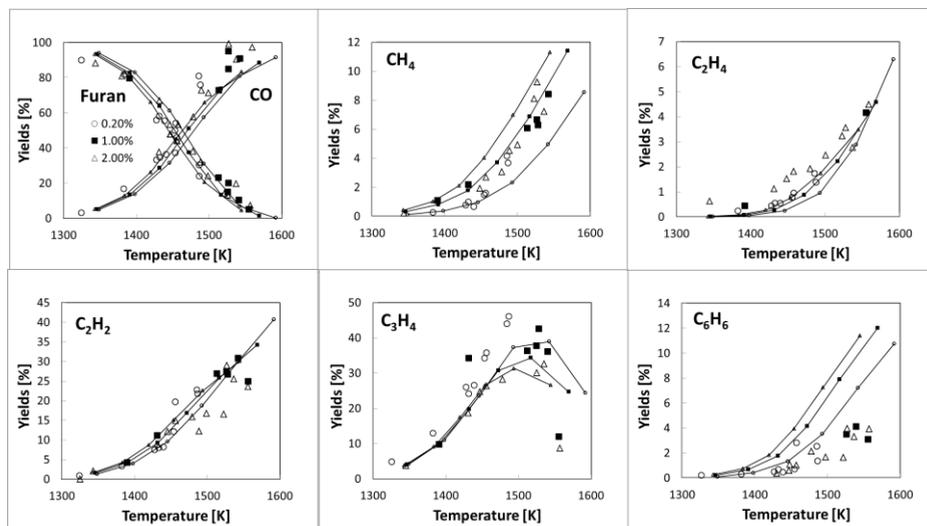


Figure 2. Furan pyrolysis diluted in Ar at ~20 atm. Comparison of experimental (symbols) and predicted molar yields at 0.2-1-2% furan (lines with small symbols). [10]

Lifshitz et al. [9] did not find ketene, either in the GC or in the GC-MS analyses. Similarly, they do not report benzene formation, expected product of the recombination reaction of propargyl radicals.

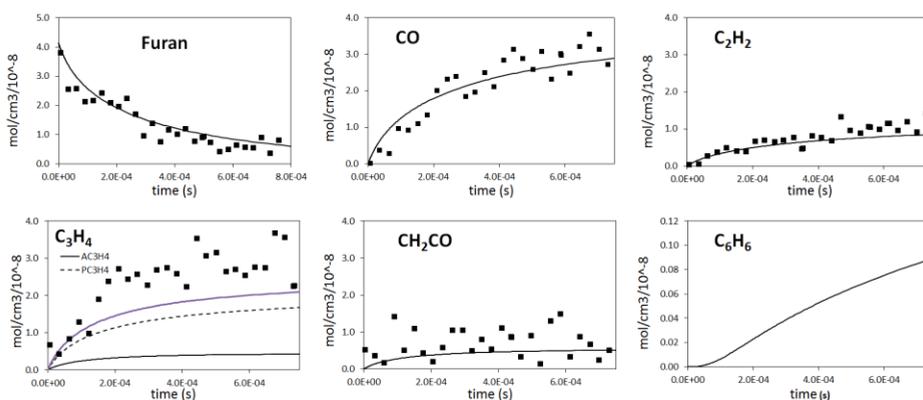


Figure 3. Furan pyrolysis diluted with 98% Ne at 1533 K and 0.26 atm. Comparison of experimental (symbols) and predicted molar yields (lines with small symbols). [4]

Further high temperature (1300-1700 K) and low pressure (175-250 Torr) shock tube experiments of furan pyrolysis were performed by Fulle et al. [4], using laser-schlieren (LS) densitometry and time-of-flight (TOF) mass spectrometry. Comparisons with these data are reported in Figure 3.

### Methylfuran

Lifshitz et al. [13] studied the pyrolysis of 2-methylfuran behind reflected shock waves in a pressurized driver single pulse shock tube over the temperature range 1100-1400 K and with overall densities of  $\sim 3 \times 10^{-5}$  mol/cm<sup>3</sup>. A large number of products resulting from unimolecular cleavage of the ring and consecutive free radical reactions were obtained under shock heating. Figure 4 shows a detailed and satisfactory comparison between experimental data and model predictions.

