

Rupali Tripathi

**Detailed Chemical Kinetic
Modeling of Biofuels and their
Blends with Conventional Fuel
Components**

Detailed Chemical Kinetic Modeling of Biofuels and their Blends with Conventional Fuel Components

Detaillierte Modellierung der Reaktionskinetik von Biokraftstoffen und ihren Mischungen mit konventionellen Kraftstoffkomponenten

Von der Fakultät für Maschinenwesen der Rheinisch-Westfälischen
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Berichte aus der Energietechnik

Rupali Tripathi

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Zusammenfassung

Kraftstoffe aus nicht-essbarer Biomasse stellen als nachhaltige Energieträger eine mögliche Alternative zu konventionellen Kraftstoffen dar. Eine wichtige Voraussetzung hierfür ist das detaillierte Verständnis ihres Oxidationsverhalten, welches stark von der Kraftstoffstruktur abhängt. Zur umfassenden Untersuchung der Oxidation einer Klasse von Furanen und Tetrahydrofuranen werden daher in der vorliegenden Arbeit detaillierte Reaktionsmechanismen entwickelt und darauf aufbauend die Zusammensetzung von Kraftstoffmischungen systematisch für konkrete Anwendungen optimiert.

Im ersten Teil wird der Effekt der Beimischung des Oktanzahlverbessers 2-Methylfuran zu der reaktiveren Komponente von Primären Bezugskraftstoffen, *n*-Heptan, untersucht. Hierzu wurde ein detaillierter Reaktionsmechanismus formuliert, welcher die relevanten Reaktionspfade der Oxidation von 2-Methylfuran und *n*-Heptan enthält, und auf Basis neuer Messungen und experimenteller Literaturdaten validiert. Beide Kraftstoffkomponenten zeigen ein nichtlineares Mischungsverhalten. Die detaillierte chemische Analyse zeigt, dass hierfür keine direkte Interaktion von 2-Methylfuran und *n*-Heptan, sondern die Rolle von 2-Methylfuran als Radikalbinder in der Mischung verantwortlich ist. Der zweite Teil der Arbeit analysiert den Einfluss der molekularen Kraftstoffstruktur auf die Reaktivitäten von 2-Methyltetrahydrofuran und 3-Methyltetrahydrofuran. Für beide Kraftstoffe wurden zunächst Reaktionsmechanismen entwickelt und mittels experimentell ermittelter Zündverzugszeiten sowie Flammendaten aus der Literatur validiert. 2-Methyltetrahydrofuran weist dabei eine geringere Reaktivität als 3-Methyltetrahydrofuran auf, wofür die Lage der Seitenkette als der entscheidende Faktor identifiziert wird. Im letzten Teil der Arbeit wird schließlich die Zusammensetzung potentieller Kraftstoffmischungen optimiert. Die Identifikation geeigneter Kraftstoffkandidaten erfolgt mittels eines eigens entwickelten Tools. Dieses erlaubt die Berechnung der physikalisch-chemischen Kraftstoffigenschaften auf Basis vordefinierter Mischungsregeln und darauf aufbauend die Auswahl geeigneter Kraftstoffkomponenten für die vorgegebenen Randbedingungen der Mischung. Die Kraftstoffauswahl ergibt hierbei, dass durch Beimischung von Alkoholen oder Ketonen zu konventionellem Ottokraftstoff ein hohes Potential zur Steigerung des Motorwirkungsgrades besteht.

Abstract

Fuel components derived from non-edible biomass are regarded as sustainable substituents for conventional fuels. A major prerequisite for their application in engines, however, is the understanding of their detailed oxidation behavior, which strongly depends on the fuel structure. In the present work, the oxidation behavior of a group of bio-derived furans and tetrahydrofurans is investigated by developing their detailed chemical kinetic mechanisms. Furthermore, to identify potential fuel blends for the desired applications, a systematic optimization approach is proposed.

The first part of this thesis is a detailed investigation of the effect of blending an octane booster, 2-methylfuran, with the more reactive primary reference fuel candidate, *n*-heptane. A detailed model comprising the chemistry relevant for 2-methylfuran and *n*-heptane was formulated, which predicts newly measured and literature data well. A non-linear mixing behavior was observed, and the detailed chemical analysis reveals no direct interaction between these two fuels, but the effect of 2-methylfuran as a radical scavenger is responsible for this trend. The second part of the thesis addresses the question, how a small change in molecular structure can lead to a substantial change in the reactivity. The oxidation behavior of two structural isomers, 2-methyltetrahydrofuran and 3-methyltetrahydrofuran, is investigated numerically and experimentally. The developed detailed chemical kinetic models show good agreement with experimental ignition delay measurements and flame data from the literature. The influence of molecular structure on ignition propensity was investigated by comparing the ignition delay times of these two components. A comparative reaction path analysis ensures that the location of the side chain is the decisive factor for their ignition propensity. The last part of the thesis focuses on the optimization of potential gasoline blending agents. For this purpose, a large database containing the physical and chemical properties of about 500 fuel components was established. In order to identify the potential candidates, a simple automatic tool was developed, whose main functions involve the physicochemical property calculation of the blends based on pre-defined blending rules and selecting the potential candidates for a set of constraints on these properties. Fuel candidates comprising the alcohol and ketone functional groups were observed to have good potential for blending with gasoline for superior efficiency.

Publications

Peer reviewed papers

R. Tripathi, L. Cai, J. Beeckmann, H. Pitsch (2019): Optimization of potential fuel components for blending with market gasoline, *in preparation*.

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Conference papers

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Oral presentations

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Abbreviations

PCCI - premixed charged compression ignition

RCCI - reactivity controlled compression ignition

GCI - gasoline compression ignition

2-MF - 2-Methylfuran

2-MTHF - 2-methyltetrahydrofuran

3-MTHF - 3-methyltetrahydrofuran

RON - research octane number

LHV - lower heating value

SI - spark ignition

DCN - derived cetane number

LBV - laminar burning velocity

2,5-DMF - 2,5-dimethyltetrahydrofuran

EI-MBMS - electron ionization molecular-beam mass spectrometry

GC - gas chromatography

BDE - bond dissociation energy

CI - compression ignition

PAH - poly aromatic hydrocarbons

HM - hydrogen migration

CE - Concerted elimination

WE - waddington elimination

WCE - waddington concerted elimination

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RCM - rapid compression machine

ST - shock tube

NTC - negative temperature coefficient

THF - tetrahydrofuran

MBMS - molecular-beam mass spectrometry

EI - electron ionization

2-BTHF - 2-butyltetrahydrofuran

MON - motor octane number

QSPR - quantitative structure-property relationship

OI - octane index

OS - octane sensitivity

NO_x - nitrogen oxides

CO₂ - carbon dioxide

PM - particulate matter

uHC - unburnt hydrocarbon

CO - carbon monoxide

CN - cetane number

ID - ignition delay

H₀V - heat of vaporization