

Reihe 3

Verfahrenstechnik

Dipl.-Ing. Manuel Dahmen,
Heinsberg

Nr. 954

Model-Based Design of Pure and Multicomponent Cellulosic Biofuels for Advanced Engine Concepts

Berichte aus der
Aachener Verfahrenstechnik - Prozesstechnik

RWTH Aachen University

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Model-Based Design of Pure and Multicomponent Cellulosic Biofuels for Advanced Engine Concepts

Modellbasierter Entwurf von lignocellulosebasierten Biokraftstoffen für fortschrittliche Motorenkonzepte

Von der Fakultät für Maschinenwesen der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades eines Doktors der Ingenieurwissenschaften genehmigte Dissertation

vorgelegt von

Manuel Dahmen

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Univ.-Prof. Dr.-Ing. (USA) Stefan Pischinger

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This thesis describes model-based strategies for the identification of pure and multicomponent cellulosic biofuels that exhibit tailored properties for use in high-efficiency, low-emission internal combustion engines. Based on the principles of computer-aided molecular design, algorithmic exploration of the molecular search space by means of carbon- and energy-efficient refunctionalization of bio-derived platform chemicals is combined with quantitative structure-property relationship (QSPR) and group contribution modeling of key physicochemical fuel properties including the derived cetane number. The resulting virtual fuel screening approach is applied to the task of identifying oxygenated fuel candidates for both spark-ignition and compression-ignition engines. Optimization-based formulation of 100%-renewable biofuel blends is performed by means of integrated product and pathway design. Application of the novel design methodology yields biofuel mixtures that exhibit both the desired physicochemical properties and attractive process-related properties.

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Vorwort

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Heinsberg, im September 2017

Manuel Dahmen

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Notation

Abbreviations

AD	applicability domain
ADC	Advanced Distillation Curve
AI	artificial intelligence
AIC	Akaike's information criterion
AIC _c	Akaike's information criterion corrected for small sample size
ARE	average relative error
ASG	ASG Analytik-Service GmbH
cMON	correlated motor octane number
cRON	correlated research octane number
C	carbon atom
CAMD	computer-aided molecular design
CFR	cooperative fuels research
CI	compression-ignition
CN	cetane number
CPD	conceptual process design
CPM	conversion pathway map
CRPM	chemical reaction pathway map
CV	cross-validation
DCN	derived cetane number
DIPPR	Design Institute for Physical Properties
DMTHF	dimethyltetrahydrofuran
ETBE	ethyl-tert-butyl ether
FIM	Fisher information matrix
FIT	Fuel Ignition Tester
GC	group contribution
GC ⁺	group contribution plus
GCM	group contribution method
H	hydrogen atom

HCCI	homogeneous charge compression ignition
HMF	hydroxymethylfurfural
IQT	Ignition Quality Tester
LHV	lower heating value
LLE	liquid-liquid equilibrium
LMO-CV	leave-many-out cross-validation
LOO-CV	leave-one-out cross-validation
MLR	multiple linear regression
MON	motor octane number
MTBE	methyl-tert-butyl ether
MTHF	methyltetrahydrofuran
NLP	nonlinear program
NMR	nuclear magnetic resonance
O	oxygen atom
ON	octane number
PC	principal component
PCA	principal component analysis
PCI	premixed compression-ignition
PLS	partial least squares
PNFA	process network flux analysis
QSAR	quantitative structure-activity relationship
QSPR	quantitative structure-property relationship
RCCI	reactivity controlled compression ignition
RMSE	root-mean-square error
RNFA	reaction network flux analysis
RON	research octane number
RVP	Reid vapor pressure
SCA	stochastic cluster analysis
SI	spark-ignition
TMFB	Tailor-Made Fuels from Biomass
TSI	threshold sooting index
VLE	vapor-liquid equilibrium