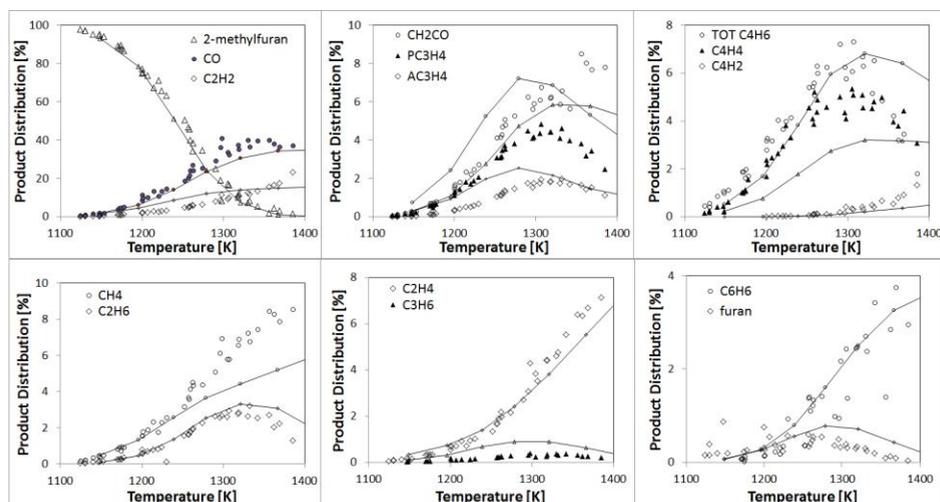


Figure 4. Methylfuran pyrolysis in 99.5% Ar at  $\sim 3$  atm. Comparison of experimental (symbols) and predicted molar yields (lines with small symbols). [13]

### Dimethyl-furan

The pyrolysis of 2,5-dimethylfuran was studied behind reflected shock waves in a single pulse shock tube at 1070-1370 K and overall densities of  $\sim 3 \times 10^{-5}$  mol/cm<sup>3</sup> by Lifshitz et al. [14]. A large number of products are formed from the cleavage of the ring and the successive free radical reactions. Unimolecular processes via methyl group migration from C(2) to C(3) in the ring with the elimination of CO produce four pentadiene (C<sub>5</sub>H<sub>8</sub>) isomers. The unimolecular decomposition process of 2,5-dimethylfuran to form CH<sub>3</sub>CO and C<sub>4</sub>H<sub>5</sub> is an important initiator of the free radical reactions. Dehydrogenation of the methyl group in the molecule is another channel for initiation of free radical reactions in the system. The dimethylfuryl radical, which is obtained in the dehydrogenation process, decomposes to produce, among other products, C<sub>5</sub>H<sub>7</sub>, which is the precursor of cyclopentadiene. The major decomposition product found in the post shock mixtures is carbon monoxide [14].

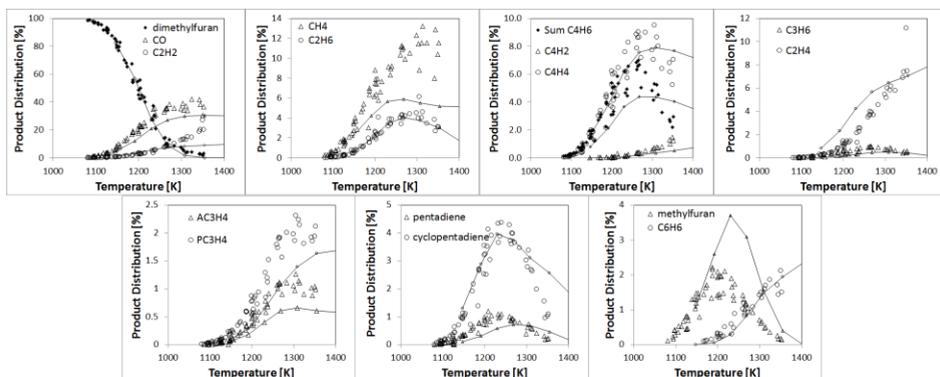


Figure 5. Dimethylfuran pyrolysis in 99.5% Ar at  $\sim 3$  atm. Comparison of experimental (symbols) and predicted molar yields (lines with small symbols). [14]

The 2,5-dimethylfuran pyrolysis diluted with  $N_2$  was recently studied in a bench-scale flow reactor equipped with a dedicated GC analysis section [15] enabling a very detailed quantitative on-line analysis of the reactor effluent. The reactor temperature was varied from 873 K to 1098 K at a fixed pressure of 1.7 bar and a residence time of  $\sim 300$  ms. Figure 6 compares experimental and predicted dimethylfuran conversion, while Figure 7 shows a comparison between experimental and predicted molar yields of several major and minor species. At high DMF conversions, a large amount of benzene, toluene, indene, and polyaromatics is formed. This high sooting tendency even under diluted conditions poses a threat for the use of 2,5-dimethylfuran as a fuel.

