COST Action CM0901 Detailed Chemical Models for Cleaner Combustion

BOOK OF ABSTRACTS

IV Annual Meeting

Dipartimento di Chimica
Università degli Studi di Perugia
Perugia, Italy
September 16-18, 2013

Edited by Nadia Balucani

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Virt&l-Comm is a new international online electronic scientific magazine offering a forum for presenting the work carried out by Virtual Innovation, Research, Teaching & Learning Communities. This magazine is the result of a joint endeavour of the COMPCHEM Virtual Organization (VO), of the European Chemistry Thematic Network (ECTN) Association and of the University of Perugia spinoff Master-Up.

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Virt&l-Comm publishes at present two issues per year to promote Molecular and Materials Science, Teaching and Learning, Computer Science research. The magazine is also specialized in education and innovation and focuses on Service Oriented approaches. Therefore, in addition to articles, news, projects, reports of (successful or failed) attempts to build services relevant to the field of interest, lists of best practices, products used, the advantages and disadvantages of the solutions adopted will be considered for publication. In particular, all the information useful to build the puzzle of innovative complex applications in education (EDU), information and communication tecnology (ICT) and research and development (R&D) in Molecular and Materials science are welcome.

BOOK OF ABSTRACTS

of the

IV Annual Meeting

of the

COST Action CM0901
Detailed Chemical Models for Cleaner Combustion

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Welcome to Perugia!

Inhabited since the XI century BC, Perugia developed as one of the main Etruscan cities, being one of the 12 confederate cities (lucomonie) of Etruria. After entering the Roman domain following the Battle of Sentinum (295 BC), Perugia assisted Rome in the Second Punic War and was actively involved in the war between Octavian and Marcus Antonius. After a long siege, it was reduced and destroyed by Octavian. It was subsequently rebuilt and called Augusta Perusia. Under the popes since the IX century, by the XI century Perugia had become a Comune with an independent life, warring against neighbouring cities like Assisi, Spoleto, Todi, Siena, Arezzo. On occasion of several tumults in Rome, the popes found asylum in Perugia. Five conclaves (leading to the election of Honorius III in 1216, Clement IV in 1285, Celestine V in 1294 and Clement V in 1305) took place in Perugia.

Perugia is a well-known cultural and artistic center. Pietro Vannucci (called Perugino), was active in Perugia. Perugino was the mentor of Raphael, the great Renaissance artist, who spent many years in the town. Pinturicchio was another famous painter active in Perugia.

Among the best sights of Perugia, the ***Palazzo dei Priori*** *(seat of the independent Comune, built at the end of the XIII century and hosting the Collegio della Mercanzia and Collegio del Cambio, whose frescoes by Perugino represent one of the masterpieces of the Italian Renaissance),* ***Fontana Maggiore*** *(one of the most important examples of the medieval Italian Sculpture),* ***Rocca Paolina*** *(built at the end of the Salt War over the houses and streets of an entire neighborhood where the rebels were used to live; the 'underground town' is open and used as a pedestrian shortcut from parking lots to the top of the town), the* ***Etruscan Arch*** *(built in the III century BC), the Cathedral, the churches of San Francesco al Prato, Sant'Ercolano, San Domenico, San Pietro, Sant'Angelo (the oldest church in town built in the V-VI centuries).*

Perugia is a university town, hosting the University of Perugia founded in 1308 (ca 35,000 students), the University for Foreigners (ca 5,000 students), the Academy of Fine Arts "Pietro Vannucci" founded in 1573, the Music Conservatory of Perugia, founded in 1788. There are annual festivals and events: the Eurochocolate Festival (October), the Umbria Jazz Festival (July), and the International Journalism Festival (in April).

Perugia and Assisi together are candidates as European Capital of Culture 2019.

Introduction to the COST Action CM0901 Detailed Chemical Kinetic Models For Cleaner Combustion

General background

It is now well established that the use of traditional fossil fuels is largely responsible for causing global warming, acid rain, tropospheric ozone enhancement etc. Yet 91% of the world's primary energy supply was derived from combustion in 2005 and this situation is unlikely to change in the near term. In Europe, about 12% of the overall emissions of carbon dioxide (CO_2), the main reenhouse gas, comes from the fuel consumed by passenger cars. Road transport is the dominant source of ozone precursors, accounting for 34% of their emissions. Despite increasing concerns about this problem, there is still not enough known about the hazards associated with the combustion of natural gas and petroleum-based fuels and with that of the proposed alternatives. This is due to a poor understanding of the presently exploited combustion processes.

As an example, industry is developing more efficient and cleaner gas turbines and new types of engines such as the Homogeneous Charge Compression Ignition (HCCI) one. The HCCI engine combines the advantages of spark ignition engines with those of compression ignition or Diesel ones. The homogenous fuel/air mixture or charge guarantees low particulate emissions. High dilution leads to very low NOx production, while still maintaining the high working efficiency of the Diesel engine. However the main challenge for the successful operation of HCCI engines is the difficulty in controlling the moment of auto-ignition, which is directly governed by chemistry.

Such new developments have prompted the recent growth of industrial projects targeted to the development of detailed chemical kinetic models for the combustion of hydrocarbons. However, the focus of these models is mostly to simulate the main combustion parameters (auto-ignition delay times, laminar flame speed, heat release), which are needed for the design of engines or turbines and to estimate the fuel consumption and the formation some of the main regulated pollutants (carbon monoxide, nitrogen oxides, unburned hydrocarbons and particulate matter).
The state-of-the-art shows that very little thought has been given to the prediction of hazardous minor combustion products, such as alkenes, dienes, aromatics and polyaromatics, aldehydes, enols, ketones, alcohols, oxides of sulphur, etc., which can be toxic for human health and are of great importance for air pollution, as they are involved in the formation of urban smog and acid rain. Most of the models largely quoted in the literature do not give a satisfactory description of these important intermediate species and that is partly due to an incomplete understanding of possible reaction channels and partly to a lack of accuracy in the rate coefficients.

At the same time there is an increasing emphasis in shifting from hydrocarbon fossil fuels to biofuels (particularly bioethanol and biodiesel) in order to mitigate climate change and the impending scarcity of resources. Since the principal components of plant matter, cellulose and starch have a molecular formulae $(C_6H_{10}O_5)_n$, this means that these new fuels will contain substantial amounts of oxygen which will have both positive and negative impacts on exhaust emissions. Positive - reduction in particulate emissions, negative — increased propensity to form toxic by-products such as aldehydes. Therefore, a deeper understanding of oxygenate bio-fuel combustion chemistry is also necessary to fully exploit positive aspects and minimize negative ones. Unfortunately, there is a clear scarcity of detailed models and kinetic data for oxygenated compounds. That is especially the case of alcohols, glycols and ethers — gasoline additives and substitutes.

Accordingly, a better understanding of combustion chemistry is a high priority challenge which must be taken up before any further developments of innovative combustion processes are undertaken and before biofuel usage becomes widespread. A strong improvement of the understanding of combustion reaction schemes can only be obtained through a long-term, transnational and interdisciplinary collaborative project based on a wide range of academic and industrial expertise in these different fields, as will be made in this Action. The need for a COST Action in this field is made even more impellent by the recent decisions of the US government and the launch of US scientific networks of several universities and national laboratories aimed at developing economically valuable computational chemistry models for gasoline, diesel and jet fuels. At the European level several calls were issued by the last Framework Programme in the area of "Sustainable development, global change and eco-systems". While the development of cleaner engines for road and maritime transport were promoted by the NICE, GREEN, RENEW and HERCULES integrated projects and the ECO-ENGINES Network of Excellence, their interest in combustion chemistry was mostly marginal. Current European Union (EU) FP7 programmes are only concerned with bio- and renewable-fuels production and the development of power trains using them. However the innovative character of investigating combustion chemistry to promote the development of cleaner engines has been already recognized at European level by awarding an advanced researcher ERC grant (Clean-ICE). Therefore, an Action of the Chemistry and Molecular Science and Technology domain can offer the proper collaborative European environment for bridging theory with modeling and experiment and conjugating fundamental with applied research in testing cleaner combustion technologies. This COST Action does not cut across any ongoing initiatives in Europe - no other COST Chemistry Action exists with a similar scientific content.

Objectives

The main objective of this Action is to develop cleaner and more efficient combustion processes through the design and implementation of better defined and more accurate detailed chemical kinetic models. The main deliverable of the present Action will be the design of a prototype model for the combustion of alternative fuels capable of increasing our understanding and possessing genuine predictive power.

At the scientific level the secondary objectives of this Action are:

- Improved Chemical Kinetic Models: Enlargement of the range of families of initial reactants for which well-validated combustion models are available. Gaining improved understanding of the reaction pathways and relative efficiency specific to alcohols, esters, glycols, ethers and other oxygenates. Development of methods to facilitate the use of quantum chemistry and dynamics calculations in the exploration of reaction channels, in particular for the combustion of large molecular weight compounds which most closely represent real fuels and for those species such as enols which have only recently been identified in flames and plasma discharges and whose gas-phase chemistry is almost completely unknown.
- Minor Combustion Product Prediction: Improvement of the prediction of those hazardous minor products of combustion which are of principal concern; for example, alkenes, dienes, aldehydes, ketones, alcohols, aromatics and polyaromatics, nitrogen oxides, soot. Development of a network of contacts with researchers in atmospheric chemistry through mutual exchanges of research personnel and other means with a view to identify products for which more accurate predictions will have the larger impacts. An effort will be made to promote a more comprehensive analysis of the minor species formed during combustion process.
- More Accurate Parameters: Determination of thermochemical parameters and rate coefficients for elementary steps crucial for successful simulation, using high-level classical, semiclassical and quantum dynamical methodologies combined with statistical approaches for the appropriate range of temperature.

- Validation Experiments: Enlargement of the range of experimental conditions and devices for which data for validation of models are available, and, which mimic more closely the pressures and to a lesser extent the temperatures encountered in industrial combustion units.

As a network, this Action aims to:

- Cooperation: Bring together the leading European groups across disciplines, but within the range of expertise needed to tackle the problem of modeling cleaner combustion through cooperative distributed computing (on the European computing Grid) and experimenting.
- Information Exchange: Share information relating to ongoing experiments and computations to maximise the integration and potential value of said work which is currently taking place largely in isolation.
- Training: Train young scientists in a strongly interdisciplinary field of research.
- Improved gender ratio: Attempt to make the field more attractive to female researchers by highlighting the lead role played by women in this Action and ensuring that all committees etc. adhere to the most positive gender ratio possible.
- Increased Interaction: Facilitate the exchange of researchers, particularly those newly embarked on their training, between laboratories from COST countries, so as to maximise the exposure that they receive to different aspects of a common problem.
- New Common Proposals: Act as a platform for initiating possible common proposals for EU FP7 programmes, including Marie-Curie Initial Training Networks.
- Dissemination: Disseminate the fruits of the Action to the wider scientific and engineering communities.
- Industrial Cooperation: Ensure the rapid translation of new knowledge in the field towards actual industrial application.
- Competitiveness: Promote the competitiveness of European academic and industrial partners in the field at the worldwide level.

Program of the 4th annual meeting of the COST Action CM0901 "Detailed chemical kinetic models for cleaner combustion"

16-18 September 2013

Department of Chemistry, University of Perugia, Italy

Monday, 16 September 2013

8:15 - 9:00 - Registration

9:00 – 9:15 Welcome
F. Battin-Leclerc and N. Balucani

Working Group 1: Enlargement of the range of families of initial reactants for which well-validated detailed combustion models are available

Chair: T. Faravelli

9:15 – 9:30 Experimental and kinetic modelling study of C3-C5 *n*-aldehydes auto-ignition and pyrolysis in shock tubes
M. Pelucchi[1], K. P. Somers[2], U. Burke[2], C. Saggese[1], A. Frassoldati[1], K. Yasunaga[3], E. Ranzi[1], H. J. Curran[2], T. Faravelli[1]
[1] Department of Chemistry, Materials, and Chemical Engineering, Politecnico di Milano, Milano, Italy
[2] Combustion Chemistry Centre, National University of Ireland, Galway, Ireland
[3] Department of Applied Chemistry, National Defense Academy, Yokosuka, Japan

9:30 – 9:45 Experimental study of pollutants formation in laminar premixed flames of tetrahydrofuran family fuels
L.-S. Tran, M. Verdicchio, P.-A. Glaude, F. Battin-Leclerc
Laboratoire Réactions et Génie des Procédés (LRGP), CNRS, Université de Lorraine, Nancy, France

9:45 – 10:00 Modeling the decomposition chemistry of renewable fuels
K. M. Van Geem[1], R. De Brucker[1], H. H. Carstensen[1], J. Simmie[2], G. B. Marin[1]
[1] Laboratory of Chemical Technology, Ghent University, Belgium
[2] Combustion Chemistry Centre, NUI Galway, Ireland

10:00 – 10:15 On the mechanism of partial methane oxidation
A. Fomin[1], M. Poliak[1], I. Rahinov[2], V. A. Alekseev[3], A. A. Konnov[3], V. Tsionsky[1], S. Cheskis[1]
[1] School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv, Israel
[2] Department of Natural Sciences, The Open University of Israel, Raanana, Israel
[3] Lund University, Lund, Sweden

10:15 – 10:30 First principles kinetics of alkyl radicals

A. Ratkiewicz

University of Bialystok, Bialystok, Poland

10:30 – 10:45 Methane oxidation under fuel-rich conditions using pulsed-flame setup

A. Fomin[1], T. Zavlev[1], V. Tsionsky[1], I. Rahinov[2], S. Cheskis[1]

[1] School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv, Israel

[2] Department of Natural Sciences, The Open University of Israel, Raanana, Israel

10:45 – 11:00 The role of CO_2 and H_2O on ignition chemistry in MILD (diluted, pre-heated) combustion condition

M. de Joannon[1], P. Sabia[1], R. Ragucci[1], A. Cavaliere[2]

[1] Istituto di Ricerche sulla Combustione, CNR, Naples, Italy

[2] DICMAPI, University Federico II, Naples, Italy

11:00 – 11:30 Poster session and coffee break

Chair: F. Battin-Leclerc

11:30 – 12:00 Topical lecture: Methodology for emission prediction at the exit of a turbofan combustor based on chemical reactor network and detailed chemical kinetics of aviation fuels

M. Yahyaoui[1], A.-S. Ananthakrishnan[2], E. Joubert[1], I. Lombaert-Valot[1]

[1]EADS Innovation Works, Suresnes, France

[2]Institut Supérieur de l'Aéronautique et de l'Espace, Toulouse, France

Working Group 2: Writing models of the formation and consumption of oxygenated pollutants

Chair: H. Curran

12:00 – 12:15 A kinetic modeling study of major C1-C6 and PAH species in propyne and allene pyrolysis

G. Vourliotakis[1], M. Braun-Unkhoff[2], M.A. Founti[1]

[1] National Technical University of Athens, Laboratory of Heterogeneous Mixtures & Combustion Systems, Athens, Greece

[2] DLR, German Aerospace Centre, Institute of Combustion Technology, Stuttgart, Germany

12:15 – 12:30 Kinetic modelling and experimental study of a fuel rich, premixed n-heptane flame

L. Seidel[1], K. Moshammer[2], X. Wang[1], T. Zeuch[3], F. Mauss[1], K. Kohse-Höinghaus[2]

[1] Chair of Thermodynamics / Thermal Process Engineering – BTU-Cottbus, Cottbus, Germany

[2] Department of Chemistry, Bielefeld University, Bielefeld, Germany

[3] Institut für Physikalische Chemie – Georg-August-Universität Göttingen, Göttingen, Germany

12:30 – 12:45 Evaluation of straw with absorbed glycerol destruction during combustion and pyrolysis by TG-FTIR and TG-GC/MS

N. Striūgas, G. Stravinskas

Lithuanian Energy Institute, Kaunas, Lithuania

12:45 – 13:00 A combined modeling and experimental study of the combustion of 1,3-butadiene/butanol

M. Braun-Unkhoff[1], T. Kathrotia[1], N. Hansen[2]

[1] *Institute of Combustion Technology, German Aerospace Center (DLR), Stuttgart, Germany*

[2] *Sandia National Laboratories, Livermore (CA), USA*

13:00 – 13:15 Laminar burning velocities of C4 - C7 ethyl esters: Experiments and modeling

G. Dayma[1,2], F. Halter[1], F. Foucher[1], C. Mounaïm-Rousselle[1], P. Dagaut[2]

[1] *University of Orléans, Orléans, France*

[2] *CNRS, Orléans, France*

13:15 – 13:30 Premixed flames of dimethyl carbonate with air

M. E. Bardin, V. A. Vinokurov, E. V. Ivanov, E.J.K. Nilsson, A. A. Konnov

Division of Combustion Physics, Department of Physics, Lund University, Lund, Sweden

13:30 – 15:00 Lunch

Chair: A. Konnov

15:00 – 16:00 Fuel flexibility of Siemens industrial gas turbines

J. Larfeldt

Siemens Industrial Turbomachinery, Finspang, Sweden

Working Group 2: Writing models of the formation and consumption of oxygenated pollutants

Chair: H. Curran

16:00 – 16:15 A detailed kinetic modeling study of the combustion of C1-C2 oxygenated fuels in laminar premixed flames

A. Gazi, G. Vourliotakis, G. Skevis, M. A. Founti

National Technical University of Athens, Laboratory of Heterogeneous Mixtures & Combustion Systems, Athens, Greece

16:15 – 16:30 Sensitivity analysis of methanol flames with air and under oxy-fuel conditions

J. D. Nauclér[1], L. Sileghem[2], E. J. K. Nilsson[1], S. Verhelst[2], A. A. Konnov[1]

[1] *Combustion Physics, Department of Physics, Lund University, Lund, Sweden*

[2] *Department of Flow, Heat and Combustion Mechanics, Ghent University, Gent, Belgium*

16:30 – 16:45 Investigation of the effect of hydrogen on particle formation from hydrocarbons

M. Fikri[1], M. Aghsaee[1], H. Böhm[1], H. Jander[2], A. Eremin[3], C. Schulz[1]

[1] *IVG, Institute for Combustion and Gas Dynamics – Reactive Fluids, and CENIDE, Center for Nanointegration, University of Duisburg-Essen, Germany*

[2] *Institut für Physikalische Chemie, University of Göttingen, Germany*

[3] *Institute for High Energy Density, Russian Academy of Sciences, Moscow, Russia*

16:45 – 17:15 Poster session and coffee break

Working Group 3: Improvements of the models for formation of polyaromatic compounds and soot

Chair: M. Alzueta

17:15 – 17:30 Interactions between SO_2 and ethylene. Experimental and modeling study
M. Abián, A. Millera, R. Bilbao, M. U. Alzueta
Aragón Institute of Engineering Research (I3A), Chemical and Environmental Engineering Department, University of Zaragoza, Spain

17:30 – 17:45 Numerical and experimental investigation and soot formation and particle size distributions in laminar premixed flames
S. Salenbauch, I. Frenzel, D. Trimis, C. Hasse
TU Bergakademie Freiberg, Germany

17:45 – 18:00 Electrochemical testing of metal dissolution kinetics in bioethanol fuels
S. J. Asadauskas, S. Lichusina, A. Griguceviciene
Institute of Chemistry, Center for Physical Sciences and Technology, Vilnius, Lithuania

Tuesday, 17 September 2013

Working Group 3: Improvements of the models for formation of polyaromatic compounds and soot

Chair: M. Alzueta

9:00 – 9:15 Experimental and modeling study of acetylene conversion in a tubular reactor: Polycyclic aromatic hydrocarbon (PAH) and soot formation
N.E. Sánchez[1], C. Saggese[2], A. Frassoldati[2], A. Cuoci[2], T. Faravelli[2], E. Ranzi[2], A. Callejas[1], A. Millera[1], R. Bilbao[1], M.U. Alzueta[1]
[1] Aragón Institute of Engineering Research (I3A), Department of Chemical and Environmental Engineering, University of Zaragoza, Zaragoza, Spain
[2] Politecnico di Milano, Milano, Italy

9:15 – 9:30 Carbon tracking during lab-scale pyrolysis and combustion of refuse derived fuels
R. B. Silva[1], C. Arnal[3], S. Martins-Dias[1], M. Costa[2], M. U. Alzueta[3]
[1] IBB- Institute for Biotechnology and Bioengineering, Centre for Biological and Chemical Engineering, Instituto Superior Técnico, Lisbon, Portugal
[2] Mechanical Engineering Department, Instituto Superior Técnico, Lisbon, Portugal
[3] Aragón Institute of Engineering Research (I3A), University of Zaragoza, Zaragoza, Spain