Latin

A	matrix of stoichiometric coefficients
<i>AICc</i>	Akaike's information criterion corrected for small sample size

b	product flow	kmol/h
\mathbf{b}	vector of product flows	kmol/h
\mathbf{c}	vector of weights (PLS)	
C	pathway conversion	
$C_{ant,1} - C_{ant,7}$	parameters for the extended Antoine equation	
$C_{cost,a} - C_{cost,h}$	parameters for the COSTALD method	
$C_{dip,1} - C_{dip,4}$	parameters for the DIPPR 105 equation	
d	descriptor value	
\mathbf{d}	vector of descriptor values	
D	descriptor contribution (model parameter)	
\mathbf{D}	vector of descriptor contributions (model parameters)	
DCN	derived cetane number	
\dot{E}_{fuel}	energy flow of fuel produced	MJ/h
\mathbf{E}	matrix of \mathbf{X} residuals (PCA / PLS)	
f	molar flow over pathway	kmol/h
\mathbf{f}	vector of molar flows over all pathways	kmol/h
$f_{COSTALD}$	COSTALD equation	kmol/m ³
f_{HF}	Hoffmann-Florin equation	kPa
f_{dp}	tangent plane distance function	
F^α	F-distribution with confidence level α	
F	entry of the Fisher information matrix	
\mathbf{F}	Fisher information matrix	
g	group occurrence	
Δg	Gibb's energy change of mixing	J/mol
\mathbf{g}	vector of group occurrences	
G	group contribution (model parameter)	
\mathbf{G}	vector of group contributions (model parameters)	
H	enthalpy	kJ/kg, MJ/kg, kJ/mol, J/kmol
\mathbf{H}	Hessian matrix	
HHV	higher heating value	kJ/mol
\mathbf{I}	identity matrix	
K	sensitivity coefficient for octane index	
K	equilibrium ratio	
L	likelihood function	

LHV	lower heating value	MJ/kg, J/kmol, kJ/mol
m_{CO_2}	mass of carbon dioxide per MJ of fuel	g/MJ
\dot{m}_{fuel}	total mass flow of fuel produced	kg/h
$\dot{m}_{fuel,min}$	minimum total mass flow of fuel to be produced	kg/h
m_{H_2}	mass of hydrogen per mass of fuel	kg/kg
M	molar mass	g/mol, kg/kmol
n	amount of substance	mol
n_C	number of carbon atoms (descriptor)	
n_C	number of palette compounds in a CPM	
\dot{n}_{fuel}	total mole flow of fuel produced	kmol/h
n_{H_2}	moles of hydrogen per mole of fuel	mol/mol
$n_{H_2,max}$	maximum hydrogen demand of fuel production (moles of hydrogen per mole of fuel)	mol/mol
\dot{N}	mole flow of vapor	kmol/s
N_c	number of compounds, i.e., length of property vector \mathbf{y}	
N_d	number of descriptors	
N_m	number of parameters in group contribution model	
N_{pc}	number of principal components in the model	
N_{pls}	number of PLS components in the model	
N_N	number of nodes in a CPM	
N_P	number of pathways in a CPM	
p	pressure	bar, kPa, Pa
\mathbf{p}	column of the loading matrix (PCA / PLS)	
P	parameter in group contribution or QSPR model	
\mathbf{P}	loading matrix (PCA / PLS)	
PC	set of palette compounds	
q	ignition delay prediction from perfect model	ln(ms)
\mathbf{r}	vector of model residuals (PLS)	various
R	universal gas constant	J/(mol·K)
$RMSE$	(weighted) root-mean-square error	
\mathbf{s}	vector of sensitivities	
std	standard deviation of a vector	various
S	pathway selectivity	

S	diagonal matrix of singular values	
<i>SCBO</i>	sum of conventional bond orders (descriptor)	
$t^{1-(\alpha/2)}$	two-tails Student's t-distribution with confidence level α	
<i>t</i>	time	s
<i>t</i>	entry of a score vector	
t	column of the score matrix (principal component)	
<i>T</i>	temperature	K, °C
T	score matrix (PCA / PLS)	
T^2	Hotelling's T^2 diagnostic (PCA)	
$T_{10(m)}/T_{50(m)}$	temperature on the distillation curve where 10 mol-% / 50 mol-% / 90 mol-% of the fuel have been evaporated	°C
$T_{10(v)}/T_{50(v)}$	temperature on the distillation curve where 10 vol-% / 50 vol-% / 90 vol-% of the fuel have been evaporated	°C
<i>u</i>	model input	
u	vector of model inputs	
U	matrix of left singular values	
<i>v</i>	specific volume	m ³ /kg
<i>v</i>	entry of eigenvector	
v	eigenvector	
<i>var</i>	variation (PCA)	%
<i>V</i>	volume / molar volume	m ³ , cm ³ /mol, m ³ /kmol
V	matrix of right singular values	
V_f	volume fraction distilled	
V_F	entry of the covariance matrix	
V_F	covariance matrix	
$V_R^{(0)}$	auxiliary variable in COSTALD method	
$V_R^{(\delta)}$	auxiliary variable in COSTALD method	
V_{shift}	normalized volume increment	
wt_{O_2}	oxygen content (weight fraction)	
W	weight matrix (PLS)	
x'	mole fraction liquid phase	
x''	mole fraction vapor phase	
<i>x</i>	entry of a descriptor matrix/vector	