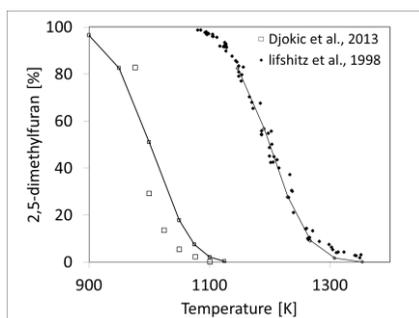


Figure 6. Comparison of experimental and predicted 2,5-dimethylfuran conversion. [14-15]

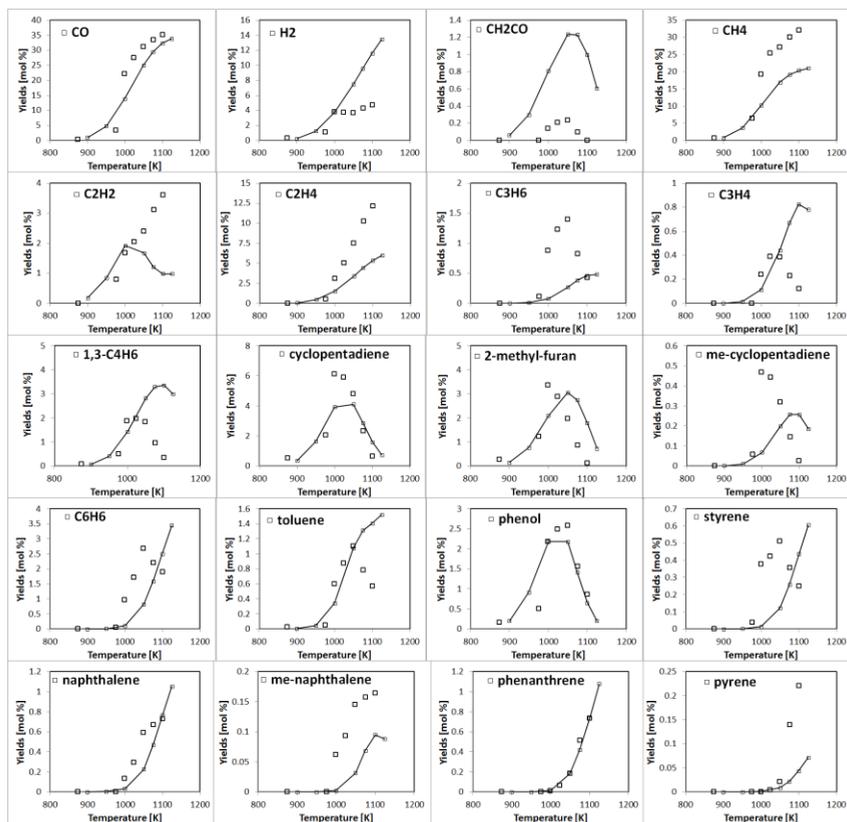


Figure 7. Dimethylfuran pyrolysis diluted with 88%  $N_2$  at 1.7 atm. Comparison of experimental (symbols) and predicted molar yields (lines with small symbols). [15]

## Conclusions

This kinetic work presents a lumped kinetic model of pyrolysis of furan components. Several comparisons between experimental measurements and model predictions support the validity of the model, while large uncertainties are evident in the experimental data. Recently, Sirjean and Fournet [7] questioned about the temperatures of Lifshitz experiments, suggesting to increase 50-80 °C the experimental temperatures. On the contrary, Figure 6 shows that, while there is a good agreement between predicted DMF conversion and Lifshitz experiments [14], the DMF conversion in the Ghent reactor [15] seems higher than the predicted one. Finally, experimental data on the ignition delay times of furan in oxidation conditions seem to indicate a lower reactivity of furan components [16].

## References

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