9:30 – 9:45 Modelling of soot formation and oxidation in benzene and hexane diffusion flames
M. Sirignano, A. D' Anna
DIC.MA.PI, Università degli Studi di Napoli Federico II, Napoli, Italy

9:45 – 10:00 Effect of flue gas recirculation on particulate matter emissions from a domestic pellet-fired boiler
U. Fernandes, M. Henriques, M. Costa
Mechanical Engineering Department, Instituto Superior Técnico, Technical University of Lisbon, Avenida Rovisco Pais, Lisboa, Portugal

10:00 – 10:15 Dehydrogenation and aromatization of growing soot particles
C. Russo, F. Stanzione, A. Tregrossi, A. Ciajolo
Istituto di Ricerche sulla Combustione, IRC-CNR, Napoli, Italy

10:15 – 10:30 Combustion intermediates relevant to gas phase soot precursor's formation in acetylene flames
I. Naydenova[1], E. Goos[2], T. Petrova[1], U. Riedel[2], I. Ganev[1]
[1] Technical University of Sofia, College of Energy and Electronics, Department Industrial Power Engineering, Sofia, Bulgaria
[2] DLR, German Aerospace Center, Institute of Combustion Technology, Stuttgart, Germany

10:30 – 11:00 Poster session and coffee break

Working Group 4: Improvements of models for mechanism reduction uncertainty analysis

Chair: A. Tomlin

11:00 – 11:15 The value of uncertainty studies for the evaluation and improvement of combustion models
A.S. Tomlin
Energy Research Institute, University of Leeds, UK

11:15 – 11:30 Consistent chemical mechanism from collaborative data processing: H_2/CO mixtures
N.A. Slavinskaya[1], U. Riedel[1], H. Lerch[2], W. Speight[2], A. Packard[2], M. Frenklach[2]
[1] German Aerospace Center (DLR), Institute of Combustion Technology, Stuttgart, Germany
[2] University of California, Berkeley

11:15 – 11:30 Comparison of chemical kinetic mechanisms for lean methane/propane mixture ignition at high pressures
R. Bardolf, F. Winter
Vienna University of Technology, Vienna, Austria

11:45 – 12:00 Modeling of Particle Size Distribution Function of Incipient Soot Formed In Laminar Premixed Flames
C. Xu, F. Mauss
Thermodynamics and Thermal Process Engineering, Brandenburg University of Technology, Cottbus,Germany

12:00 – 12:15 Kinetic analysis of ethyl iodide pyrolysis based on shock tube measurements
T. Varga[1], I. Gy. Zsély[1], T. Turányi[1], T. Bentz[2], and M. Olzmann[2]
[1]Institute of Chemistry, Eötvös University (ELTE), Budapest, Hungary
[2]Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

12:15 – 12:30 Global sensitivity analysis of dimethyl ether oxidation in an atmospheric pressure laminar flames using open-source software tools: a case study
J. Dlabka[1], M. Vašinek[1], L. Pečínka[1], V. Nevrlý[1], A. S. Tomlin[2], Z. Zelinger[3]
[1] VŠB – Technical University of Ostrava, Faculty of Safety Engineering, Ostrava, Czech Republic
[2] Energy Research Institute, University of Leeds, UK
[3] Academy of Sciences of the Czech Republic, J. Heyrovský Institute of Physical Chemistry, Praha, Czech Republic

12:30 – 12:45 Reaction mechanism reduction and optimization by evolutionary algorithms
N. Sikalo, O. Hasemann, C. Schulz, I.Wlokas, A. Kempf
IVG, Institute for Combustion and Gasdynamics, University of Duisburg-Essen, Germany

12:45 – 15:00 Lunch

15:00 – 22:00 Excursion to Assisi and Social Dinner

Wednesday, 18 September 2013

Chair: N. Balucani

9:00 – 10:00 Plenary Talk: Low temperature kinetics studies of reactions relevant for combustion
S. Le Picard
Département de Physique Moléculaire, Institut de Physique de Rennes, UMR6251 du CNRS - Université de Rennes 1, Rennes, France

Working Group 4: Improvements of models for mechanism reduction uncertainty analysis

Chair: A. Tomlin

10:00 – 10:15 The effect of argon dilution on the structure of dimethylether cup-burner flame
V. Nevrlý[1], *P. Bitala*[1], *J. Dlabka*[1], *L. Pečínka*[1], *M. Vašinek*[1], *A. Cuoci*[2], *A. Frassoldati*[2], *Z. Zelinger*[3]
[1] *VŠB – Technical University of Ostrava, Faculty of Safety Engineering, Ostrava, Czech Republic*
[2] *Politecnico di Milano, Milano, Italy*
[3] *Academy of Sciences of the Czech Republic, J. Heyrovský Institute of Physical Chemistry, Praha, Czech Republic*

10:15 – 10:30 On the structure of hydrogen, carbon monoxide and methanol combustion models
J. Tóth, A. László Nagy, I. Gyula Zsély
Department of Analysis, Budapest University of Technology and Economics, Budapest, Hungary

10:30 – 10:45 Evaluation of the influence of thermodynamic data for propane and propene ignition delay times
L. León[1], E. Goos[2], C. Klauer[1], L. Seidel[1], F. Mauss[1], T. Zeuch[3]
[1] *Chair of Thermodynamics / Thermal Process Engineering – BTU-Cottbus, Cottbus, Germany*
[2] *Institute of Combustion Technology, DLR German Aerospace Center, Stuttgart, Germany*
[3] *Institut für Physikalische Chemie – Georg-August-Universität Göttingen, Göttingen, Germany*

Working Group 5: Experimental and theoretical determination of thermochemical parameters and rate coefficients for elementary steps crucial for successful simulation, but for which important uncertainties remain

Chair: M. Olzmann

10:45 – 11:00 Elementary chemical steps in combustion – From biofuels to NOx formation
M. Olzmann
Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

11:00 – 11:15 Ab initio characterization of the cresol potential energy surface
H.-H. Carstensen[1], M.-F. Reyniers[1], G. B. Marin[1], A. M. Dean[2]
[1] *Laboratory for Chemical Technology (LCT), Ghent University, Gent, Belgium*
[2] *Chemical and Biological Engineering Department – Colorado School of Mines, CO, USA*

11:15 – 11:30 The chemical kinetics of the reaction R• + HBr(HI) → RH + Br(I)• in the range 293-623 K for R• = C_2H_5•, i-C_3H_7, n-C_3H_7•, and t-C_4H_9•
N. Leplat, A. Wokaun, M.J. Rossi
Laboratory of Atmospheric Chemistry (LAC), General Energy Research (ENE) Division, Paul Scherrer Institut (PSI), Villigen, Switzerland

11:30 – 12:00 Poster session and coffee break

12:00 – 12:15 Reaction dynamics of oxygen atoms with unsaturated hydrocarbons: primary radical and molecular products, branching ratios and role of intersystem crossing
P. Casavecchia, F. Leonori, N. Balucani
Dipartimento di Chimica, Università degli Studi di Perugia, Perugia, Italy

12:15 – 12:30 Reaction kinetics, photochemistry and CI-engine study of γ-valerolactone
S. Dóbé, M. Farkas, Á. Bereczky, G. L. Zügner, Á. Illés, G. Lendvay, K. Lukács, I. Szilágyi, E. Szabó, D. Zsibrita
Institute of Materials and Environmental Chemistry, MTA TTK, Budapest, Hungary

12:30 – 12:45 Ketene Formation from P_2O_3/P_2O_5-catalyzed Pyrolysis of Acetic Acid
N. Sebbar[1], J. Appel[2] and H. Bockhorn[1]
[1] KIT- Karlsruhe Institute of Technology, Engler-Bunte-Institut, Verbrennungstechnik, Karlsruhe, Germany
[2] Clariant Produkte (Deutschland) GmbH , Group Process Development, Werk Gendorf, Industrieparkstraße 1, D- 84504 Burgkirchen, Germany

12:45 – 13:00 Investigation of methylfuran pyrolysis at Swiss Light Source
E. Goos[1], P. Hemberger[2], A. Bodi[2], U. Riedel[1], T. Gerber[2]
[1] DLR German Aerospace Center, Stuttgart, Germany
[2] Paul Scherrer Institut (PSI), Villigen, Switzerland

13:00 – 13:15 Molecular dynamics investigations on xylenes and dimethylfuran at the VUV beamline at Swiss Light Source
T. Gerber, P. Hemberger, Y. Liu, G. Knopp, A. Bodi, P. Radi
Paul Scherrer Institut, Molecular Dynamics, Villigen, PSI, Switzerland

13:15 – 13:30 The decomposition kinetics of xylyl radicals
D. Polino[1], C. Cavallotti[1], R. Sivaramakrishnan[2], S. J. Klippenstein[2], J.V. Michael[2]
[1] Politecnico di Milano, Milano, Italy
[2] Chemical Sciences & Engineering Division, Argonne National Laboratory, Argonne, IL, USA

13:30 – 13:45 A theoretical study of the O + O_2 isotope exchange reaction
G. Lendvay
Research Center for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary

14:00 – 17:30 Final Management Committee Meeting

Poster Session

Production and characterization of oxygenated soot surrogates from carbon black and comparison with real diesel soot

M. Alfè[1], V. Gargiulo[1], C. Arnal[2], M. Alzueta[2], A. Ciajolo[1]
[1] *Istituto di Ricerche sulla Combustione (CNR), Napoli, Italy*
[2] *Aragón Institute of Engineering Research (I3A), Chemical and Environmental Engineering Department, University of Zaragoza, Spain*

Reactivity of two different carbonaceous materials with NO

C. Arnal, M.U. Alzueta, A. Millera, R. Bilbao
Aragón Institute of Engineering Research (I3A), Department of Chemical and Environmental Engineering, University of Zaragoza, Zaragoza, Spain

Crossed molecular beam study of the radical + radical reaction N + OH

N. Balucani[1], A. Bergeat[2], S. Falcinelli[3], F. Leonori[1], D. Stranges[4], P. Casavecchia[1]
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[4] *Dipartimento di Chimica, Università "La Sapienza", P.le A. Moro 5, Rome I-00185, Italy*

Hexadecane Mechanisms: comparison of hand-generated and automatically generated with pathways

E.S. Blurock[1], I.E. Mersin[2,3], H.S. Soyhan[3], A.A. Konnov[2]
[1] *REACTION, Lund, Sweden*
[2] *Combustion Physics, Lund University, Sweden*
[3] *Sakarya University Mechanical Engineering Department, Turkey*

Effects of water vapor on a methane and hydrogen flame

M. Christensen, V. A. Alekseev, E. J. K. Nilsson, A. A. Konnov
Division of Combustion Physics, Department of Physics, Lund University, Lund, Sweden

Validation of chemical mechanisms in rich methane flame using laser absorption spectroscopy diagnostics

A. Fomin[1], I. Rahinov[2], V.A. Alekseev[2], S. Cheskis[1], A.A. Konnov[2]
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[2] *Division of Combustion Physics, Lund University, Lund, Sweden*

Shock tube studies and modeling of the pyrolysis of 2,5-dimethylfuran

L. Genthner[1], P. Friese[1], J. Kiecherer[1], M. Olzmann[1], B. Sirjean[2,3], R. Fournet[2,3]
[1] *Karlsruher Institut für Technologie, Karlsruhe, Deutschland*
[2] *CNRS, LRGP, Nancy, France*
[3] *Universite de Lorraine, LRGP, Nancy, France*

Experimental and theoretical study of $O(^3P) + C_2H_4$ multichannel reaction dynamics

F. Leonori[1], L. Angelucci[1], N. Balucani[1], A. Occhiogrosso[1], R. Petrucci[1], P. Casavecchia[1*] B. Fu[2], Y.-C. Han[2], J. M. Bowman[2]
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New improvements in the direction of analyzing more detailed mechanisms with thepackage ReactionKinetics

A. László Nagy, P. Dávid, J. Tóth
Department of Stochastics, Budapest University of Technology and Economics, Budapest, Hungary

The role of combustion intermediates in soot precursor's formation chemistry

I. Naydenova[1], I. Angelov[1], M. Braun-Unkhoff[2], I. Ganev[1], U. Riedel[2], M. U. Alzueta[3]
[1] Technical University of Sofia, College of Energy and Electronics, Department Industrial Power Engineering, Sofia, Bulgaria
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Crossed molecular beam study of the $O(^3P)$ + propene reaction: Primary products and branching ratios

V. Nevrly[1], A. Bergeat[2], N. Balucani[3], S. Falcinelli[4], F. Leonori[3], P. Casavecchia[3]
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Optimization and uncertainty quantification of a wet CO combustion mechanism

Carsten Olm[1,2,3], Tamás Varga[1,2], István Gy. Zsély[1], Éva Valkó[1,2], Tibor Nagy[1] and Tamás Turányi[1]
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[2] MTA-ELTE Research Group on Complex Chemical Systems, Budapest, Hungary
[3] Chair of Numerical Thermo-Fluid Dynamics, TU Bergakademie Freiberg, Germany

Crossed molecular beam study of the $O(^3P)$ + CH_3CCH reaction

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Development of a hydrogen combustion mechanism using an optimization approach

T. Varga[1,2], T. Nagy[1], R. Pálvölgyi[1], I. Gy. Zsély[1], C. Olm[1,2], G. Vincze[1], É. Valkó[1,2], H. J. Curran[3], T. Turányi[1]
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Experimental and modeling study of the structure of laminar premixed flames of tetrahydrofuran/Oxygen/Argon

M. Verdicchio, L.-S. Tran, P.-A. Glaude, B. Sirjean, F. Battin-Leclerc
Laboratoire Réactions et Génie des Procédés (LRGP), CNRS, Université de Lorraine, Nancy, France

Automatic generation of kinetic models for the oxidation of large alkylbenzenes

V. Warth, B. Husson, R. Bounaceur, P.-A. Glaude, O. Herbinet, F. Battin-Leclerc
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LIST OF CONTRIBUTIONS

Invited Experts

Oral Contributions

Poster Contributions

Invited experts

Fuel flexibility of Siemens industrial gas turbines

Jenny Larfeldt
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Finspang. Sweden

The variety of gaseous fuels that Siemens Industrial Turbomachinery (SIT) is requested to consider during sales enquiries has prompted product development that have allowed to continuously increase SIT gas turbine fuel flexibility. The development has been performed experimentally as close to the real gas turbine as possible implying combustion conditions of 20 bars pressure and excess air ratio of about 2. Numerical simulations are used for guidance on what to expect regarding emissions and combustion related problems such as flashback and flameout compared to standard fuel. Since gas turbine operation involves varying load conditions including ignition, the fuels are today carefully evaluated on a case by case basis.

Low temperature kinetics studies of reactions relevant for combustion

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The use of the CRESU (a French acronym for Reaction Kinetics in Uniform Supersonic Flow) technique coupled with lasers techniques or mass spectrometry allows to study reaction kinetics of neutral-neutral (1) or ion-molecule reactions (2) at very low temperatures, down to 6 K. This technique has had a major impact in astrochemistry and planetology because of the presence of many low temperature environments in space. Our results have shown for instance, that radical-radical, radical-unsaturated molecule and even radical-saturated molecule reactions can be rapid down to the temperatures of dense interstellar clouds (10—20 K).

Low temperature experimental results also provide a stringent test for the theoretical treatment of chemical reactions, thus furnishing detailed information on the quality of a calculated potential energy surface (3). Interestingly, many reactive systems which play an important role in combustion chemistry are of the same relevance in astrochemistry. For instance, understanding the formation of complex molecules and carbonaceous particles in astrophysical environments is currently one of the major topics of this field. Progress in modelling the formation and growth of PAHs in combustion has motivated astrophysicists to propose essentially the same chemistry in space, with PAHs considered as the building blocks of stellar dust. Some interstellar objects such as carbon-rich stars indeed, bear some resemblance to those in combustion. Many other environments however, are much colder with temperatures as low as less than 10 K, and combustion chemical schemes can no longer be applied as the kinetics of many elementary reactions show a very different temperature dependence when reaching this very low temperature regime.

In this contribution, I will present some recent results and perspectives in the field of reaction kinetics at low temperature (≤ 300 K) involving elementary reactions of interest for both fields, astrophysics and combustion.

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Oral Contributions WG1

Working Group 1: Enlargement of the range of families of initial reactants for which well-validated detailed combustion models are avail

Experimental and kinetic modelling study of C_3-C_5 n-aldehydes auto-ignition and pyrolysis in shock tubes

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Alessio Frassoldati[1], Kenji Yasunaga[3], Eliseo Ranzi[1], Henry J. Curran[2], Tiziano Faravelli[1]

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Oxygenated hydrocarbons are implicated in the combustion processes of several fossil fuels either as additives or as intermediate species which can persist at the end of combustion and emerge as pollutants. Aldehydes such as formaldehyde and acetaldehyde are amongst the organic compounds whose emissions from combustors are regulated due to their adverse effects on human health and air quality. With a shift towards using oxygenated biofuels and the interest in the combustion of large molecular weight alcohols (propanol, butanol, pentanol) there is a need to further assess the combustion properties of these species, widely proven to be primary stable intermediates formed during the high temperature oxidation process.

There have been a number of fundamental combustion studies on C_3–C_4 aldehydes [1–7], while no relevant or specific oxidation studies on C_5 aldehydes are available in the recent literature. This kinetic study aims to provide new fundamental data for the combustion and pyrolysis of n-butanal and n-pentanal which in turn form the basis of the validation of two comprehensive chemical kinetic models for the high temperature oxidation of C_3–C_5 aldehydes.

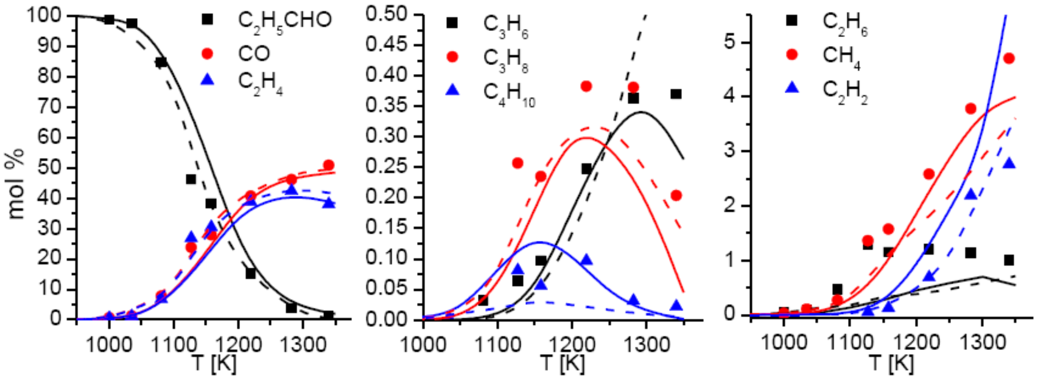

Figure 1: Species profiles from SPST by Lifshitz *et al.*[2], of 1% propanal mixture in Ar. POLIMI (dashed lines) and NUIG (solid lines) model predictions.

Ignition delay time measurements for pure *n*-butanal and *n*-pentanal (1%)–O_2/Ar were carried at equivalence ratios of 0.5, 1.0 and 2.0, at reflected shock pressures of 1 and 3 atm and at reflected shock temperatures of 1100–1850 K using the low pressure shock tube facility described in details by Smith *et al.* [8]. In addition, species profiles were obtained experimentally in a Single Pulse Shock Tube (SPST) previously described by Hidaka *et al.* [9]. Mixtures of 3% *n*-butanal and *n*-pentanal in argon (97%) have been tested at reflected shock pressure of 1.1–2.6 atm, at temperatures in the range 1096–1368 K and at effective heating times of 1.7–2.3 ms.