\bar{x}	mean of column-vector of descriptor data	
x	column-vector of descriptor data	
x'	vector of mole fractions liquid phase	
X	matrix of descriptor data	
y	fuel property (various)	various
\tilde{y}	known fuel property data (various)	various
$\bar{\tilde{y}}$	mean of column-vector of known fuel property data (various)	various
y	vector of fuel property data (various)	various
\tilde{y}	vector of known fuel property data (various)	various
Δy	confidence interval for the prediction	ln(ms)
Y	pathway yield	
z	mole fraction of the blend	
z	vector of mole fractions of the blend	

Greek

α	confidence level	
α	incremental step	
β	vector of regression coefficients (PLS)	
γ	activity coefficient	
$\bar{\delta}$	similarity threshold	
δ	Euclidean distance in the PC space	
δ	vector of Euclidean distances in the PC space	
$\Delta\theta$	confidence interval for model parameter	
$\tilde{\epsilon}$	normally distributed measurement error (zero mean)	ln(ms)
ζ	absolute parameter correlation	
η_{LHV}	LHV efficiency	MJ/MJ
Θ	parameter of group contribution model	
Θ	vector of model parameters	
χ	auxilliary variable	
λ	air-fuel equivalence ratio	
λ	eigenvalue	
μ	dynamic viscosity	Pa·s
ν	kinematic viscosity	mm ² /s
v	stoichiometric coefficient	
ξ	mass fraction of the blend	
ρ_L	liquid density	kg/m ³

ρ_m	molar liquid density	kmol/m ³ , mol/cm ³
σ	surface tension	N/m, mN/m
$\tilde{\sigma}$	measurement standard deviation	ln(ms)
$\tilde{\sigma}$	vector of measurement standard deviations	ln(ms)
τ	IQT ignition delay	ms
ϕ	objective function in parameter estimation	
φ	length of vector	
ω	acentric factor	

Subscripts

$5NTN$	five nearest training neighbors
a	first-order structural group index
$a2$	second-order structural group index
$a3$	third-order structural group index
b	descriptor index
$boil$	normal boiling point
bp	bubble point pressure (approximated Reid vapor pressure)
c	combustion cycle index (measurement index)
$crit$	critical state
D	distillate
ext	external validation set
f	enthalpy of formation
h	pathway index
i	index (component / compound)
j	index (component / compound)
k	pathway index
l	index
L	liquid
max	maximum value
min	minimum value
$melt$	melting point
nAB	number of aromatic bonds (descriptor)
$nCCDB$	number of carbon-carbon double bonds (descriptor)
nTC	number of tertiary carbon atoms (descriptor)

nQC	number of quaternary carbon atoms (descriptor)
p	model parameter index
$P1$	biomass fractionation and depolymerization pathway
q	model parameter index
$Reid$	Reid vapor pressure
$S1$	biomass supply pathway
$S2$	hydrogen supply pathway
$thre$	threshold value
vap	enthalpy of vaporization
V	vapor
x	number of carbon atoms
y	number of hydrogen atoms
z	number of oxygen atoms

Superscripts

*	optimal value
0	reference state
cum	cumulative
j	eigenvector/eigenvalue index
lb	lower bound
$norm$	normalization factor
S	vapor pressure
t	model candidate index
$test$	test set (external validation set)
ub	upper bound

