

FIRST-PRINCIPLES KINETIC MODEL FOR 2-METHYL-TETRAHYDROFURAN PYROLYSIS AND COMBUSTION

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Abstract

2-methyl-tetrahydrofuran (MTHF) is a promising next-generation bio-derived fuel. This study presents new experimental data regarding its reactivity under pyrolytic (plug flow reactor) and combustion conditions (low-pressure premixed MTHF flame). A first-principles kinetic model was developed using quantum chemical calculations and the automatic model generation code EXGAS. The model was used to simulate the obtained experimental data. Model calculated and experimental mole fraction profiles are in good agreement. Sensitivity and rate of production analysis reveal that MTHF conversion in pyrolysis is sensitive towards unimolecular decomposition of MTHF to 4-pentenol. The consumption of MTHF in the investigated combustion conditions is dominated by hydrogen abstraction reactions.

Keywords

2-methyl-tetrahydrofuran, pyrolysis, combustion, detailed kinetic model

Introduction

Cyclic ethers, such as 2-methyl-tetrahydrofuran (MTHF), are considered as next-generation bio-derived fuels. They can be produced from non-edible biomass by catalytic and fermentative conversion routes, with levulinic acid and γ -valerolactone as possible intermediates (Geilen et al., 2010).

The practical implementation of bio-derived fuels requires careful evaluation of the stability of the molecule, assessment of its combustion characteristics and tendency of soot formation. Several fundamental studies regarding the combustion of cyclic ethers have recently been conducted (Tran et al., 2015) (Moshammer et al., 2013).

This work aims at extending the experimental database for MTHF pyrolysis and combustion. Furthermore, a new

detailed kinetic model for MTHF combustion has been developed and was used to simulate and interpret the performed experiments.

The proposed kinetic model can be extended towards other promising bio-derived fuels, such as 2,5-dimethyl-tetrahydrofuran. The kinetic model can be used as a building block for biomass pyrolysis and gasification mechanisms as cyclic ethers are abundantly present in the biomass molecular structure.

Experimental

The pyrolysis chemistry of MTHF was investigated in a tubular plug flow reactor. The inlet mixture consisted of

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MTHF diluted in N₂ and the effect of reactor temperature on reactor effluent composition was evaluated.

The combustion chemistry of MTHF was investigated using a low-pressure (6.66 kPa) pre-mixed flame. The MTHF flame was stabilized on a McKenna burner. Temperature profiles and product mole fraction profiles were measured as a function of distance above the burner.

Kinetic model development

A first-principles kinetic model has been developed to describe the pyrolysis and high temperature combustion of MTHF. The mechanism consists of three main parts.

It contains a base mechanism, developed by Tran et al. (2015), which describes the combustion and pyrolysis of tetrahydrofuran and small hydrocarbons/oxygenates.

Furthermore, it includes a primary mechanism which describes the combustion and pyrolysis chemistry of MTHF and derived radicals. Kinetic and thermodynamic parameters were taken from quantum chemical calculations or estimated using an analogy with tetrahydrofuran.

Finally, a secondary mechanism, with reactions detailing the consumption of products that originate from the decomposition of MTHF, was generated automatically using EXGAS (Warth et al., 1998) and was added to the kinetic model.

Results and discussion

The kinetic model is in good agreement with the obtained experimental data as shown in Figure 1 and Figure 2.

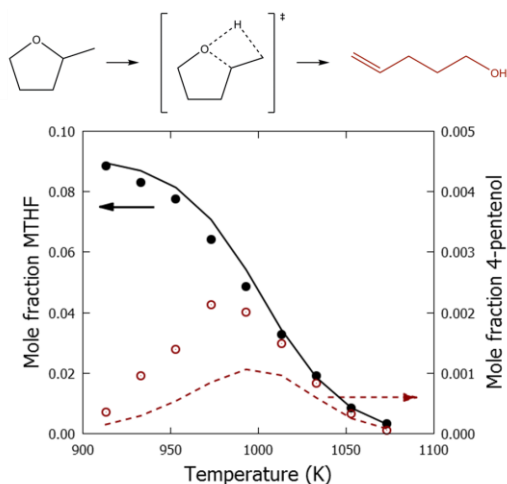


Figure 1 Experimental (symbols) and model calculated (lines) mole fraction profiles as a function of temperature for MTHF pyrolysis in a tubular reactor

MTHF pyrolysis has a high selectivity towards alkenes, CO, ketene, formaldehyde and acetaldehyde. Minor fractions of 4-pentenol were detected in the reactor effluent. The latter product is formed by the unimolecular decomposition of MTHF, see Figure 1. Conversion of

MTHF is found to be sensitive towards this reaction. A similar reaction was shown to be important in the pyrolysis of γ -valerolactone (De Bruycker et al., 2015).

About 50 species were identified and quantified in the low pressure premixed flame. The major products are displayed in Figure 2.

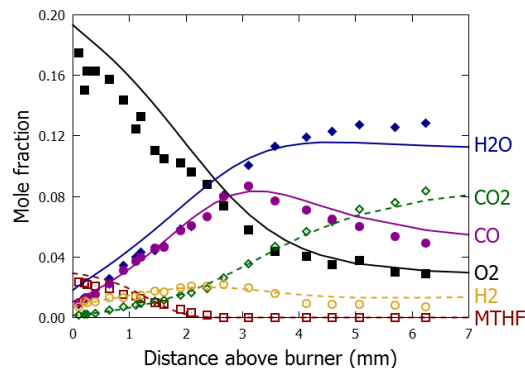


Figure 2 Experimental (symbols) and model calculated (lines) mole fraction profiles as a function of height above burner in stoichiometric MTHF flames

MTHF is mostly consumed by hydrogen abstraction reactions. Subsequent decomposition can form resonantly stabilized radicals such as allyl, butenyl, 2-oxo-ethyl and 2-oxo-propyl radicals. Consumption of these radicals by recombination reactions are important reaction paths according to the kinetic model.

Conclusions

The pyrolysis of MTHF has been investigated in a tubular reactor and the combustion of MTHF has been investigated in premixed flames. A first-principles kinetic model was developed and used to interpret the experimental results. Decomposition of MTHF by unimolecular reactions is non-negligible in low temperature pyrolysis conditions. Consumption of MTHF is dominated by hydrogen abstraction at the investigated combustion conditions, for which the kinetics have been determined using ab-initio calculations.

Acknowledgments

The authors acknowledge the financial support from the Long Term Structural Methusalem Funding by the Flemish Government, the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013) / ERC grant agreement n° 290793, the Research Board of Ghent University (BOF) and the Fund for Scientific Research Flanders (FWO). The work in the Laboratoire Réactions et Génie des Procédés-Nancy was funded by the European Commission through the "Clean ICE" Advanced Research Grant of the European Research Council.

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