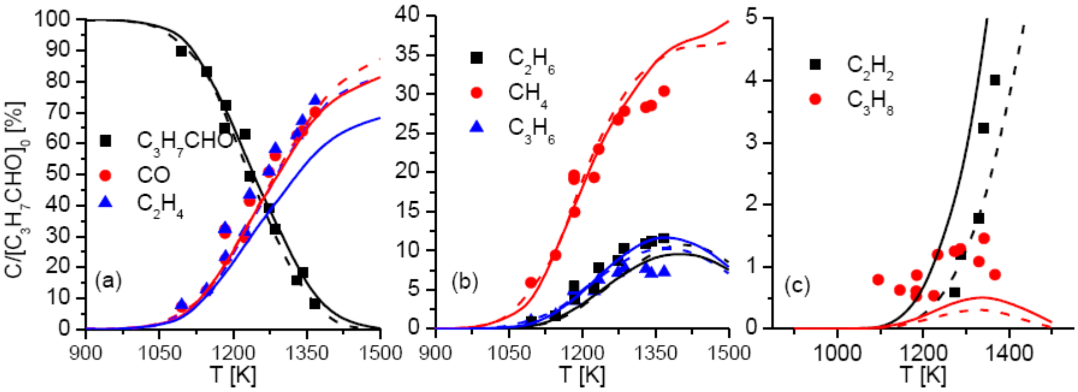

Figure 2 (a-c): Species profile from SPST for 3% n-butanal in Ar. POLIMI (dashed lines) and NUIG (solid lines) model predictions.

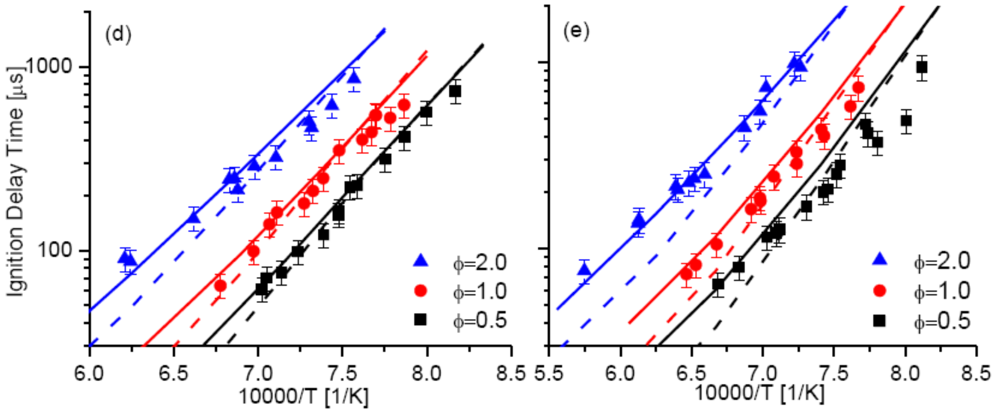

Figure 3 (d,e): Experimental ignition delay times (15% error bars) for mixtures of 1% *n*-butanal in Ar, φ=0.5, 1.0, 2.0. p_5=1 atm (d) and 3 atm (e), POLIMI (dash), NUIG (solid).

detailed mechanism has been developed at the Combustion Chemistry Centre (NUI Galway, Ireland) and a lumped one developed within the research activity of the CRECK Modeling group (Politecnico di Milano, Italy). The figures presented show examples of agreement between experimental results and model predictions. The models show the capability to reproduce the main experimental observations. Detailed analysis of the results will be presented in the final paper.

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Experimental study of pollutants formation in laminar premixed flames of tetrahydrofuran family fuels

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The cyclic ethers of tetrahydrofuran family, e.g. 2-methyltetrahydrofuran (MTHF), 2,5-dimethyltetrahydrofuran (DMTHF), have been recently considered as potential additives to gasoline or diesel fuel and can be produced from biomass. Tetrahydrofuran (THF) is quite well suited as a model fuel for these cyclic ethers, which have been also identified among the emissions produced during the combustion and auto-ignition of alkanes and alkenes by isomerization of alkylhydroperoxy radicals. The subsequent reaction of these cyclic ethers can then influence the overall chemical kinetic mechanisms of combustion of alkanes and alkenes. For all these reasons, it is important to understand the combustion and the oxidation of cyclic ethers. Currently, very little data is available for the combustion of these fuels, especially under laminar premixed low-pressure flame conditions.

In the present study, the combustion chemistry of THF and MTHF were experimentally investigated under similar conditions in laminar premixed low-pressure flames (6.7 kPa; 78 % Ar diluent; φ=0.7, 1.0, and 1.3). Analyses were made by gas chromatography (GC) with a heated (at 423 K) on-line connection to the quartz probe, using three types of columns: Carbosphere, HP-Plot Q, and HP-Molsieve and two types of detectors: flame ionization detection (FID) coupled with a methanizer and thermal conductivity detection (TCD). Stable species were identified by the determination of their individual retention times and by mass spectrometry (GC/MS). The flame temperatures were measured by a rhodium-platinum thermocouple, with a correction using the electrical compensation method for radiative heat losses.

Mole fraction of reactants, mains products (CO, CO_2, H_2, and H_2O), and C_1-C_6 hydrocarbons and oxygenated intermediates were measured as a function of the distance to the burner. A comparison of the combustion of THF and MTHF was also performed regarding the mole fraction of species formed in flames by these two fuels. Some examples are displayed in figure 1. This figure shows that the fuel is completely consumed and the maximum of intermediate formation is reached closer to the burner in the THF flame than in the MTHF one. Ethylene is the most abundant one of all intermediates, with a similar production in both flames. The formation of C_3 aromatic precursors, allene and propyne, benzene and acetaldehyde is favored in the MTHF flame. Several cyclic ethers, such as 2,3-dihydrofuran (2,3-DHF), 2,5-dihydrofuran (2,5-DHF), furan, THF (intermediate in the MTHF flame) and MTHF (intermediate in the THF flame), were identified and quantified in the THF and MTHF flames.

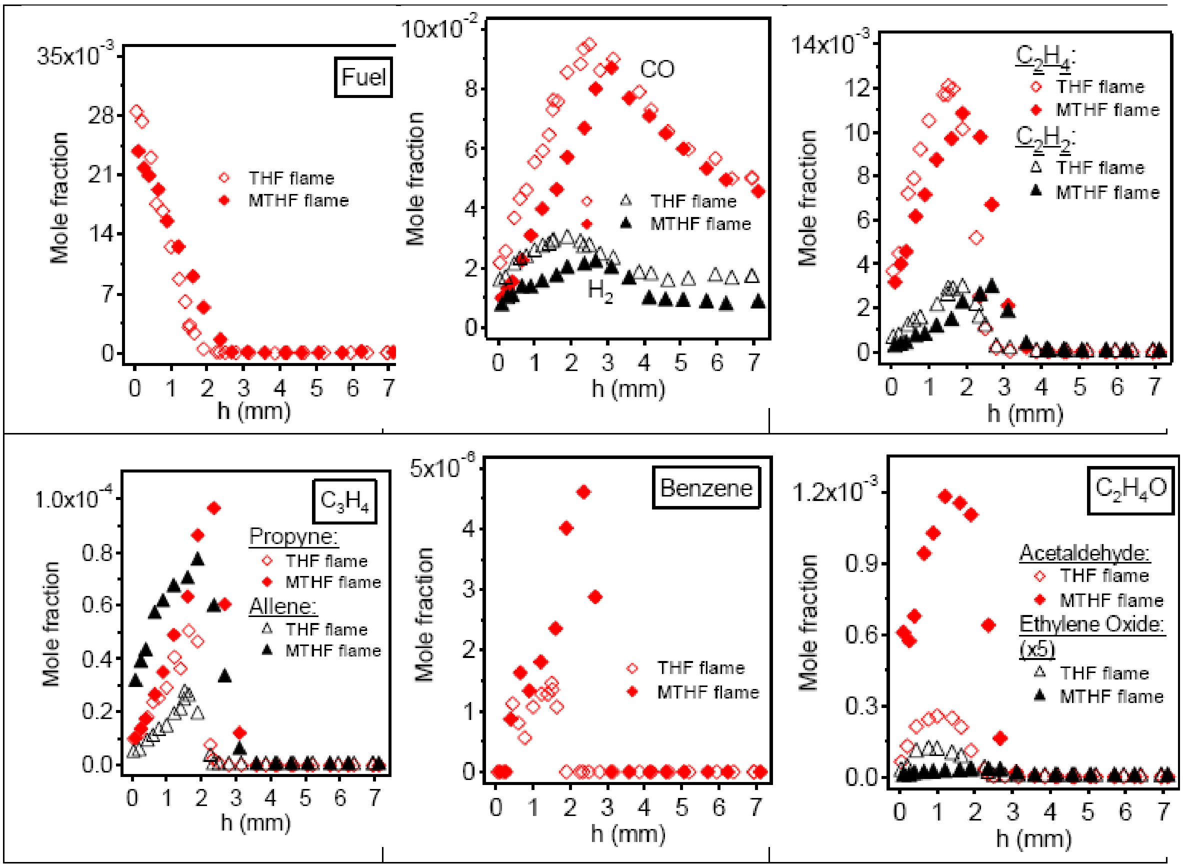

Figure 1: Comparison between THF and MTHF (φ=1.0) for the mole fraction of fuel and of some intermediates measured as a function, to the distance to the burner (h).

The potential pathways of which can be envisaged for the formation of intermediates are discussed and a preliminary modeling mainly based on an EXGAS generated mechanism has also been performed in the case of THF.

This work was funded by the European Commission through the "Clean ICE" Advanced Research Grant of the European Research Council.

Modeling the decomposition chemistry of renewable fuels

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In this contribution we will evaluate the decomposition chemistry of different candidates of renewable fuel (additives) ranging from longer alcohols (butanols, pentanols) to esters (saturated, unsaturated, cyclic) and furans both experimentally and theoretically.
New experimental data have been acquired on a modified setup that is both equipped with a plug flow reactor made out of quartz and Incoloy800HT. The latter allows to determine valuable kinetic data and at the same time evaluate the importance of surface reactions on the decomposition chemistry which could be important for real engines.
The application Gaussian-09 was used to carry out the computation of geometries, frequencies and energies of all the species. The model chemistries CBS-QB3, CBS-APNO and G3 were employed to determine the species enthalpy, H, and free energy, G, at 298.15 K giving a reasonable compromise between accuracy and computational expense [1-5]. In order to verify our method the Thermo module of Multiwell [6] was used to calculate thermodynamic parameters under the rigid rotor harmonic oscillator approximation. In appropriate cases the barriers to internal rotations were computed by relaxed dihedral angle scans at the B3LYP/6-311G(2d,d,p) level and the results treated as 1-dimensional hindered rotors. The ab-initio calculations will be used to show the differences in how these different renewable components decompose under our conditions.

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On the mechanism of partial methane oxidation

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Vladimir Tsionsky[1], and Sergey Cheskis[1]

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The main purpose of this work is to investigate the process of partial methane oxidation, where the methane is oxidized just up to carbon monoxide, CO, and not up to CO_2. This partial oxidation becomes possible under very fuel-rich conditions. Better understanding of methane oxidation under these conditions will allow to develop new technologies for conversion of natural gas to syngas. Syngas production from natural gas can be established as a first stage of the so-called Gas-to-Liquid process (GTL).

Usually, the GTL process involves two stages: the first is the conversion of methane to syngas (a mixture of CO, H_2 and H_2O) and the second is the so-called Fischer-Tropsch process or similar, where syngas is converted to liquid hydrocarbons. There are several methods to carry out the first stage of GTL, the most advantageous of which, seems to be partial oxidation, as it does not require additional energy sources and results in an H_2 to CO ratio, favorable for the subsequent Fischer-Tropsch process. The main challenge to be met for practical realization of partial oxidation, and is being addressed in this research, is the demand for technology suitable for the stabilization of the self-sustaining process of oxidation of very fuel rich methane/oxygen mixtures, which cannot be ignited by traditional means.

In the present work we studied the partial methane oxidation using two approaches: premixed pulsed propagating flame (PPPF) and premixed low pressure flame stabilized on modified McKenna burner.

A PPPF is based on flame propagation in a narrow tube from the igniter to the source of combustible gas. When the rate of gas flow is insufficient for flame stabilization, the flame is observed as pulses separated by regular intervals. The flame front propagates through the tube opposite to the gas flow, with a repetition rate of 0.5 - 5 pulses/s depending on experimental parameters. We believe that the PPPF can be very suitable for partial oxidation of methane. By varying the tube temperature a super-adiabatic regime (preheating of the combustible gases) can be easily realized, which allows ignition of very fuel-rich mixtures. The first results obtained by this method, including product composition as a function of the equivalence ratio will be presented, discussed and compared to model predictions.

In a low-pressure system, the flame front is also wide enough to recover detailed information on the concentration profiles of various species. We used a modified McKenna burner with a central tube to study very fuel-rich mixtures. Flames with practically any fuel/oxygen ratio can be stabilized with this burner configuration exploiting the stabilizing influence of the outer flame, which has a methane-to-oxygen ratio close to the stoichiometric one.

Several laser spectroscopy methods were used for concentration measurements in low pressure flames. Concentration of the HCO radical was measured as function of the equivalence ratio and compared to model calculation.

First principles kinetics of alkyl radicals

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Being the initial product from the radical attack on the alkanes, alkyl radicals are important intermediates in the decomposition of organic fuels, mostly consisting of the long chain hydrocarbons. To optimize its usage a detailed knowledge of the alkyl radicals kinetics is needed. Their chemistry is largely governed by unimolecular reactions, namely intramolecular H atom migration and direct decomposition (beta scission) of the C-C bond, which can be competitive with oxidation processes (especially with reaction with O_2) to form peroxy radicals, which leads to autoignition. Since only a limited amount of experimental kinetic data is available, cost effective theoretical methods are necessary to provide a clear picture of the radical processes. The Reaction Class Transition State Theory (RC-TST) extrapolates a known rate constant to that of any arbitrary reaction in the same class using correlations, which are constructed under the Transition State Theory framework. The key idea of this application is that reactions in the same class have the same reactive moiety whose chemical bonding changes during the course of the reaction, and thus, they are expected to have similarities in their potential energy surfaces along the reaction pathways/valleys.

The RC-TST method was applied to both H migration and □-scission reaction classes. From the individual product channel rates constants, branching ratios of the multichannel decomposition and isomerization of alkyl radicals are evaluated. The method's reliability is assessed by comparison with experimental data for the n–octyl radicals. Such a selection is given by both the importance of the octane, which is one of the most important constituents of the gasoline and a reference component in liquid fuel surrogates; as well as the availability of the experimental data to compare the RC-TST results with. Theoretically calculated branching ratios for both individual n-octyl radicals and total branching ratios are reported. Thermoneutral reactions, for which experimental data are not available, were found to be of importance to understanding radical processes; these are mainly responsible for observed differences between theory and experiment. Furthermore, theoretical data are also validated on the macroscopic level with the EQUIL program. Results are in reasonable agreement with observations, thus proving that *ab initio* methods can be considered a feasible tool for the modeling of chemical processes based on gas phase radical chemistry. The simulation of a chemical reactor built on *ab initio* calculations and kinetic models only, without adjusted parameters or experimental values, is within the reach of the current methodology.

Methane oxidation under fuel-rich conditions using pulsed-flame setup

Alexey Fomin[1], Tatiana Zavlev[1], Vladimir Tsionsky[1], Igor Rahinov[2], Sergey Cheskis[1]

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Natural gas consists mainly of methane, the combustion of which has long been subject of extensive studies. Syngas production from natural gas can be established as a first stage of the so-called Gas-to-Liquid process (GTL). However, most of the mechanisms of methane oxidation were developed for high temperature, near stoichiometric or fuel-lean combustion. On the other hand, oxidation under very fuel-rich conditions is of interest as a possible way for the conversion of natural gas to syngas (mixture CO, H_2 and water). Better understanding of methane oxidation under very fuel-rich conditions will allow the development of new technologies for conversion of natural gas to syngas.

The main challenge in non-catalytic oxidation is finding conditions in which the process occurs fast enough to become self-sustaining and provide a high product yield, while still maintaining the conditions of partial oxidation and preventing full oxidation of methane to CO_2 and H_2O. Monitoring of stable molecules involved in this chemistry is usually more difficult than monitoring of active radical species. The reason is that stable molecules strongly absorb in the IR spectral range only, where sensitive monitoring techniques such as laser induced fluorescence cannot be easily applied. Recently our group has developed a unique capability for real time simultaneous non- intrusive measurements of CO and CO_2 concentrations.

The goal of the present work was to acquire the information about CO/CO_2 product ratio in flames with equivalence ratios up to $\phi = 3$. In the experimental part, Fiber Laser Intracavity Absorption Spectroscopy (FLICAS) and Gas Chromatography techniques were utilized for the pulsed-flame setup.

The pulsed-flame apparatus is based on a flame source where combustible gas flow rate cannot sustain a continuous-flame operation. The combustible gases (CH_4 and O_2) are mixed together in a small flame tube and flow to a resistively heated Cr - filament igniter. The ignited flame propagates through the detector and self-terminates after the combustible gas mixture is consumed. The continuous gas flow removes the combustion products and creates additional ignition in a periodic fashion.

FLICAS technique was chosen for CO/CO_2 product ratio measurements, since it provides very high sensitivity and simultaneous detection of both gases. In this technique, the absorbing medium is placed inside a laser cavity, forcing the laser light to pass the sample many times. While being ultra-sensitive to narrowband absorption of the gaseous constituents, the laser gain compensates broadband cavity losses, e.g. mirror transmission. The FLICAS spectrometer is based on an external cavity Er-doped fiber laser, which is optically pumped by a single mode diode laser at 980 nm. The ends of the Er-doped fiber are polished; the entrance end is covered with high reflectivity coating at $\lambda \approx 1.5$ μm and output end is anti-reflection coated for the same spectral range. The output coupler of the laser is a flat mirror with partial reflection, wedged by 10^0 to avoid interferometric fringes. The spectrum of the laser radiation is analyzed by a high resolution spectrograph (SPEX 1000M) and recorded by an IR linear CCD camera (1024 pixels of 25 µm, Sensors Unlimited, Inc).

If the spectral saturation time of the laser emission t_s is larger, than the laser pulse duration, t_g, the effective optical path length of FLICAS, L_{eff} is:

$$L_{eff} = c * t_g * \frac{l}{L}$$

where l and L are optical lengths of the sample and of the laser cavity. The laser pulse duration is controlled by the square modulation of the pump power.

The experimental spectra of the CO and CO_2 were recorded for different equivalence ratios. The interpretation of the spectral data is presented and its potential for the model development is discussed.

Our experiments indicate linear dependence of the premixed combustible gases temperature required for the ignition on the equivalence ratio. The dependence of the CO and CO_2 concentration on equivalence ratio were measured and compared with model calculations.

The role of CO_2 and H_2O on ignition chemistry in MILD (diluted, pre-heated) combustion condition

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It is currently unquestionable that the use of new combustion technologies based on dilution and pre-heating of fuel and/or oxidant, such as MILD combustion [1], is among the most favorable methods to reducing the formation or to eliminate classes of pollutants. This is related to the peculiar reacting zone established from pre-heated and diluted reactants, characterized by relatively low, nearly homogeneous temperature and concentration distributions. These features also imply a strong flexibility with respect to the fuel thus allowing the use of low calorific values mixtures with high efficiency. In this framework MILD combustion appears to be one of the most suitable modes to recover energy from biofuels. The high content of diluent species, deriving either from presence of diluent in low calorific values fuels or from recirculation of flue gases to reach MILD combustion regime, namely H_2O and/or CO_2 makes the role of these species relevant in the oxidation chemistry in such a non standard condition [2].

The aim of the present work is to highlight the effect of the H_2O and CO_2 on ignition kinetics of two reference fuels. More specifically, ignition delay time has been evaluated from experimental point of view in a tubular flow reactor [2] using propane and a model gas surrogating the gaseous fraction of biomass pyrolysis products containing C1-C2 species (biogas), CO and CO_2. The experimental analysis has been carried out at atmospheric pressure and inlet temperature ranging from 1000K to 1300K in presence of high dilution of either N_2, or CO_2 or H_2O. In particular, different dilution levels (90-97%) and C/O ratio (0.05-1.5) have been analyzed. As example, the ignition delays of the biogas, measured for C/O=0.2 and a dilution of 90% of the different diluent considered have been reported in the fig.1 with symbols. It has been found that for a fixed inlet temperature the ignition delay time measured in presence of CO_2 or H_2O is longer than the one measured using nitrogen as diluent and the extent of increase depends on fuel and diluent itself. However, such an increase of ignition delay does not prevent the use of MILD combustion processes, even if they rely on massive CO_2 and H_2O recirculation, in practical applications.