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Abstract

The present thesis describes model-based strategies for the identification of pure and multicomponent cellulosic biofuel candidates that exhibit tailored properties for use in high-efficiency, low-emission internal combustion engines. Following a description of the theoretical foundations of fuel design, an algorithm for the targeted generation of candidate structures is proposed that facilitates an exploration of the molecular search space by means of a rule-based approach resembling carbon- and energy-efficient chemo-catalytic refunctionalization of bio-derived platform chemicals. Model-based evaluation of the obtained structures is based on a group contribution method that is capable of predicting the derived cetane number (DCN) of oxygenated hydrocarbon species directly from molecular structure. Furthermore, the virtual fuel screening relies on tailored quantitative structure-property relationship (QSPR) models which can predict a range of important physicochemical fuel properties based on molecular descriptors computable from the two-dimensional molecular graph. The analysis of two comprehensive case studies reveals that compact ketones, furans and esters represent knock-resistant compounds which also exhibit favorable thermophysical properties deemed important for the in-cylinder mixture formation process in spark-ignition (SI) engines. In contrast, cyclic and acyclic ethers of moderate size readily auto-ignite and therefore represent first choice candidates for compression-ignition (CI) engines. Moreover, the high fuel oxygen contents, the low viscosities and the high volatilities of the ether compounds are expected to result in low levels of engine-out soot emissions. Finally, an optimization-based approach for the formulation of multicomponent biofuels by means of integrated product and pathway design is presented. Here, the objective is to maximize a process-related quantity, i.e., the energy of fuel produced (in terms of the lower heating value), and the constraints in the problem formulation allow to define target ranges for the blend's physicochemical properties. To account for non-ideal mixture behavior with respect to two important properties of SI engine fuels, i.e., the Reid vapor pressure and the distillation curve, the nonlinear program includes the UNIFAC group contribution model. Application of the new design methodology to a case study underlines the significance of performing combined product and pathway design, since only few investigated blends are found to exhibit both the desired fuel properties and attractive process-related properties.

Kurzfassung

Die vorliegende Arbeit beschreibt modellbasierte Strategien zur Identifikation lignocellulosebasierter Kraftstoffkandidaten mit vielversprechenden Eigenschaften für den Einsatz in hoch-effizienten und schadstoffarmen Verbrennungsmotoren. Auf Basis theoretischer Grundlagen zum molekularen Maßschneiden von Kraftstoffen wird dabei zunächst ein Algorithmus zur zielgerichteten Molekülstrukturgenerierung vorgestellt, der den Suchraum mittels eines regelbasierten Ansatzes systematisch aufspannt und dabei dem Konzept einer selektiven Refunktionalisierung biobasierter Plattformchemikalien folgt. Für die modellbasierte Bewertung der so erhaltenen Strukturen liefert die vorliegende Arbeit einen essentiellen Baustein in Form einer Gruppenbeitragsmethode zur Vorhersage der abgeleiteten Cetanzahl (engl. Abk. DCN). Daneben fußt die virtuelle Kraftstoffsuche vor allem auf maßgeschneiderten quantitativen Struktur-Eigenschafts-Beziehungen (engl. Abk. QSPR), die wesentliche Kraftstoffeigenschaften als Funktion molekularer Deskriptoren beschreiben. Die Analyse umfangreicher Fallstudien zeigt, dass kompakte Ketone, Furane und Ester sehr klopfeste Verbindungen darstellen, die zudem günstige Eigenschaften für die Gemischbildung im Ottomotor aufweisen. Für den Dieselmotor hingegen kommen vor allem cyclische und acyclische Ether mittlerer Größe in Frage, da diese Stoffe eine hohe Zündwilligkeit besitzen. Die hohen Sauerstoffgehalte, die vergleichsweise niedrigen Siedepunkte und die geringen Viskositäten der Etherkraftstoffe lassen zudem niedrige Partikelemissionen bei der Verbrennung im Dieselmotor erwarten. Schließlich wird ein optimierungsbasierter Ansatz vorgestellt, der ein integriertes Produkt- und Pfadentwurfsproblem zur Formulierung von Kraftstoffmischungen mit gewünschten Eigenschaften löst. Im Zielunktional der Optimierung steht dabei mit der produzierten Energiemenge des Kraftstoffs (gemessen am Heizwert) eine prozessrelevante Größe. Die in den Nebenbedingungen des Problems auftretenden Stoffdatenmodelle erlauben die Beschränkung physikalisch-chemischer Kraftstoffeigenschaften und umfassen die UNIFAC-Gruppenbeitragsmethode, um die Einflüsse von nicht-idealem Mischungsverhalten auf Dampfdruck und Destillationskurve zu beschreiben. Die Anwendung der neuen Entwurfsmethode auf eine Fallstudie verdeutlicht die Wichtigkeit einer integrierten Betrachtung von Produkt- und Pfadentwurf, denn nur eine kleine Zahl der untersuchten Gemische weist neben den wünschenswerten Kraftstoffeigenschaften auch attraktive Prozesseigenschaften auf.