Numerical simulations for studying the evolution both of propane and the model gaseous fuel oxidation process in the same working conditions of experimental tests have been carried out by means of several kinetic models available in literature. It has been shown that models are able to reproduce the main features of ignition and oxidation process also in such a not standard condition, even though they significantly underestimate ignition delay values. This behavior is well shown by the numerical results reported in fig.1 with solid and dashed line. Thus, a detailed kinetic analysis has been carried out with the aim to evidence the main routes in which CO_2 and H_2O could interfere with. CO_2 and H_2O can modify the evolution of the combustion process for both kinetic and thermodynamic reasons. Beside a different heat capacity of such species, they can be involved in direct or indirect way in the fuel oxidation reaction.

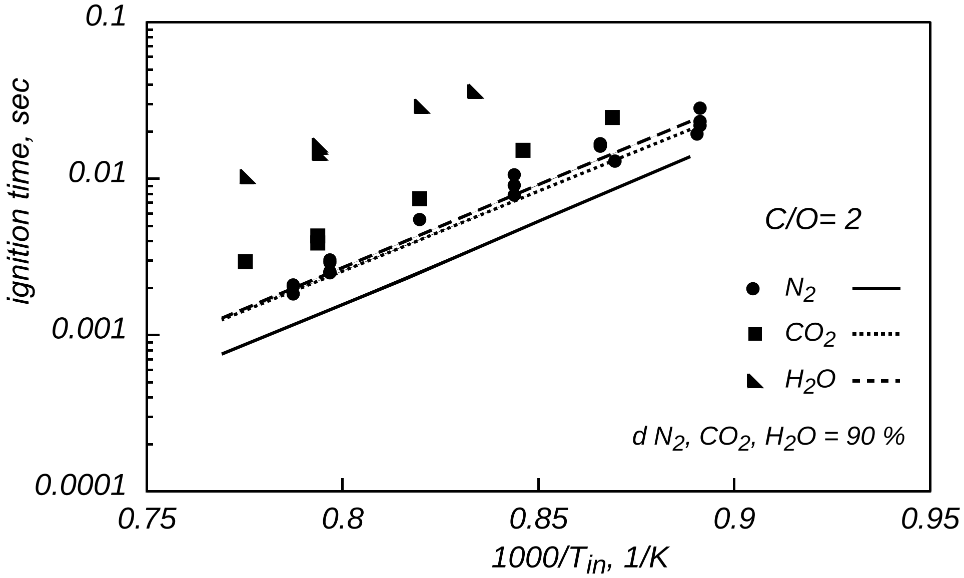

Figure 1. Experimental and numerical ignition delay of biogas in presence of N_2 or CO_2 or H_2O as diluent

The numerical analysis has evidenced the complex effect of the diluent typology on evolution of chemical process that depends on the temperature range considered. More specifically, is has been shown that CO_2 and H_2O strongly alter the competition between the oxidation and recombination/pyrolytic reaction channels also acting on H_2/O_2 oxidation systems.

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Methodology for emission prediction at the exit of a turbofan combustor based on chemical reactor network and detailed chemical kinetics of aviation fuels

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The alternative fuels for aviation would play a key role in the future, first by lowering the pressure on fossil fuels and also by decreasing the global emitted CO_2 from aviation transport. Recently, several alternative fuels production pathways have been emerged, some of them are already certified to be used as aviation fuels (Fischer-Tropsh fuels, HEFA) and some others are following the certification process and could be certified in the future. These emerging fuels are different in terms of components (part of different families, ramification, aromatics, carbon chain length, etc.) and properties and should give different combustion products at the exit of the engine combustor. To be evaluated in terms of the combustion products, detailed chemical kinetics (thousands of elementary reactions) have to be used, which could not be feasible if combined within CFD. The present work is summarising a project research, which aims at developing an emission prediction procedure at the exit of a turbofan. The approach is based on physical-chemistry models more accurate than the empirical methods and more simplified than the high fidelity approaches used by the engine manufacturers. The adopted approach will allow performing quick prediction of emissions within the engine cycle and parameters variation. The pollutant formation inside the combustion chamber is result of two main overall parameters: turbulence (mixing, evaporation, flows) and chemistry. Instead combining these complex phenomena to predict pollutant formation which needs high computation performance and long calculation time, the adopted approach here treats the turbulence separately inside the combustion chamber, and based on the resulting reactive flow, the combustion chamber is divided into numerous equivalent zones. Each equivalent zone is then represented by an ideal chemical reactor. So, the combustion chamber is represented by a Chemical Reactor Network (CRN) [1-3]. The CRN is validated on the ICAO data base (EI_{NOx} and EI_{CO}) measured at the exhaust of aircraft engine. Once the CRN is validated, and depending on the burnt fuel, the detailed chemical kinetics are used to predict the pollutant formation and define the differences regarding the used fuels.

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Oral Contributions WG2

Working group 2: Writing models of the formation and consumption of oxygenated pollutants

A kinetic modeling study of major C_1-C_6 and PAH species in propyne and allene pyrolysis

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Despite the continuously growing share of renewable energy sources in total energy supply, global economy will be still, at least for the foreseeable future, largely based on conventional, fossil primary energy sources (coal, oil and gas) [e.g. 1, 2]. Hence, efficient operation of combustion systems is required, with a further optimization of the fuel breakdown process under a wide range of operating conditions while minimizing the potentially harmful carbonaceous species (aromates, soot) formation.

Usually, small hydrocarbon products are formed during fuel decomposition and may act as important precursor species in the formation of single-ring aromatics (benzene, toluene, styrene, etc.), thought to be, especially benzene, the rate-limiting step in the formation of PAH and soot [e.g. 3, 4]. Among the several proposed benzene formation chemical pathways , those featuring C3 species and, in particular, the propargyl radical recombination reaction, appear to dominate, for a wide variety of aliphatic fuels under several combustion conditions [e.g. 4, 5].

Allene and propyne constitute the smallest pair of isomers encountered in combustion studies and provide an early insight into the effects of structural differences in combustion performance and emissions. Their consumption reactions are primary sources of the key propargyl and allyl radicals, both participating in cyclization steps, and are closely linked to benzene, PAH and molecular growth and soot formation processes. For these reasons, combustion chemistry of allene and propyne is critical for the breakdown of higher hydrocarbon fuels and for molecular growth processes.

Developments in isomer identification experimental techniques have resulted in the emergence of novel experimental datasets of C_3H_4 species flames (e.g. stoichiometric and rich low pressure allene, propyne premixed flames [6, 7]). Recently, a series of pyrolysis experiments of propyne and allene have been conducted at the Louisiana State University in an isothermal laminar-flow reactor at temperatures of 970 – 1270 K and a residence time of 0.3 s [8, 9, 10]. Analysis of several stable reaction products of C_3H_4 fuels pyrolysis by a GC/FID/MS and a HPLC with diode-array ultraviolet-visible absorbance detection setup [see e.g. 11] has led to the identification of about 40 H/C species in the allene and 56 H/C species in the propyne experiment.

The objective of the present work is to utilize existing, detailed, in-house developed mechanisms [12, 13, 14], for modelling key C1-C6 hydrocarbon products and major PAH species profiles obtained from allene and propyne pyrolysis. The mechanism is further developed on the basis of the above C_3H_4 pyrolysis datasets. Results are critically assessed while extensive rate-of-production and sensitivity analyses are utilized in order to identify key controlling processes. The importance of initial propyne destruction paths that largely control the availability of CH_3 and C_3H_3 radicals and directly influence the formation rates of two-, three- and four-ring PAH species, has been shown. Further work would include the modeling of more two-ring PAHs as well as higher PAH species.

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Kinetic modelling and experimental study of a fuel rich, premixed n-heptane flame

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A detailed reaction mechanism is evaluated by the comparison of simulated species mole fraction profiles against more than 70 experimental species profiles measured in a fuel rich (φ=1.7), premixed flat low-pressure (4 kPa) n-heptane/O_2/Ar flame.

Introduction

In the past, premixed n-heptane flames have been investigated at different conditions [1-4]. The work of Douté et al. [1] from 1997 provided for the first time species species concentration profiles information for premixed n-heptane/O_2/Ar flames (at 6 kPa, φ=0.7-2.0). In addition the authors discussed the species involved in the formation of benzene. El Bakali et al. 1999 [2] investigated fuel rich (φ=1.9) atmospheric n-heptane/O2/Ar flames, in which the isomers are distinguished and the importance of allene in benzene formation is mentioned and the mechanism developed in [1] was extended to atmospheric pressure. Further the work of Song et al. [3] and Yoa [4] et al. investigated the effect of MTBE and ethanol addition on the flame structure using synchrotron radiation.

The present work focuses on detailed species measurement and modelling of the n-heptane flame.

Experiment

A laminar low-pressure n-heptane/O_2/Ar flame with equivalence ration of φ=1.7 was investigated at 4 kPa. Time-of-flight molecular-beam mass spectrometry (MBMS) with electron impact ionization (EI) was used to analyze and quantify mole fraction profiles of reactants, products, and most intermediate species including radicals involved in the combustion process.

Mechanism modelling

The experiments are modelled with an detailed reaction mechanism. The reaction scheme is composed of two submechanism. The C1-C4 chemistry is based on the mechanism of Hoyermann et al. [5] with recent updates for butane [6] and butene isomers. The n-heptane sub-mechanisms is based on prior work [7], more detailed sub-mechanisms of olefins are used based on the extensive studies of Ranzi and his co-workers [8].

Results

Figure 1 and 2 show exemplary results for 7 out of 77 measured species profiles. The overall agreement is found to be good for most of the species.

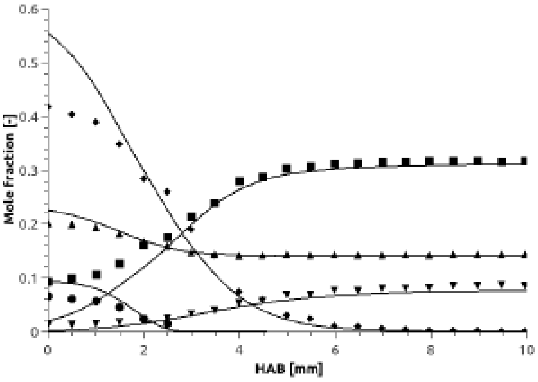

Fig 1: Experiments:◆O_2, ▲Ar, ●C_7H_{16}, ■CO, ▼CO_2 Lines: model predictions

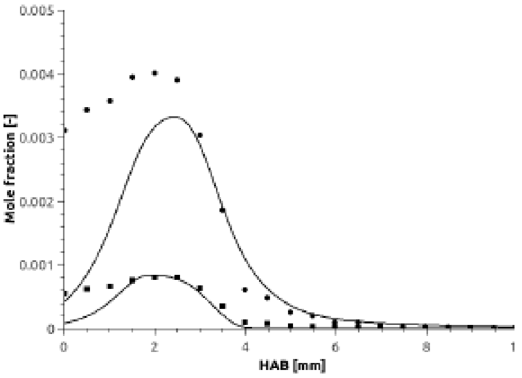

Fig 2: Experiments: ●CH2O, ■CH3CHO; Lines: model predictions

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Evaluation of straw with absorbed glycerol destruction during combustion and pyrolysis by TG-FTIR and TG-GC/MS

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In small countries like Lithuania, with rather no own resources of fossil fuels, interest in alternative energy sources are noticeable. In order to become energetically independent and economically sound, the energy sector development in these countries is heading towards utilization of renewable resources for biofuel production. As an alternative fuel for thermal energy production, instead of wood, cereals harvest waste (straw) is being used recently. Combustion of straw, prepared as pellets or briquettes, is performed in specially designed low capacity boilers. Despite of the interest on the biofuel from straw, an increased attention on the by-products (glycerol) of the biodiesel production still remains. With increase of biodiesel production year by year more attention on new possibilities for glycerol utilization are sought. One possible use of glycerol is as a binder material for straw or other biomass pellets production. The optimum value of fuel properties with the maximum mass fraction of 10 % of glycerol has been shown in the work of L. Raslavicius [1]. According the author, further increase of glycerol amount reduces physical-mechanical properties, but emission (CO, SO_2, and NO_x) from combustion of such fuels falls under requirements. Despite the fact that glycerol is low-cost raw material for biofuel production, direct combustion of glycerol may cause unwanted emissions, especially due to formation of carbonyl compounds [2-3]. From previous investigations on the combustion of raw glycerol and co-combustion of glycerol with heavy fuel oil in spatial furnaces the formation of acrolein at unstable combustion regimes were noticed [4]. From the pure glycerol combustion analysis it was found that this cancerogenic compound completely decomposes at high temperatures and was not analytically detected.

The scope of this work is investigation of formation and development of most toxic carbonyl group compound during combustion and thermal destruction of straw pellets with respect to the absorbed amount of raw glycerol, atmosphere and heating rate by thermogravimetry and evolved gas analysis (TG-FTIR and TG-GC/MS) methods.

Thermal behavior of the straw pellets containing 0 and 14 wt.% of glycerol were analysed using a Netzsch STA 449 F3 Jupiter thermal analyser. Nitrogen gas (60 ml/min) was used as inert atmosphere while synthetic air as an oxidizing environment. Evolved gas analysis during TG temperature program was performed by TG-coupled FTIR spectrometer Bruker Tensor 27 and gas chromatograph Agilent 7890A with quadrupole mass spectrometer 5975C (heated gas transfer lines, 300°C). Infrared spectra were recorded at 30 seconds interval in the MIR 4000-650 cm^{-1}. TG-GC/MS analysis was performed both in quasi-continuous and event-controlled triggering modes in the 13-300 m/z range.

Some of obtained results are presented in the figures 1 to 3. The Fig. 1 presents behavior of mass loss during combustion and pyrolysis of samples w/ and w/o absorbed glycerol. The temperature profile of evolution of selected infrared wavelengths of acrolein and glycerol during oxidation and pyrolysis are presented in Fig. 2. The abundance of specific m/z for acrolein and glycerol during TG run are evaluated in the Fig. 3.

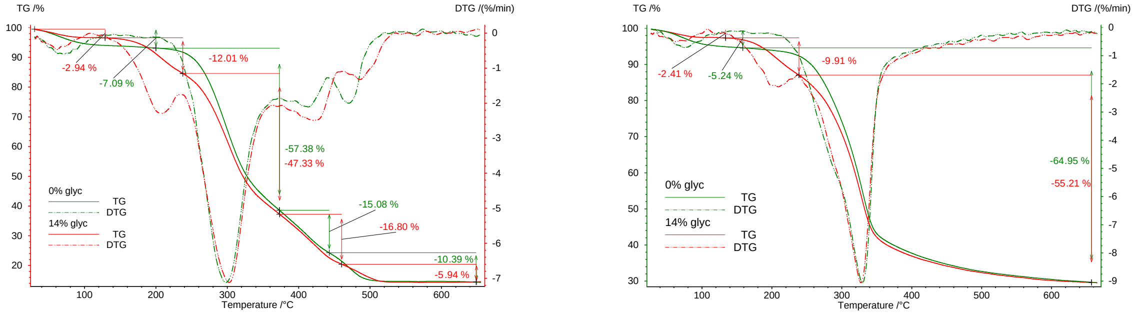

Fig.1. TG and DTG curves for wheat straw w/ and w/o absorbed glycerol during oxidation (left) and pyrolysis (right)

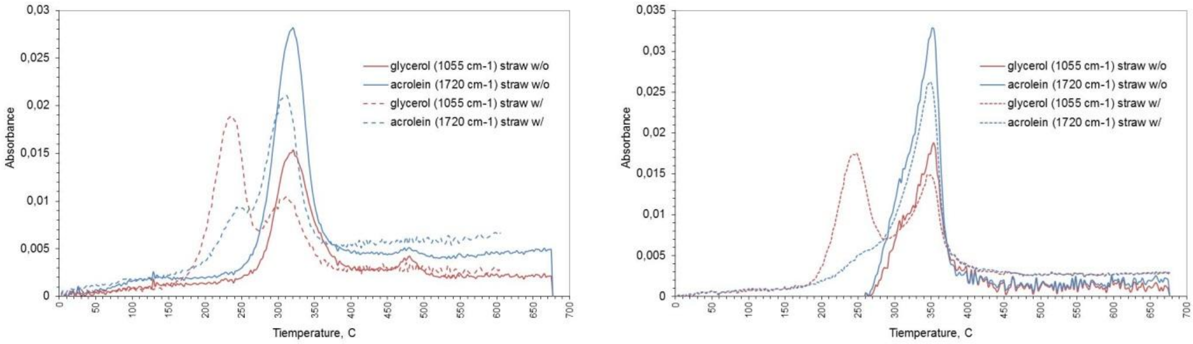

Fig.2. Evolution of acrolein and glycerol specific IR wavelengths for wheat straw w/ and w/o absorbed glycerol during oxidation (left) and pyrolysis (right)

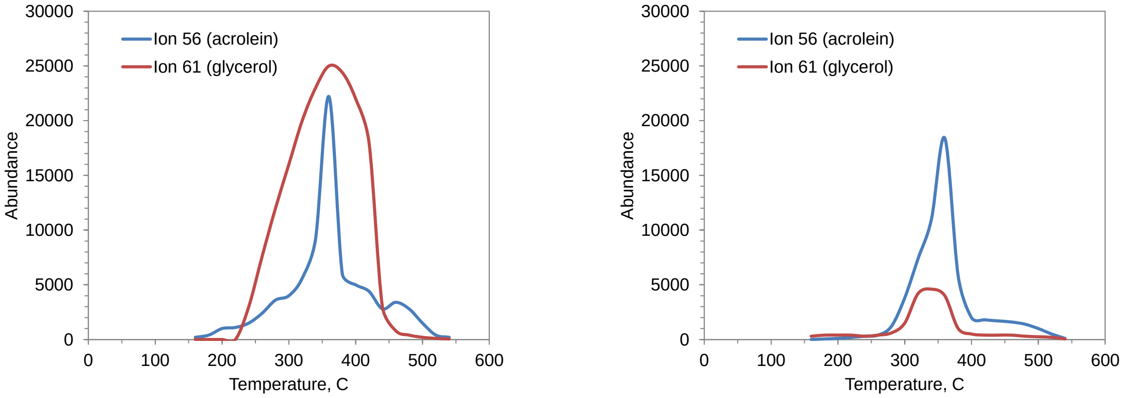

Fig.3. Evolution of acrolein and glycerol specific m/z for wheat straw w/ (left) and w/o (right) absorbed glycerol during pyrolysis

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A combined modeling and experimental study of the combustion of 1,3-butadiene/butanol

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The combustion of butanol has gained much interest as butanol offers a renewable way to serve as an additive to gasoline [1] and, furthermore, it promises a less sooting behavior than hydrocarbons [2]. Studying formation and destruction pathways of soot is in the focus of numerical investigations. The addition of small hydrocarbons (1,3-butadiene) to single-ring aromatics (benzene) are considered as major steps in PAH formation and growth reactions [3-4].

The objective of the present work is to develop a detailed combustion chemistry model for a combined 1,3-butadiene/ butanol flame, which allows to identify the important pathways for butadiene and butanol oxidation as well as for formation of aromatic species and their precursors.

Detailed kinetic modeling results are compared against flame-sampled molecular-beam mass spectrometry data obtained in several laminar premixed flames [1, 4-6]. The latest experimental data are obtained by utilizing photoionization by tunable vacuum-ultraviolet synchrotron radiation, which allows for the identification and separation of combustion species by their characteristic ionization energies.

The chemical kinetic model under development is based on the reaction set used previously [7]. The key features of the updated model are the detailed description of 1,3-C4H6 consumption and an accurate treatment of several reactions involving known benzene precursors. Also, the C3H4 chemistry was critically reviewed and a butanol sub-model added.

The predicted mole fraction profiles are at least in satisfactory but mostly in good agreement with the measured ones. Reaction flux and sensitivity analysis will be used to get more insight into the combustion of the fuel.

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Laminar burning velocities of C4 - C7 ethyl esters: Experiments and modeling

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In order to better understand the combustion characteristics of ethyl esters, possible second generation biofuels, unstretched laminar burning velocities of C_4 to C_7 ethyl ester-air premixed laminar flame were measured in a spherical combustion chamber [1, 2]. Laminar flame speeds have already shown their practical interest in spark-ignited engines development and they are more and more used as a validating support to kinetic mechanisms. But what is the gain of using laminar burning velocities to develop or validate such mechanisms? This is a question this presentation will try to answer through the study of the effect of fuel structure as well as the effect of pressure, from 1 to 10 bar, fresh gas temperature, from 323 to 473 K, and equivalence ratio in the range 0.7-1.4.

The laminar flame burning velocity measurements were performed using a stainless steel spherical combustion chamber with an inside volume of 4.2 L. Four windows provided optical accesses into the chamber. Before filling, a vacuum was created inside the chamber. The volume of air was introduced into the chamber with a thermal mass flow controller. Synthetic air (79.5% N_2 and 20.5% O_2) was used in the experiments. The liquid fuel was injected through coriolis mass flow meters (Bronkhorst France). Injected air was directed to the exit of the coriolis flow meters to convey the injected liquid. Before entering the chamber, the mixture was heated up to 450 K to guarantee full vaporization of the liquid. The temperature of the chamber was regulated at the desired value (323 - 423 K). Inside the chamber, an electric fan mixed all the gases. A delay before ignition was used to avoid any perturbation during the flame propagation experiments. Two tungsten electrodes, with a 1 mm gap, connected to a conventional capacitive discharge ignition system, were used for spark production at the center of this chamber. Measurements were limited to flames having diameters less than 50 mm, corresponding to a total volume of burned gases < 1.6% of the chamber volume. During the initial stage of the flame expansion, the total pressure inside the chamber can be considered constant. For each condition, the measurements were repeated three times. The standard deviation corresponding to the scattering in experiments was ± 2 cm/s. Flame images were obtained by shadowgraphy. Parallel light was created from an Ar-Ion laser source with two plano-convex lenses (25 mm and 1000 mm focal lengths respectively). To analyze the temporal evolution of the expanding spherical flame, the shadowgraphic images were recorded by using a high speed video CMOS camera (Photron APX) operating at 10000 frames per second with an exposure time of 20 µs.

As commonly observed for alkanes for instance, an increase of pressure was found to decrease the laminar burning velocity whereas an increase in fresh gas temperature was found to increase the laminar burning velocity. According to the equivalence ratio, the usual bell-shaped curve was observed with a maximum obtained around phi = 1.1. At Tu = 423 K and P = 1 bar, ethyl acetate was found to have the lowest flame velocity regardless to the equivalence ratio whereas ethyl valerate has the highest under lean conditions and ethyl propionate under rich conditions.

The oxidation of these four ethyl esters was modeled using a unique new detailed chemical kinetic reaction mechanism (1845 reactions involving 232 species). As can observed from Figure 1, the proposed mechanism shows good agreement with the present experimental data as well as data from the literature. Reaction path analyses and sensitivity analyses were conducted to interpret the results. C4 to C7 ethyl esters flame speeds were found to be essentially sensitive to small species kinetics regardless to fuel structure, equivalence ratio, pressure or initial temperature.

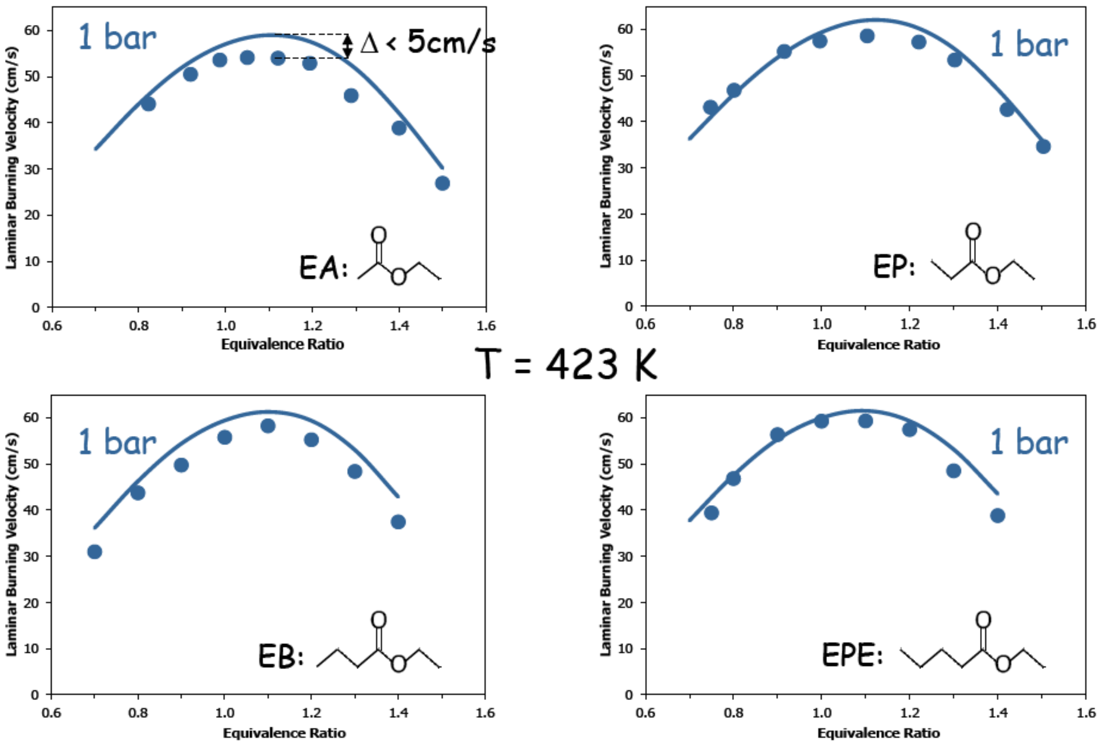

Fig 1: Ethyl acetate, ethyl propionate, ethyl butyrate and ethyl valerate laminar burning velocities in air according to the equivalence ratio at P = 1 bar, T_u = 423 K.

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Premixed flames of dimethyl carbonate with air

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Essential oxygenates were developed in the 1970s as substances that increase the octane number of gasoline to improve combustion efficiency, reduce emission of exhaust gases of cars and improving the environmental characteristics of the exhaust gases, as well as a mean for replacement of antiknock compounds such as tetraethyl lead. One of these oxygenated additives is dimethyl carbonate (DMC), which is useful because of its high oxygen content. Evaluation of DMC production technology and fuel properties has become important to the oil industry, because recent economic studies have shown that it is more economical to use DMC in reformulated gasoline than MTBE produced from butane [1]. Opposed flow diffusion flames of dimethyl carbonate were studied by Sinha and Thomson [2] but no laminar burning velocities have been reported.

In the present work the heat flux method [3] was used to study laminar burning velocities of DMC+air. Simulations of the DMC combustion process were performed using the chemical kinetics mechanism by Glaude et al. [4]. Experiments and modeling were carried out at temperatures ranging from 298K to 358K. The accuracy of the experimental laminar burning velocities was ±1 cm/s.

The adiabatic laminar burning velocity of a combustible mixture is a key parameter governing many properties of combustion, such as the shape and stabilization of a flame. The heat flux method use a perforated plate burner, where a flame is stabilized on a brass plate of 2-mm thickness, perforated with a hexagonal pattern of small holes. The temperature in the burner plate approaches a distribution only dependent on the radius, which then corresponds to the heat loss from the flame to the burner. The temperature distribution is measured by means of small thermocouples attached to the burner plate.

Figure 1 present the results; the symbols represent the experimentally determined laminar burning velocity as a function of DMC concentration, while the lines are from the simulations. The effect of unburned gas mixture temperature on the laminar burning velocity was analyzed using the correlation $u_L = u_{L0}(T_u/T_{u0})^{\alpha}$. The correlation coefficient α as a function of equivalence ratio is presented in Figure 2. From the two figures it is evident that while the detailed chemical kinetics model over predict the absolute values on the laminar burning velocity, it shows good agreement with respect to the temperature correlation.

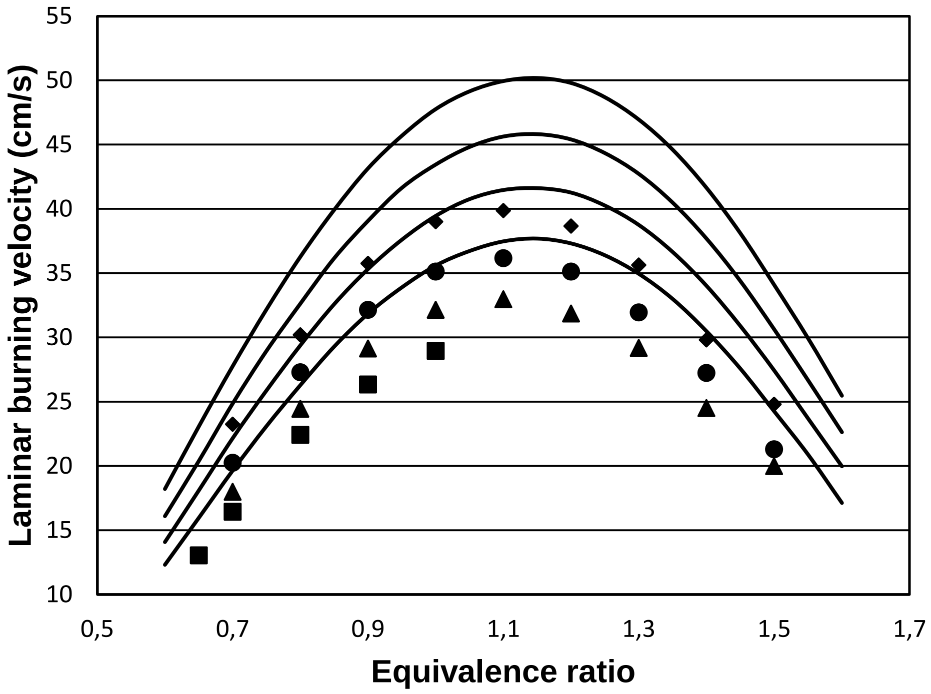

Figure 1. Experimental (symbols) and simulated (lines) laminar burning velocities of DMC+air at 298-358K. 298K (squares), 318K (triangles), 338K (circles), 358K (rhombs).

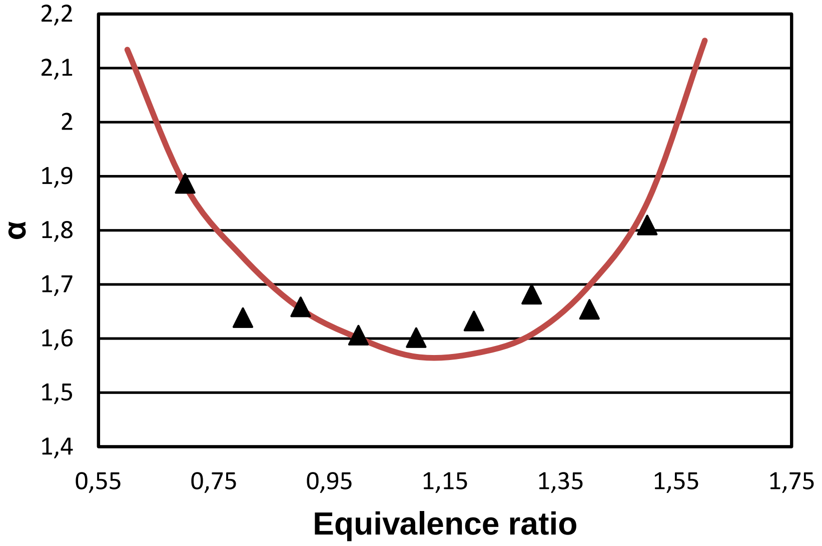

Figure 2 The correlation coefficient α as a function of equivalence ratio. Experimental data (triangles), Modeling data (line).

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A detailed kinetic modeling study of the combustion of C1-C2 oxygenated fuels in laminar premixed flames

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The increased utilization of biofuels, and in particular the use of bio-alcohols and bio-diesel in the transportation sector, has sparked an interest in the combustion of relevant major fuel components. Additionally, oxygenated exhaust species in engines, e.g. small aldehydes, are directly linked with the use of practical bio-fuels and are expected to be regulated by future emission standards. The assessment of the effect of specific fuel components on overall engine efficiency and performance, as well as on pollutants formation, needs to be tackled through a detailed kinetics approach that inherently permits such a correlation. Several reaction mechanisms are available in the open literature for a variety of such fuels and their components, while features of relevant models and performance are under continuous review, e.g. [1-4]. These recent significant advances in thermo-chemical and kinetic parameters assessment with respect to C_1-C_2 chemistry, necessitate continuous re-evaluation of existing mechanistic approaches. In parallel, the increasing wealth of experimental speciation data from fundamental configurations, and especially premixed flames [e.g. 5], and the numerous experimental campaigns at engine level utilizing neat bio-fuels or blends of practical and oxygenated fuels, can directly support the development of a flexible combustion chemistry model able to describe the oxidation of a range of fuels and for a range of operating conditions.

Towards this direction, a single, in-house developed, detailed chemical kinetic mechanism [6, 7], is utilized in the present work in order to model and analyze five (5) stoichiometric or near stoichiometric low-pressure laminar premixed flames of C_1-C_2 oxygenated fuels, see Table 1. In particular, flames of the two smallest aldehydes, (formaldehyde and acetaldehyde) and the two smallest alcohols (methanol and ethanol) are considered. Formaldehyde is an important intermediate species in the combustion of methanol, while both aldehydes have a prominent role in the oxidation process of lean, stoichiometric and rich ethanol mixtures. The mechanism is shown to satisfactorily reproduce major reactants decay as well as major and intermediate species profiles. Reaction path and sensitivity analyses are utilized in order to scrutinize the controlling elementary steps and to reveal part of the mechanism for further improvement.

The above work is directly related to WP2 (Writing of models of the formation and consumption of oxygenated pollutants) of the present COST CM0901 action, since the improvement of model predictions of combustion products from bio- and alternative fuels will play an important role in the selection of energy vectors for future usage. Towards this direction, test of different fuel mixtures (such as GtL) for their primary combustion behavior (i.e. ignition delay time and laminar flame speed), appropriate surrogate choice (a mixture of alkanes, alkenes, oxygenates, naphthanics etc), and improvement of the common C1-C4 underlying chemistry, is in complete line with the vision of the COST network and further enhances our efforts for building a common European reaction data base.

Flame	**Fuel**	□	**p (mbar)**	**Ref.**
FF1	**CH_2O**	1.09	30	[8]
FA1	**CH_3CHO**	1.00	50	[9]
FM1	**CH_3OH**	0.89	53.3	[10]
FE1	**C_2H_5OH**	1.00	50	[11]
FE2	**C_2H_5OH**	1.00	50	[12]

Table 1 The premixed flames computed in the present work.

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Sensitivity analysis of methanol flames with air and under oxy-fuel conditions

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As the chemistry is altered under oxy-fuel combustion, studies of properties and the chemistry of fuels and intermediates under oxy-fuel conditions are of importance. This paper is part of a study of C1-C2 alcohols under oxy-fuel condition [1, 2].

Methanol is both a fuel, and a major intermediate in combustion of other fuels. Given that methanol contains only one carbon in its structure, methanol is an excellent model fuel for studying alcohol chemistry under oxy-fuel conditions.

Measurements of laminar burning velocities for methanol flames under oxy-fuel conditions for atmospheric pressure and elevated temperatures are performed using the heat flux method. The experimental results were compared with modeling using the kinetic mechanism by Li et al. [3]. This mechanism is well established for methanol combustion and validated for combustion where the diluting gases are N_2 or Ar [4]. Experimental results from the present study are shown with the modeling results in Fig. 1. The chemical kinetics modeling consistently over predicts the laminar burning velocity for the investigated range of equivalence ratios and temperatures.

The measured laminar burning velocities for methanol burned with an oxidizer mixture of 35% O_2 in CO_2 are lower than for methanol in conventional air combustion measured with a similar heat flux setup [4]. The same behavior was seen for ethanol flames in air and oxy-fuel environment [1, 5, 6]. The modeled adiabatic temperature for the methanol flames under oxy-fuel conditions is only slightly higher than for methanol and air, 2290 K and 2220 K respectively for ϕ=1.0 and 318 K. The difference of 70 K between the oxy-fuel and air flames

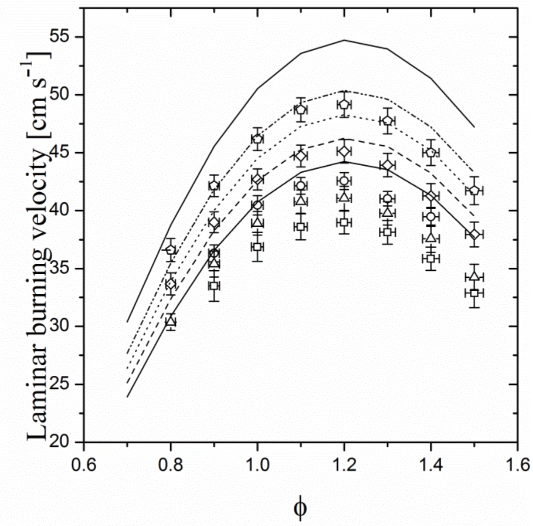

Figure 1: Laminar burning velocity vs. equivalence ratio for methanol+O_2+CO_2 flames. Squares: 308 K, triangles: 318 K, circles: 328 K, diamonds: 338 K, pentagons: 358 K. Lines are modeling, solid: 308 K, dash: 318 K, dot: 328 K, dot/dash: 338 K and solid: 358 K.

is negligible compared to the flame temperature. With this at hand, any differences in laminar burning velocity predictions probably will not stem from radiative properties or shifts in reactivity because of temperature differences.

Figures 2-3 shows the twenty most sensitive reactions for methanol flames at ϕ=1.0 and 318 K, for oxy-fuel and air combustion respectively in the Li et al. mechanism. There are no major differences in sensitive reactions which show that the chemistry is treated similar in the model, for both cases. The same sensitive reactions are shared but with different sensitivity. The sensitivity is generally higher for the most sensitive reactions under oxy-fuel conditions.

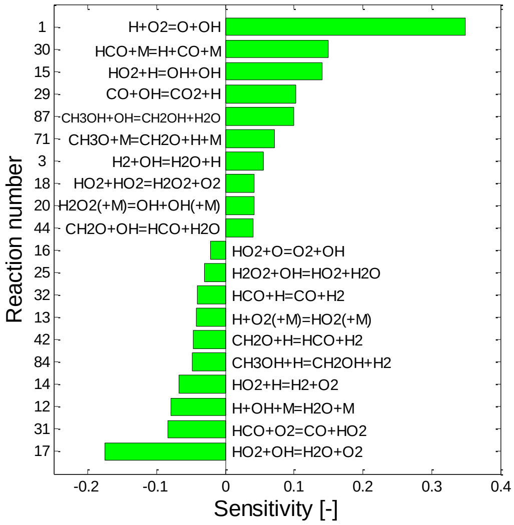

Figure 2: The twenty most sensitive reactions from Li et al. mechanism for methanol under oxy-fuel conditions at ϕ=1.0 and 318 K.

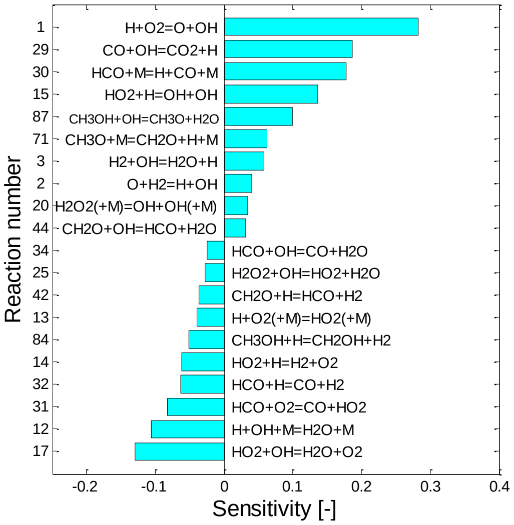

Figure 3: The twenty most sensitive reactions from Li et al. mechanism for methanol + air at ϕ=1.0 and 318 K.

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Investigation of the effect of hydrogen on particle formation from hydrocarbons

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Carbon nanoparticles play an important role both as an undesirable combustion-generated pollutants as well as valuable industrially-produced material. The modeling of their formation process is therefore of great interest. During the formation of carbon particles by combustion or pyrolysis of hydrocarbons, reactions involving hydrogen play a key role in the growth of molecular species [1]. According to the commonly accepted HACA mechanism (Hydrogen Abstraction Carbon Addition) proposed by Wang and Frenklach [1], hydrogen plays a crucial role. The process of soot particle growth can be represented as a sequence of a hydrogen abstraction from a gaseous hydrocarbon followed by addition of a gaseous acetylene to the newly formed radical site. The aim of this study is the experimental and numerical investigation of soot particle formation under the influence of *chemically bonded* and *free molecular hydrogen*. For this task, a precursor that contains chemically-bonded hydrogen (C_2H_2) [2] and two hydrogen-free precursors (CCl_4, C_3O_2) were selected for the experiments with variable addition of molecular hydrogen.

Gas-phase pyrolysis of these precursors and gas mixtures was investigated in a shock tube that is equipped with a high-repetition-rate time-of-flight mass spectro-meter. This method allows the simultaneous detection of several species with a repetition rate of 10 µs [3] within the 1 ms test time provided after the initialization of the reaction through the shock-induced heat up of the gas mixture in the shock tube. Figure 1 shows the periphery around the mass spectrometer.

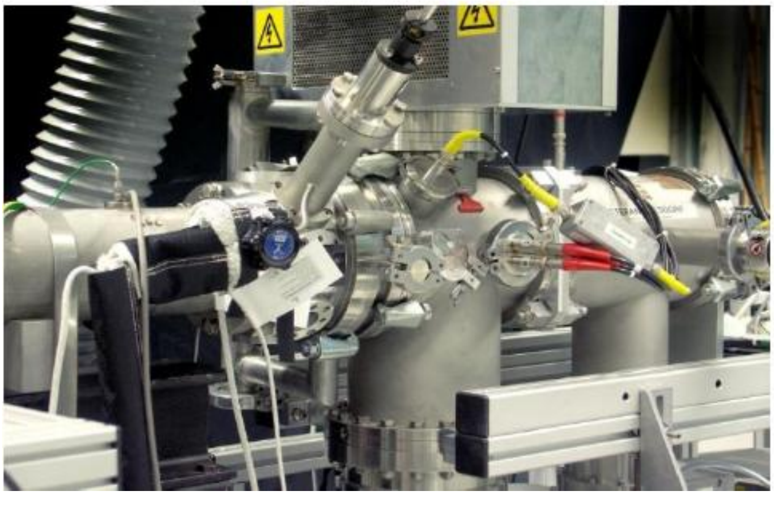

Figure 1: Mass-spectrometer coupled to the end flange of the shock tube.

To investigate subsequent growth processes at high temperature, extinction measurements were performed to determine the inception times and diameters of primary particles. In this way, the entire process from the primary decomposition of he precursors to the final particle formation was characterized.

The results show that the mechanism of formation of higher clusters in C_3O_2 is significantly different from that of CCl_4. While cluster formation in C_3O_2 proceeds via the C_2 dimer, in contrast, in the case of CCl_4 the clusters grow via C_2Cl_2. The investigations showed that chemically-bonded hydrogen has a different effect on the rate of formation and on the size of the particles formed from C_3O_2 pyrolysis in the presence of an equivalent amount of molecular hydrogen. For the numerical description of the underlying processes, a detailed mechanism of the homogeneous and heterogeneous reaction mechanism was developed and validated against the experimental data. The model was able to describe both the chemical decomposition of the precursors and the formation of carbon particles.

Additionally, the effect of molecular hydrogen on acetylene pyrolysis was investi-gated. In the experiments and simulations, increased concentrations of C_2H_2, and decreased concentration of C_4H_2 and larger polyacetylenes were found when H_2 was added. Numerically, it was found that the impact of H_2 on carbonaceous reaction products, important for soot precursor formation was as follows: The presence of H2 reduced the consumption of acetylene, and reduced the concentration of the respective polyacetylenes, PAHs, and carbon clusters. This is attributed to an enhanced consumption of the crucial carbon-adding (di)radicals C_2H, PAH●, C_2, that are required for the fast build-up of carbonaceous material by H_2, resulting in less reactive species. Figure 2 shows an example of concentration-time profiles measured with and without addition of molecular hydrogen in acetylene pyrolysis.

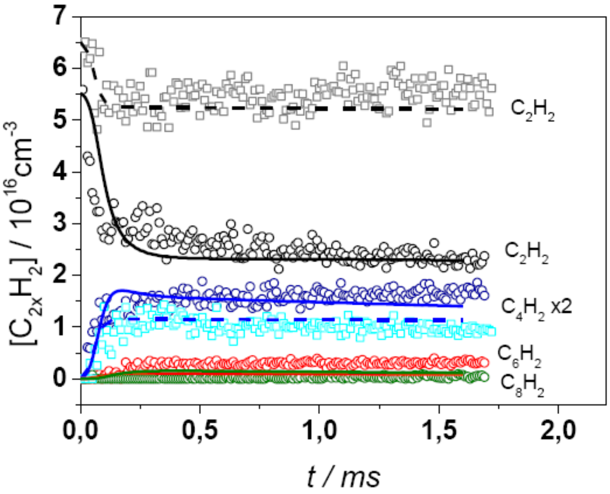

Fig. 1: Comparison of the measured and calculated concentration-time profiles of $C_{2x}H_2$ species for a mixture of 2% C_2H_2, 1% Ar and 97% Ne at T_5 = 2310 K and p_5 = 0.88 bar (circles) and a mixture of 2% C_2H_2, 4% H_2, 1% Ar and 93% Ne at T_5 = 2315 K and p_5 = 1.04 bar (squares). Solid lines and dashed lines are results of the simulations.

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Oral Contributions WG3

Working Group 3: Improvements of the models for formation of polyaromatic compounds and soot

Interactions between SO_2 and ethylene. Experimental and modeling study

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Most fossil fuels, biofuels and household waste contain sulfur, which is largely released to the gas phase during combustion processes [1]. Once released, the gaseous sulfur is oxidized rapidly to sulfur oxides, mainly sulfur dioxide (SO_2) [2]. When a flue gas recirculation (FGR) technique is applied in combustion processes, the SO_2 present in the flue gas could be removed/treated before or after recirculation the gases, which in the latter case may affect the overall combustion scheme and/or the fate of other pollutants such as soot.

In this context, the objective of this study is to identify to what extent the presence of a given compound in the recirculated mixture, in this case SO_2, can affect emissions of a given pollutant, in this case soot, and be used for its control in a combustion process. Ethylene, as one of the main soot precursors, and as being an important intermediate in many combustion processes, is used as fuel to determine the influence of the SO_2 presence and concentration on its pyrolysis with further soot formation.

Experiments are carried out in a laboratory quartz flow reactor, under well controlled conditions of temperature and inlet reactants concentrations, at atmospheric pressure, in the 975-1475 K temperature range. The concentration of ethylene is kept constant in all the experiments (30000 ppm), whereas the concentration of SO_2 is varied (0-1 %) to address its influence on soot formation. The produced gases are analyzed by a Gas Chromatograph equipped with TCD and FID detectors, a Fourier Transform Infrared Analyzer (FTIR) and infrared (IR) CO/CO_2 and NO analyzers. Soot produced is collected, quantified and characterized.

The experimental results are examined with the main objective of assessing the effectiveness of SO_2 in suppressing or boosting soot formation, and to identify the elementary steps involved in the ethylene and SO_2 conversion as function of the SO_2 present. To achieve this, the experimental results are simulated and interpreted in terms of a detailed gas-phase kinetic mechanism run with Chemkin. The reaction mechanism is taken from the work of Glarborg et al. [3] to describe the combustion of small hydrocarbons, with minor modifications and updates [4], together with the sulfur reaction subset developed by Alzueta et al. [5], subsequently updated by Giménez-López et al. [6]. The resultant gas phase chemical kinetic mechanism is being modified and updated to introduce a subset for the sulfur radicals–unburnt hydrocarbons interactions, in the frame of reactions of sulfur radicals (as example SO) with unburnt hydrocarbons to generate CS that then reacts further to generate CS_2 and COS [7]:

$$SO + C_xH_y \rightarrow CS + \text{products} \rightarrow COS \text{ or } CS_2$$

Main results indicate that the presence of SO_2 in the initial reacting mixture has direct implications on soot formation, achieving different reduction levels as function of the temperature and inlet SO_2 concentration. The presence of CO and CO_2 at the reactor outlet points to the fact that oxidation reactions are taking place, and those reactions could come in competition with typical pathways leading to soot formation. The formation of sulfur compounds such as CS_2, on the one hand, decreases the amount of carbon available for soot growth and, on the other hand, gives evidence that interactions between sulfur radicals and unburnt hydrocarbons are indeed taking place.

The soot characterization results, through elemental analysis, indicate that soot is mainly composed by carbon, with presence of sulfur, when SO_2 is present during its formation.

Acknowledgements

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Numerical and Experimental Investigation of Soot Formation and Particle Size Distributions in Laminar Premixed Flames

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The legislation for particle emissions has become stricter by limiting the particle number in addition to the mass. Along with stricter emission standards, the use of biofuels in gasoline engines is of increasing importance. However, in comparison to classical gasoline, biofuels lead to different soot emissions [1, 2]. The investigation of the underlying physical and chemical effects is the long term goal of a current scientific project. The present study is a fundamental part of it.

In order to study the soot formation in complex systems like internal combustion engines the detailed understanding of the soot formation and the particle size distribution in simple laboratory flames is required. Accordingly, fuel-rich laminar premixed ethylene/oxygen/argon flames with an equivalence ratio of ϕ=2.07, ϕ=2.15 and ϕ=2.31 are studied numerically as well as experimentally here.

The applied numerical setup consists of a method of moments [3] and a Monte Carlo approach [4]. Both models include detailed formulations for the processes of nucleation, condensation, coagulation, surface reactions and surface oxidation. Quantities of interest to compare between the numerical and experimental approach are the number density, the soot volume fraction, the average particle diameter and the complete particle size distribution (PSD). Since only the Monte Carlo approach enables the detailed simulation of the PSD, the method of moments is primarily used for the precomputation of the moments of the PSD during the flame calculation. This is necessary to account for the sink in relevant species profiles due to the formation of solid particles. The Monte Carlo method is applied as a post-processing step afterwards. Since the heat losses to the burner by conduction and radiation are unknown, the measured temperature profile is used for the simulations.

The experimental studies are conducted using a commercial McKenna burner and a Scanning Mobility Particle Sizer (SMPS). To eliminate particle losses due to coagulation and diffusive wall deposition a dilution ratio higher than 10^4 is realized in the sampling probe [5]. The ceramic sample probe (10 mm OD, 9 mm ID) is placed horizontally above the burner. In order to study the evolution of the PSD in different heights above the burner (HAB), the distance between the burner and the tube is adjustable. The flame temperature measurements are conducted with a type S thermocouple with a diameter of 0.5 mm.

Figure 1 presents the numerically and experimentally determined PSDs in two HABs for the ϕ=2.31 flame. Both the experimental as well as the numerical results show the same qualitative trend. The PSD evolves to larger particle diameters at higher HABs.

However, in terms of quantity, the measured soot volume fraction is underpredicted by the computation significantly. Increasing the temperature profile by 100K, which is within the range of measurement uncertainty, leads to a good agreement between the measured and the computed PSD. It can be concluded that the numerical model is very sensitive to the used temperature profile, which suffers from significant uncertainties. A different and more promising method to determine the flame temperature is proposed by [6]. The temperature profile is adjusted to match the decay of the fuel and oxidizer there.

In addition to the temperature profile, the influence of the method of moments model accuracy on the computed PSD is studied and evaluated as well. Since the method of moments approach is coupled to the flame solver, it influences the computed species profiles of the flame and thus also impacts the PSD computed with the Monte Carlo approach.

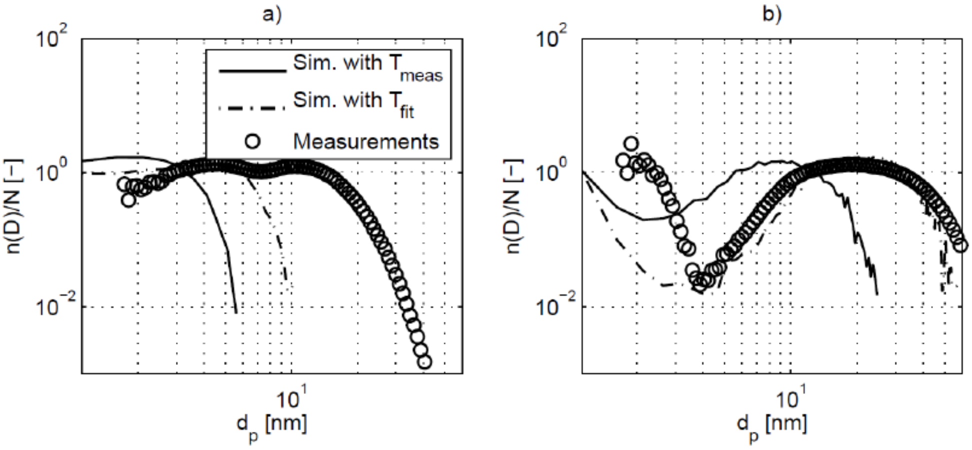

Figure 1: PSD at a) HAB=6mm and b) HAB=10mm for the ϕ=2.31 flame; points: experimental results, solid curve: simulated results with the measured (and radiation-corrected) temperature profile, dashdotted curve: the simulated results using an artificially increased temperature profile

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Electrochemical testing of metal dissolution kinetics in bioethanol fuels

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With transition to biobased energy sources, many technical properties of new fuels appear very different from those, which have been expected from traditional petroleum-based materials. In case of ethanol fuels, their ability to dissolve metals could be very high, compared to gasoline. Ethanol easily oxidizes into acetic acid, whose salts are highly soluble:

$$C_2H_5OH \rightarrow \textit{oxidation} \rightarrow CH_3COOH$$
$$2\ CH_3COOH + FeO \rightarrow (CH_3COO)_2Fe + H_2O$$

When the fuel is stored long-term in half-empty containers, oxidation proceeds more rapidly and more water is absorbed into the fuel due to its hygroscopic nature. It can also be expected that electrochemical mechanisms possibly accelerate the metal dissolution. Eventually metal acetates can be formed, which are likely to directly contribute to soot formation during the fuel combustion.

In order to study the extent of metal dissolution in bioethanol fuels, two field samples of the retail fuel with 85% bioethanol were collected in this study: B85 and S85. Also a laboratory blend was prepared from dehydrated Ethanol, Heptane and Xylene (EHX), since the retail fuels are manufactured by mixing bioethanol with ~15% conventional gasoline. In the EHX blend, ratios of heptane and xylene were selected to approach the octane number of the retail fuels, as shown in the Table.

Table Composition and key properties of the EHX blend and its components, employed in this study to simulate bioethanol-based retail fuels

Component	Octane number	Density, g/ml	wt.% in EHX
Ethanol (dehydrated)	108	0.79	85
Xylene	120	0.86	4
n-Heptane	0	0.68	11
EHX blend (theoretical values)	96	0.78	100

A 3-electrode cell was adapted to perform the measurements in low conductivity media without any supporting ions or additional electrolytes. Open Circuit Potential (OCP) and Electrochemical Impedance Spectroscopy (EIS) techniques were used to study the effects of water on metal dissolution from Low Carbon Steel (LCS) electrodes. The rates of OCP development in solutions with 0.4% and 1.0% H_2O were similar to those of the dehydrated EHX. However, the solution with 4% H_2O showed that polarization resistance (Rp), as determined from EIS data at 10 mHz, dropped significantly. Rp is recognized as the parameter, which is closely related to the strength of any passivating layers, formed between the metal surface and the electrolyte. Therefore, H_2O contents of 4% and higher may lead to much higher metal dissolution rates, which justifies the need for tight control of water contents in bioethanol fuels.

OCP and EIS tests with field samples B85 and S85 at lower than 1% H_2O additions showed that these samples follow similar kinetic trends as EHX. However, when 4% H_2O was added to those fuels, their performance became more different, see Figure.

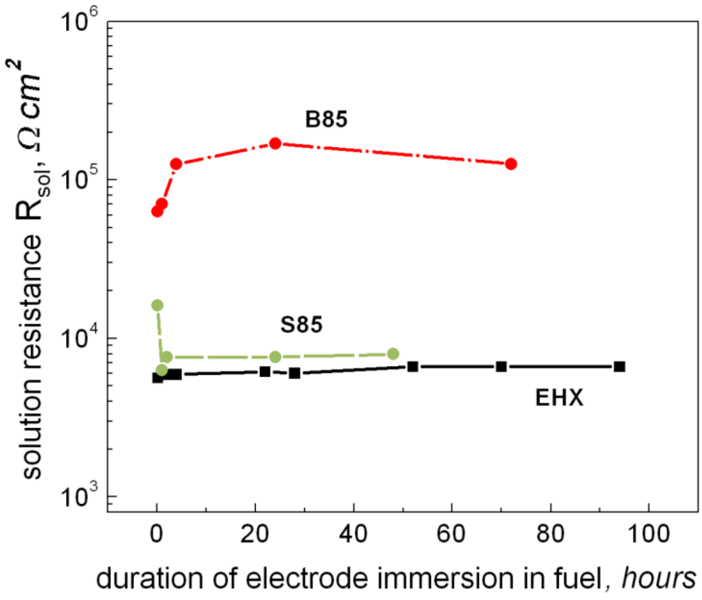

Figure Effect of 4% H_2O addition on the conductivity of bioethanol fuels during the 2-4 day exposure to steel electrode

The differences between B85 and S85 are most likely caused by different additives, such as corrosion inhibitors, used in the fuel manufacture. Nevertheless, the data still shows that the rates of metal dissolution are slow. However, it must be noted that such observations are made without any consideration of acetic acid presence. Higher acidity might lead to much faster metal dissolution, increased levels of metal salts and appearance of various side effects during the fuel combustion processes.

Experimental and modeling study of acetylene conversion in a tubular reactor: Polycyclic aromatic hydrocarbon (PAH) and soot formation

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Acetylene is the most stable and abundant hydrocarbon in many of thermochemical processes operating under fuel rich conditions [1,2]. This is due to the nature of triple carbon bond giving rise to high stability and, at the same time, to its high propensity to addition reactions [2]. Hence, acetylene combustion in fuel-rich conditions has been subject of various studies [e.g. 3,4], and it keeps on being interesting because acetylene is involved in the formation of polycyclic aromatic hydrocarbons (PAH) and soot [e.g. 5, 6].

PAH formed in these processes can cause risk on the human health. 16 PAH are considered by the United States Environmental Protection Agency (USEPA) as priority pollutants (EPA-PAH) because of their high toxic potential and their frequent presence in the atmosphere. These aromatic compounds can be released in the atmosphere as gas phase components or can remain adsorbed on particulate material, such as soot, increasing its toxic potential. This fact increases the necessity of limiting their generation, for which purpose it is required a better knowledge of their formation pathways [7].

Very recent experimental studies have been carried out on acetylene pyrolysis in a tubular reactor paying special attention on EPA-PAH and soot determination [8-10]. The present work addresses the modeling of PAH formation of the experimental data obtained in the above mentioned references [8-10]. Nonetheless, the modeling of PAH-soot formation is a very complex task, since a detailed modeling of the process needs the knowledge of the kinetic parameters of a huge number of reactions together with reliable data for the species considered, and this information is not usually available for the individual PAH considered.

In this way, a semi detailed kinetic scheme developed by Politecnico di Milano has been used in the present work. It consists of a detailed gas phase kinetic model for pyrolysis and combustion of several fuels (available online at http://creckmodeling.chem.polimi.it/) [11], which has been coupled with an updated version of the discrete sectional model [12] describing the successive soot formation. The detailed mechanism of hydrocarbons adopted for the study consists of over 10,000 reactions and more than 300 species, and was developed based on hierarchical modularity [13] and lumping procedures for several complex species. Other kinetic mechanisms, which include reaction at gas phase, [e.g. 14] have been checked for determining the extent to which the polymerization reactions leading to soot affect the agreement between experimental and simulation results.

Therefore, the aim of the present work is to achieve a better understanding of the main steps leading to EPA-PAH formation and soot inception in pyrolysis conditions and to improve the predictive ability of the kinetic mechanisms on the basis of very recent experimental data of acetylene pyrolysis at atmospheric pressure, operating under PAH-soot formation conditions in a tubular reactor [8-10]. Different acetylene inlet concentrations (10000, 20000, 30000 ppmv), reaction temperatures (873-1323 K) and residence times (≈1,5 to 4s) have been studied in these pyrolysis experiments.

Acknowledges

Authors from University of Zaragoza acknowledge the Aragón Government, the European Social Fund (ESF) and MINECO (Project CTQ2012-34423) for financial support. Ms N.E. Sánchez acknowledges the Banco Santander Central Hispano, Zaragoza University and the Colombian Institute for the Development of Science and Technology (COLCIENCIAS) for the predoctoral grant awarded.

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Carbon tracking during lab-scale pyrolysis and combustion of refuse derived fuels

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Introduction

Refuse Derived Fuels (RDF) are solid fuels prepared from non hazardous waste for further application in energy intensive industries, such as energy or cement production ones, as low cost and CO_2 neutral fuels. Among the diversity of raw materials under use for RDF production are municipal solid wastes (MSW), namely its non-recyclable nor recoverable fraction which consists of a mixture of residues of plastics, textiles and cardboard impregnated by some food and garden scrap. Given the newness and also the heterogeneity of this raw material literature is still limited regarding its combustion behaviour. High volatile content is reported [1] and its behaviour in the presence and absence of air has been studied by means of thermogravimetric analysis (TGA) [2] providing information on the temperature ranges for various reactions taking place. Aiming at increasing this knowledge, in this work authors propose a systematic overview of the main pathways followed by carbon during pyrolysis and combustion, as it is one of the main components of this alternative fuel [2]. A carbon mass balance was performed based on data obtained after experimental pyrolysis (0ºC-650ºC) followed by combustion (650ºC) of RDF and some of its main components, and is discussed based on the forms in which it was released. This work was part of a short-term scientific mission done under COST Action CM0901 (WG3) aimed at evaluating the possibility of formation of polyaromatic species (PAH) and soot in this sort of fuels.

Materials and methods

In this study three different materials were evaluated, namely one RDF produced from MSW and two of its main components: food waste and low-density polyethylene (LDPE) film waste. All materials were representatively sampled and prepared and for these tests, portion tests of 10 to 20 mg below 1 mm were used. Experiments were carried out in a fixed bed quartz reactor using an experimental setup described elsewhere [3]. The pyrolysis stage comprised materials heating up to 650ºC (10ºC/min) in the presence of an inert flow of N_2 of 1000 ml min^{-1} followed by a stabilization period (±15 min). In the combustion stage, oxygen was added (2% O_2 in N_2) keeping the total flow constant. The cooled and filtered outflow gas was analysed by a continuous analyser (Uras14/IR) that recorded CO/CO_2 composition every 5s to 10s. Other compounds formed during both pyrolysis and combustion stages were evaluated after capture from the cooled gas stream, using 5g of resin (XAD-2), placed at the outlet of the reactor. After experiments, each resin was extracted and analysed (scan mode) for identification of main compounds (among which are PAH) through GC-MS according to the procedure and using similar conditions to those described elsewhere [4]. For carbon balance, total carbon initially present was quantified through elemental analysis (LECO

TruSpec micro) of the fuels. The carbon existing in the beginning of the combustion phase (and the total carbon lost during pyrolysis) was assessed using the mass loss after TGA (Netzsch STA 449 F3) of the fuels followed along with data from elemental analysis of TGA chars. TGA experiments were performed under heating and stabilization conditions similar to those used in the reactor experiments but in the presence of a flow of 100 ml/min of N_2. The amount of carbon released in the form of CO/CO_2 was quantified through integration of the profiles obtained during heating and reaction time.

Results and Discussion

Table 1 reports the carbon mass balance obtained under the experimental conditions used. It can be seen that that during pyrolysis most of the carbon of the fuels under study (0.69 to 0.95 of the initial amounts) is released into the gas phase in face of volatilization. However it is interesting to note that a non-negligible amount comes out in the form of CO and CO_2, especially in RDF and in food waste. Auxiliary results (not shown) reveal that the most abundant specie was CO_2, probably released by temperature induced desorption in face of materials abundance in oxygen. Other forms found on RDF after GC analyses comprise mainly phthalate esters and no PAH were detected under the experimental conditions used. During combustion, most of the carbon was released in the form of CO/CO_2 (mainly in the last form) and other forms found comprise the phthalate esters.

Table 1. Overall carbon mass balance obtained during experiments.

	Carbon	**Loss on pyrolysis [0ºC-650ºC with N_2] (gC/gC_i)**	**Loss on combustion [650ºC with 2%O_2] (gC/gC_i)**
RDF	Total	0.81	0.19
	$CO+CO_2$	0.17	0.16
	Other forms	0.64	0.03
Food waste	Total	0.69	0.31
	$CO+CO_2$	0.17	0.27
	Other forms	0.52	0.04
PE film waste	Total	0.95	0.05
	$CO+CO_2$	0.06	0.05
	Other forms	0.89	0.00

Acknowledgements

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Modelling of soot formation and oxidation in benzene and hexane diffusion flames

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A detailed kinetic mechanism of aromatic growth, particulate formation and oxidation is presented and is tested in non-premixed laminar flames of benzene and hexane at atmospheric pressure. Model development has been recently updated to account for new experimental data on the formation and oxidation of high molecular mass compounds and incipient particles. Multi-Sectional approach has been adopted. In this version the model accounts for the gas-to-particle transition, the formation of first incipient particles, the evolution of the soot structure and finally the oxidation process.

The newly developed model [1] predicts the structure of the flame both for aromatic and aliphatic fuel. Also the model is able to predict the zone of formation of soot particles with a good agreement with experimental data [2] without any condition-dependent adjustments to the kinetic scheme. A wide range of particle sizes is covered from nanoparticles formed on the fuel side of the flames to larger soot particles and particle aggregates formed in the flame wings. Model gives also information on the predicted trend of the H/C ratio and morphology of the particles for the two different fuels for which no experimental data are available.

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Effect of flue gas recirculation on particulate matter emissions from a domestic pellet-fired boiler

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Introduction

Emissions of fine particulate matter (PM) can seriously affect human health. Among the major contributors of fine PM to the atmosphere are the small-scale biomass-fired boilers, which are widely used around the world. In biomass combustion, fine PM is produced from incomplete combustion (i.e., unburned matter and/or soot) and from vaporization and condensation of easily volatile ash elements [1-3]. In principle, the presence of PM in the flue gas can be minimized through combustion modifications.

Recent studies on PM emissions abatement from small-scale combustion devices include those of Qiu [4], Hukkanen et al. [5] and Lamberg et al. [6]. Qiu [4] concluded that the use of ceramic filters is very effective to meet the environment targets regarding PM emissions. Hukkanen et al. [5] evaluated the effectiveness of a commercial catalytic combustor to reduce the gaseous and PM emissions from a wood stove and concluded that the catalyst could reduce the PM emissions in 30%. Lamberg et al. [6] analysed the effects of air staging on gaseous and fine PM emissions from a small-scale pellet boiler, concluding that there is a significant potential for decreasing PM emissions from pellet combustion systems by optimizing the combustion air staging in the furnace.

The literature reveals that there are very few studies that have examined the possibility to reduce the PM emissions through combustion modifications rather than pos-combustion capture technologies. In this work, we focus on the effect of the exhaust gas recirculation (EGR) on PM emissions from a small-scale boiler.

Materials and methods

The tests were performed in a domestic pine wood pellet-fired boiler with a maximum thermal capacity of 22 kW, with forced draught. For this study, the combustion chamber of the boiler was modified to allow recirculating the exhaust gases.

PM was sampled isokinetically from the centreline of the exhaust pipe either for total mass concentration or size fractions. Total mass concentration was achieved with the aid of a total filter holder and size fractions with the aid of two impactors; specifically, a low pressure three-stages cascade impactor (LPI, TCR Tecora) and a 13-stages Dekati low-pressure cascade impactor (DLPI, Dekati Ltd.). The LPI allowed collecting three PM cut sizes during the same sampling (PM with diameters above 10 μm – PM_{10}, PM with diameters between 2.5 μm and 10 μm, and PM with diameters below 2.5 μm – $PM_{2.5}$), while the DLPI size-classified the PM according to their aerodynamic diameter in the range of 0.03 μm to 10 μm.

Results and Discussion

Figure 1 shows the gaseous and the $PM_{2.5}$ emissions as a function of the EGR for a boiler thermal input of 17 kW. Overall, the $PM_{2.5}$ emissions show a tendency to decrease with the value of EGR, reaching a minimum at EGR = 40%.

Figure 2 shows the PM size distribution for four values of EGR for a boiler thermal input of 17 kW. It is evident that with the increase in the EGR level, the fine PM (< 100 nm) tend to disappear most likely because the combustion conditions (temperature) are less suitable for the vaporization of ash elements from the fuel bed and, thus, the homogeneous condensation of these volatile elements is suppressed.

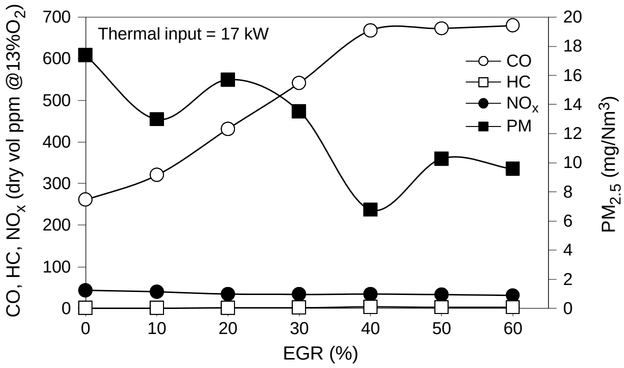

Figure 1. Gaseous and $PM_{2.5}$ emissions as a function of the EGR rate for a thermal input of 17 kW.

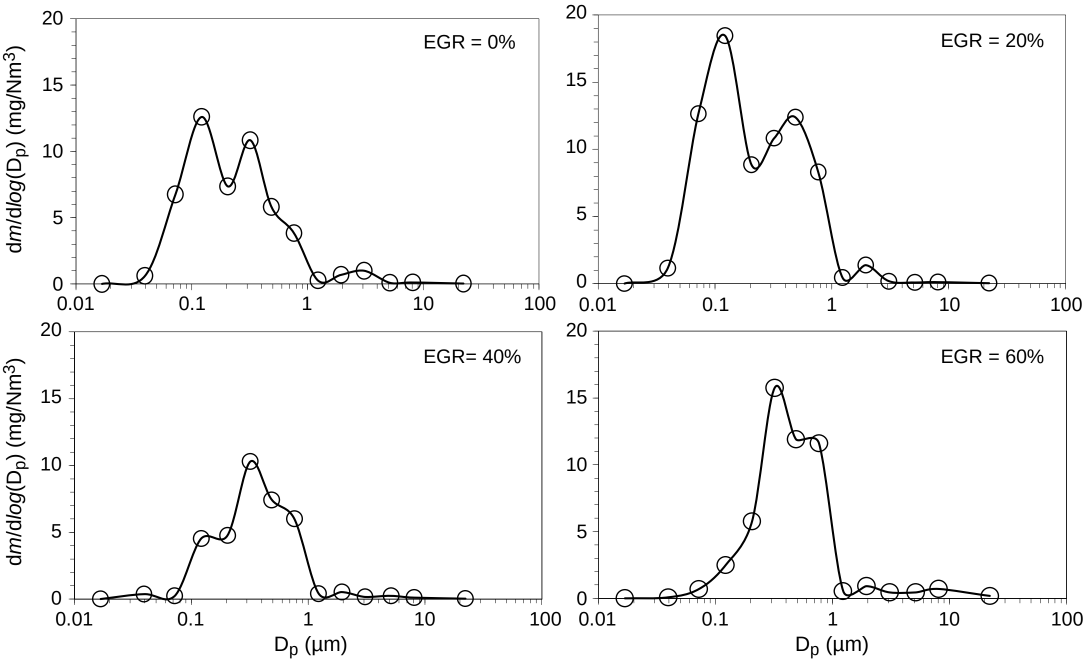

Figure 2. PM size distribution for four EGR for a thermal input of 17 kW.

Acknowledgements

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Dehydrogenation and aromatization of growing soot particles

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Carbonaceous aerosols, largely produced from the combustion of fossil fuels and widely distributed in the atmosphere, affect the solar input to the earth–atmosphere system by scattering and absorbing radiation and by providing sites for the condensation of clouds. Particulate matter emission from combustion processes may affect the hearth energy balance in different way on the climate in dependence on the chemico-physical properties as the size and the composition of the particles. Thus the optical properties, and in particular the light absorption from combustion-derived carbon-based particles (soot), are critical input in modeling the aerosols effects on radiative transfer and the anthropogenic activities impact on climate.

It has been argued that the H/C atomic ratio is a reasonable, but defective predictor of light absorption from carbon particles due to the complex effect of their composition and structural features on the optical properties [1]. Moreover, carbon particles may have H/C ratios strongly varying in dependence on their source. In our previous work the relation between the H/C ratio and the absorption coefficient of flame-formed carbon particles was studied [2]. It was shown that the mass absorption coefficient is relatively low and sensitive to H/C variations in the 0.3 down to 0.1 range whereas it steeply increases to very high values when the H/C value falls below 0.1, even for very small changes of the H/C ratio.

The effect of the type of C-H bonding (aliphatic or aromatic) on the mass absorption coefficient has been investigated in this work by quantitative FT-IR analysis of hydrogen linked to soot particles sampled in premixed ethylene flame. The discrimination between aliphatic and aromatic hydrogen of soot allowed giving some insights in the dehydrogenation process accompanying soot formation. The contribution of both aliphatic and aromatic hydrogen was found to determine the production of hydrogen-rich low light-absorbing soot in the first phase of soot formation. As soot massively formed the early depletion of aliphatic hydrogen caused the production of hydrogen-poor carbons having a high absorption coefficient. The increase of the absorption coefficient for H/C below 0.1 demonstrates that there is no relationship between optical properties and hydrogen content for hydrogen-poor carbon materials. Thus, structural transformations in size and density of aromatic layers are suggested to be the main phenomena occurring in the last phase of soot growth.

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Combustion intermediates relevant to gas phase soot precursor's formation in acetylene flames

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In this work the chemistry of various combustion intermediates has been studied concerning their role in formation and consumption of species widely accepted as gas phase soot precursors. The work was focused on acetylene flames as they are believed to have a specific chemistry that needs additional investigation. In this study a well-known chemical kinetic scheme [1] was chosen. The detailed kinetic mechanism is originally developed and validated for describing the high-temperature combustion of basic systems of type $H_2/CO/C_1$-C_4, and in this particular study it was applied for investigating the flame structure of several recently obtained $C_2H_2/O_2/Ar$ laminar flames. The model was extended with a subset of reaction pathways describing the formation and consumption of key species that are absent in the original version of the mechanism. Additionally a few subsets of the original scheme were reconsideration in order to improve the behavior of various combustion intermediates governing the aromatics chemistry processes. Furthermore, several reaction pathways for small aromatics formation were implemented together with the relevant kinetic and thermodynamic parameters. These modifications showed minor effect on the major species profiles, whereas a considerable influence was observed for various combustion intermediates, sensitive to the updated reaction sub-models.

Acknowledgments

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Oral Contributions WG4

Working Group 4: Improvements of models for mechanism reduction uncertainty analysis

The value of of uncertainty studies for the evaluation and improvement of combustion models

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The accuracy and robustness of combustion models is critical to their ability to be used in design applications for practical devices. Whilst the community has been able to provide more and more accurate descriptions of reaction pathway structures for a widening range of fuels, the quantification of these processes is extremely time consuming. Experimental studies, detailed kinetics experiments and theoretical estimations of rate parameters all have a role to play in evaluating and improving the parameterisation of these models. The incorporation of uncertainty and sensitivity analyses into the evaluation process can also help to guide more detailed studies to the improvement of those parameters which drive predictive uncertainty the most. Optimisation approaches can then be used to attempt to lower the uncertainty of key parameters based on a wide selection of information that can help to constrain them. A key question however is how such approaches could be applied in practice for larger fuels. The presentation will discuss case studies of the application of uncertainty and optimisation methods in combustion and possible future directions that could be applied to complex systems.

Consistent chemical mechanism from collaborative data processing: H_2/CO mixtures

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To reliably develop predictive reaction models for complex chemical systems requires integration of large amounts of theoretical, computational, and experimental data collected by numerous researchers. The integration entails assessment of the consistency of the data, validation of models, and quantification of uncertainties for model predictions. Approach to the development of mechanistic reaction models consists of conjecturing the reaction mechanism and comparing the predictions of the constructed model to available experimental observations. Typically, such comparisons result in mixed outcomes: some show a reasonably close agreement and some do not. In the latter case, the apparent inconsistency obtained between the model and the experiment is argued to imply either that the model is inadequate or that the experiment (or, rather, its interpretation) is incorrect. DataCollaboration module of the automated data-centric infrastructure, Process Informatics Model (PrIMe) [1-3], can establish consistency or inconsistency of a data-and-model system, when the kinetic parameters of a reaction mechanism and experimental observations used for model validation are known within its uncertainties.

In the present study, DataCollaboration [1-3] is applied to the H/CO reaction system [4] to perform a systematic uncertainty and consistency analysis of the model parameters and related experimental data (ignition delay times and laminar flame speeds), to revise and to optimise the model parameters and finally to obtain a predictive model with an evaluated uncertainty level, addressing questions of practical significance. The initial results demonstrate clear benefits of the PrIMe methods for developing predictive kinetic models, Fig.1.

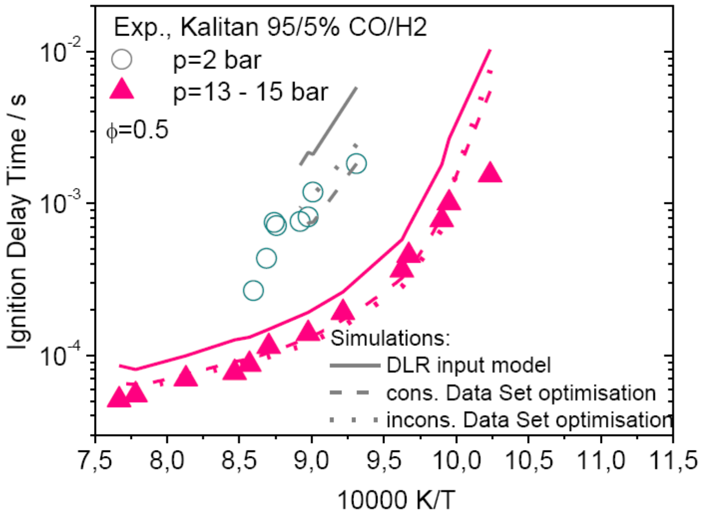

Figure 1. Comparison of the experimental ignition delay times for H_2/CO/air mixtures [5] at $\phi=0.5$ and different pressures against corresponding simulations performed with the models optimized on the consistent and inconsistent datasets.

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Comparison of chemical kinetic mechanisms for lean methane/propane mixture ignition at high pressures

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Despite the increase in power of computers, simplified chemical kinetic mechanisms are still required for CFD simulations. These simulations are an important step towards a more efficient development of new engines, e.g. lean biogas-fueled internal combustion engines. Four recently published mechanisms were chosen to perform a parameter variation study using COSILAB software. These mechanisms cover C1-C3 fuel combustion and preferably also NOx formation: NUIG NGM 3 [1] (no NOx), POLIMI CRECK C1-C3 [2], SAN DIEGO + NOX [3] and USC-MECH II [4] (no NOx).

They were compared to each other by calculating the ignition delay time obtained from a zero-dimensional homogeneous ignition process in an adiabatic batch reactor. As a model for treated biogas, methane/propane mixtures were assumed at high pressures of 70-140bar, temperatures from 700K to 1000K and air-to-fuel ratios from 1.5 to 2.

All mechanisms showed trends in the correct direction for all dependencies calculated except for NTC behavior for mixtures with higher propane content which is only described in NUIG NGM 3 and SAN DIEGO mechanism which in general agree very well with each other for the calculated conditions. Nevertheless the absolute values varied significantly for different mechanisms. Since the NTC region is not modeled by all mechanisms, ignition delay times for lower temperatures and higher propane contents varied more than for higher temperatures and lower propane contents. While all mechanisms showed a linear dependency for the variation of the air-to-fuel ratio very well, the absolute values varied even for pure methane.

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Modeling of particle size distribution function of incipient soot formed in laminar premixed flames

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Polycyclic Aromatic Hydrocarbons (PAHs) are a group of chemicals that occur naturally in coal, crude oil and gasoline. The nearly endless growth process of PAHs, where the six carbon atoms form an aromatic ring, necessitates a detailed understanding of chemical reaction pathways responsible for their formation and sequential growth, followed by the nucleation or inception of small soot particles, soot growth by coagulation and mass addition from gas phase species etc.

The transition process from planar PAHs to spherical nascent soot particles is accompanied with stocking of PAHs on top of each other. Because the growth of PAHs involves an unlimited number of different species and reactions, a detailed description of the entire process is yet not possible. But to still make a proposition about the amount of PAHs formed and their size distribution, the statistical method of Linear Lumping [1] that describes the chemical source terms of PAHs was proposed by Frenklach. Therefore the growth of PAHs can be approximately described as a rapid polymerisation [2] process. In this study, it is assumed that the rates of polymerisation of PAHs and that of particle formation from both PAHs and condensation of PAHs at the soot surface are faster than the rates of convection and diffusion. As a result, the Steady State Assumption can be introduced for every single PAH that leads to a systematical reduction and consequently a clear decrease of numerical effort. In general, this assumption is valid, if there are chemical reactions which consume a chemical specie faster than it is formed by other reactions. In multidimensional steady systems it means that the convective and diffusive terms in the conservation equations are essential smaller than the chemical terms.

According to the steady state condition, we investigate in this work the Particle Size Distribution Functions (PSDF) of the PAHs and incipient soot within a range of temperatures and compositions. Instead of endless conservation equations for every single PAH a limited number of the moments of the size distribution functions of the PAHs can be solved. In the HACA mechanism described by Frenklach [3] the accumulation of acetylenes and the aromatic ring closure is described in one reaction only, whereas in this study we divide it into two reactions in a modified HACARC mechanism [4]. This division is introduced, because the connection between the attached acetylenes and the soot surface element can be broken at high flame temperature before a new ring closure occurs. Furthermore in contrast to Mauss et al. [4], in this work, the ring closure is assumed to be irreversible.

In general, the well-known bimodality of the incipient soot PSDF can be described by using a complex log function [5]. In this work an algebraic description of the target particle diameters region based on one Difference Equation System is established and then solved with the help of Z-transform. The primary results have been evaluated against published experimental study from Wang et al. [5] and the satisfactory agreement in target range has been achieved.

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Kinetic analysis of ethyl iodide pyrolysis based on shock tube measurements

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The optimization of a kinetic mechanism of the pyrolysis of ethyl iodide was carried out based on data obtained from reflected shock wave experiments with H-ARAS and I-ARAS detection. The experiments were conducted in a stainless steel shock tube behind reflected shock waves at temperatures between 957 K and 1397 K, and pressures between 1.3 bar and 1.8 bar with argon as bath gas. The experimental details have been published in article [1]. The thermal decomposition reaction of C_2H_5I behind the reflected shock wave was monitored using H-ARAS (in 23 cases) and I-ARAS (in 6 cases) at wavelengths of 121.6 nm and 183 nm, respectively. In the kinetic analysis and mechanism optimization study, all these measurements were taken into account together with the rate coefficients measured by Michael *et al.* [2] for reaction $H_2 + I \rightarrow H + HI$. The experimental data were interpreted using the following 5-step mechanism: R1: $C_2H_5I \rightarrow C_2H_5 + I$; R2: $C_2H_5 + M \rightarrow C_2H_4 + H + M$; R3: $C_2H_5I \rightarrow C_2H_4 + HI$; R4: $H + HI \rightarrow H_2 + I$; R5: $C_2H_5I + H \rightarrow C_2H_5 + HI$. Arrhenius parameters A and E of reactions R1, R3, R4, and R5 were determined from the experimental data. The joint covariance matrix of the optimized Arrhenius parameters was also calculated. This covariance matrix was converted to the temperature dependent uncertainty parameters f of the rate coefficients and to the temperature dependent correlation coefficients between pairs of rate coefficients. Each fitted rate coefficient was determined with much lower uncertainty compared to the estimated uncertainty of the data available in the literature. The calculated uncertainty parameters correspond to the following 1σ uncertainties of the rate coefficients: 2-3% for reaction R1, 6% for reaction R4, 15-25% for reaction R3, and 5-40% for reaction R5. The C_2H_5I decomposition branching ratio, $k_{R1} / (k_{R1} + k_{R3})$, was calculated from the optimized rate parameters and it was found to be 0.965 at 900 K, decreasing nearly linearly to 0.905 at 1400 K. The extrapolated branching ratio value is 0.840 at 2000 K. This is in good accordance with several other recent measurements. Kumaran *et al.* [3] suggested branching ratio of 0.87±0.11 for temperature range 950 K – 2050 K. Yang and Tranter found that the branching ratio should be higher than 0.87. Miyoshi *et al.* [5] carried out shock tube experiments coupled to I-ARAS detection in the temperature range of 950 K – 1400 K and found branching ratio 0.92±0.06.

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Global sensitivity analysis of dimethyl ether oxidation in an atmospheric pressure laminar flames using open-source software tools: A case study

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Global sensitivity analysis enables the study of the impact of reaction rates over their whole range of uncertainty and allows couplings between parameters to be explored. The quasi-random sampling high dimensional model representation (QRS-HDMR) method [1] has proved to be an efficient tool for mapping the relationships between the inputs and outputs of models and therefore can be used to perform global sensitivity analysis of detailed chemical kinetic models. The aim of this work was to develop an intuitive interface for sensitivity analysis based on implementation of open-source software tools, thus supporting the wider applicability of the QRS-HDMR method for future studies related to the combustion community. Thus, an important objective of this work is to perform a pilot case study aimed at testing and further improving the specific-purpose software tools.

The Cantera software toolbox (version 2.0.0) [2] was employed for modeling the structure of the one-dimensional premixed flat flames and nonpremixed counterflow flames. Global sensitivity analysis is based on quasi-random sampling of the model input parameters and hence a large number of model simulations should be performed for samples of input parameters which fall within the uncertainty boundaries of the input space. This process requires automation and hence the original C++ kernel of the Cantera code was interfaced via specific-purpose Python scripts designed to perform automatically appropriate calculations for the global sensitivity study. Implementation through such scripts enables the progress of multiple simulations and data manipulation in an efficient way on an arbitrary (Windows/Unix) computational platform. Additional subroutines and libraries were developed or linked in order to provide the simulation results in the required data format for the global sensitivity study. The routines were designed to be general enough to be applied to a wide variety of combustion schemes and configurations.

Initial testing of the given set of tools was focused on the atmospheric pressure oxidation of dimethyl ether (DME) in laminar premixed and nonpremixed flames. The availability of accurate and reliable detailed chemical kinetic models of dimethyl ether oxidation is of key importance for the further development of simplified schemes that could be used for simulating practical combustion devices.

Therefore, sensitivity of selected predictive target quantities (flame temperature maxima, methane and formaldehyde concentration maxima) to potential uncertainties within the input data of available chemical kinetic scheme [3] was investigated through implementation of QRS-HDMR method, see Figure 1.

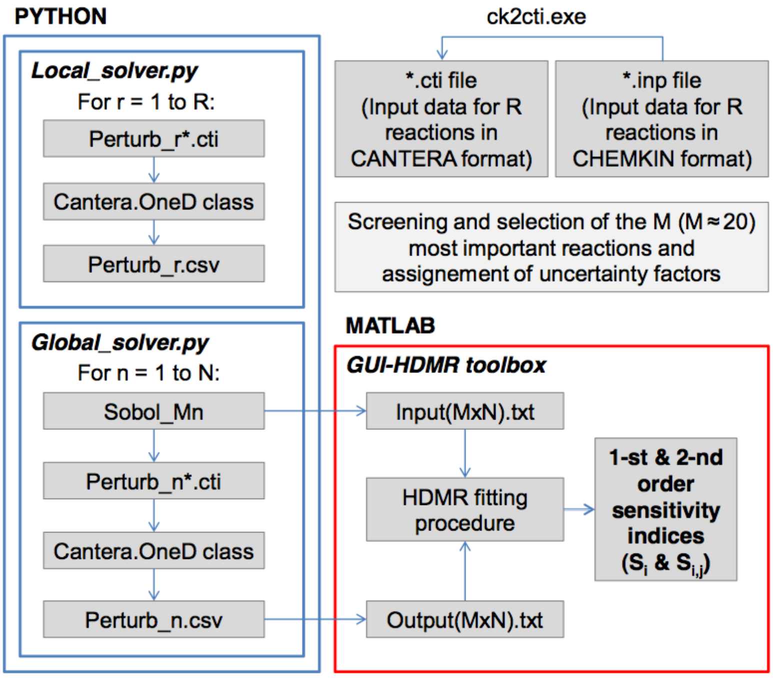

Fig. 1: The schematic overview of the implementation of the QRS-HDMR method using open-source software tools (it should be noticed that the MATLAB license is required for the final step).

High dimensional model representation provides an efficient response surface generation method well suited for calculating the variance based sensitivity indices. The MATLAB based software tool GUI-HDMR [4] was used to fit an HDMR to the input-output response surface for the target quantities and global sensitivity indices were determined with respect to the selected reaction rates (A-factors) and relevant uncertainties. Such information is crucial in order to identify the most important parameters influencing the prediction of the chosen target quantities and provide deeper insight into the complex chemistry involved in DME flames.

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Reaction mechanism reduction and optimization by evolutionary algorithms

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Combustion of fossil and bio-fuels is usually described by reaction mechanisms consisting of hundreds of species and thousands of reactions. Thus the applicability for cases which require many evaluations of detailed reaction mechanisms, like computational fluid dynamics or generation of look-up tables, is limited by the available computational resource. Assuming that in a certain range of parameters only a smaller subset of reactions dominates the process, very large reaction mechanisms can be significantly reduced still preserving the main properties of the detailed mechanism.

The reaction subset is found by a search for unimportant reactions and species, which is performed in a given range of parameters, e.g. an initial mixture composition. The tolerances for accuracy loss due to the modifications of the mechanism are set by the user at the beginning of the reduction procedure. The genetic algorithm (GA) based method searches for the reaction subset until an optimum of mechanism size and accuracy is found. The GA parameters are set to force the reduction of the mechanism. The accuracy of the mechanism is tracked by monitoring features like ignition delay time, temperature and species concentration profiles. Subsequently the reduced reaction mechanism is optimized by tuning the rate coefficients of the remaining reactions in order to restore the prediction accuracy of the detailed mechanism. The optimization procedure uses also a genetic algorithm.

We present the fully automated and parallelized reduction and optimization process of a tert-Butanol combustion mechanism [1] by the proposed evolutionary algorithm method. The evaluation of the test problem during the search and optimization is performed by the open-source kinetics library cantera [2] using a homogeneous reactor model at constant pressure. The convergence of the method is demonstrated and the influence of the GA evaluation function is discussed.

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The effect of argon dilution on the structure of dimethylether cup-burner flame

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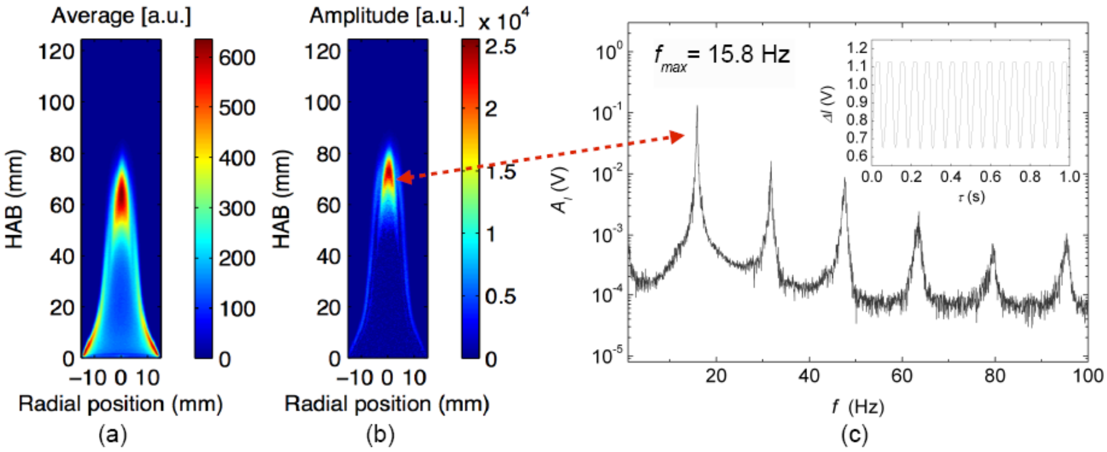
The effect of argon dilution on the structure of nonpremixed hydrocarbon flames (see e.g. [1]) and the relationship of oxygen concentration in coflowing air and pulsation frequency of cup-burner flame were reported previously [2]. However, in the case of oxygenated fuels, effect of dilution can imply qualitatively different behavior of buoyancy dominated flames, as further discussed in this work.

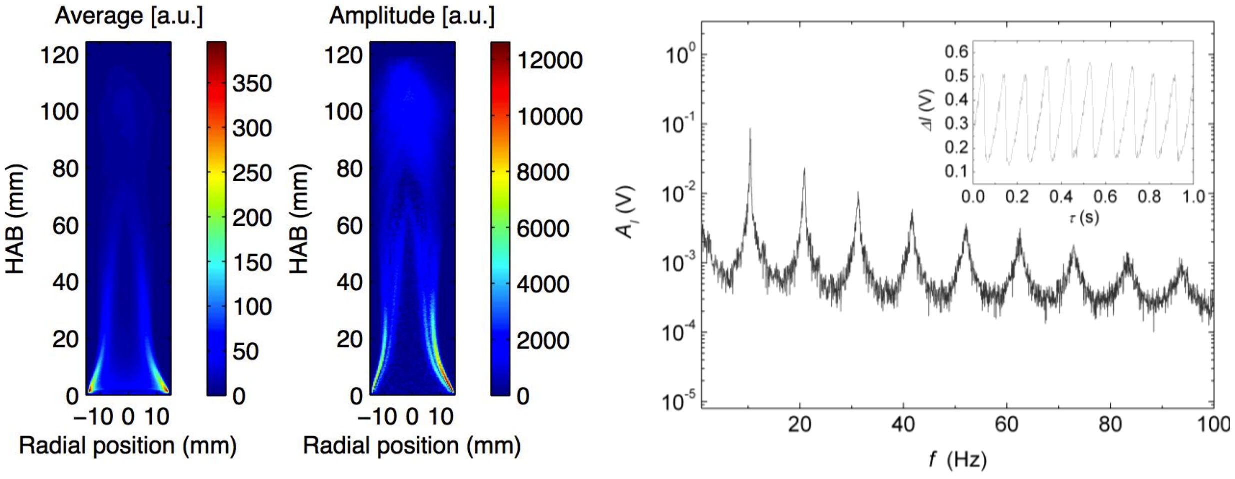
Experimental observations employing spectrally-filtered imaging followed by the spatially resolved fast Fourier transform (FFT) analysis were performed in order to describe the unsteady structure of the reaction zone of dimethylether (DME) cup-burner flames burning in undiluted ($X_{\mathrm{Ar}} = 0$) and diluted ($X_{\mathrm{Ar}} = 0.3$) air. Optical bandpass filter transmitting light at the wavelength range of 380±10 nm was used for this purpose. Two-dimensional maps of temporally averaged intensities and local FFT amplitudes shown as the color plots below were determined based on the post-processing of data acquired by the imaging system at the frame rate of 25 FPS. The main pulsation frequency were obtained based on FFT analysis of signal from the Si photodiode (wide-angle point detector) operating at 500 Hz, as depicted in the Figure 1 c) and Figure 2 c).



(a) (b) (c)

Fig. 1: The plot of temporally averaged local intensities (a) and FFT amplitude (b) at the main pulsation frequency (f_{max}) of undiluted flame with the corresponding frequency spectrum and signal curve (c).

In the case of undiluted flame, signal from electron multiplying charge coupled device camera is dominated by the chemiluminescence ($B^2\Sigma \rightarrow X^2\Pi$ emission band of CH radical) from the stable attached flame base and highly luminous soot emission from the flickering flame tip exhibiting local maxima of FFT amplitude, see the red arrow in Figure 1. Significantly different oscillatory behavior was observed in the case of argon diluted flame (Figure 2).



(a) (b) (c)

Fig. 2: The plot of temporally averaged local intensities (a) and FFT amplitude (b) at the main pulsation frequency (f_{max}) of argon diluted flame with the corresponding frequency spectrum and signal curve (c).

Formation of the periodically pulsating plume, see apparent local maxima downstream of the relatively stable flame tip region in Figure 2 a) and b), was not observed in the case of methane cup-burner flames. In order to investigate the origin of such hydrodynamic instabilities, detailed chemical kinetic scheme of DME oxidation [3] was implemented into the OpenSMOKE library (see [4] and the references given therein) suitable for unsteady laminar flame simulations in the OpenFOAM® framework. Such approach enables to elucidate the features observed experimentally and provides additional information concerning the coupling between the phenomena of chemical kinetics and fluid flow physics involved in the buoyancy driven laminar nonpremixed flames.

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On the structure of hydrogen, carbon monoxide and methanol combustion models

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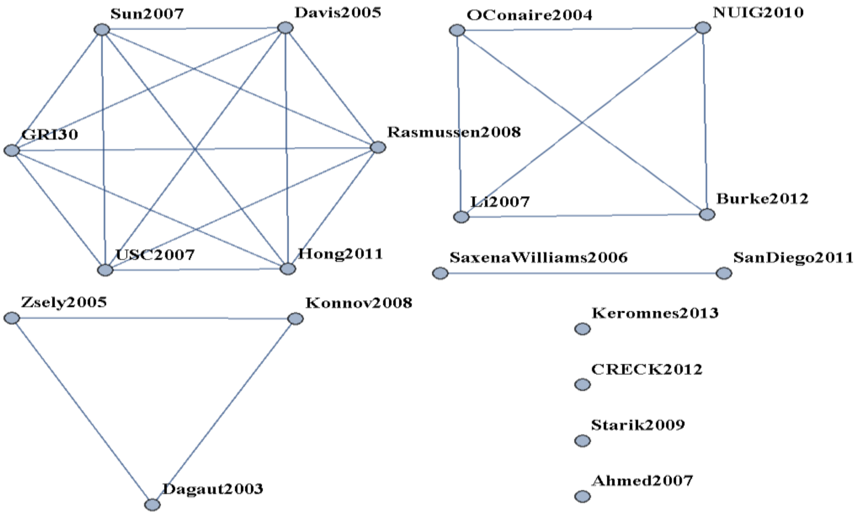
Using `ReactionKinetics`, a *Mathematica* based package 39 detailed models for combustion of hydrogen, carbon monoxide and methanol are investigated [1]. Essential structural characteristics – such as FHJ graph and its largest component, Volpert graph and its indexing starting from different initial species, deficiency, reversibility – are extracted, and similarities and differences of the mechanisms – such as species, reaction steps – are highlighted. The results are in correspondence with quantitative investigations [2,3]: the structure of the models of hydrogen combustion are more stabile, whereas in the case of methanol the authors of different models are very far from agreement. Such studies can be used before or parallel with usual numerical investigations, such as pathway analysis, sensitivity analysis, parameter estimation, or simulation. Structural relations between hydrogen combustion models are shown in the Figure.



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Evaluation of the influence of thermodynamic data for propane and propene ignition delay times.

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Reliable quantitative information on the thermodynamic properties of organic compounds especially for radical and chain-hydrocarbons is quite limited. Experimentally, it is difficult to obtain the equilibrium data directly. In the situation where experimental data are not available, most often these data are estimated or predicted. In view of this, many different theoretical techniques, have been proposed, that can compute and evaluate enthalpies, entropies, and other properties.

However, due to the different techniques available, the values computed may vary for the difference sources. New developed computational methods for properties predictions have been developed and new values of thermodynamic data are available [1].

In this study, the influence of thermodynamic data on propane and propene chemistry for shock tube experiments [2,3] has been investigated. The species sensitive for enthalpy change over ignition delay time for propene were detected with the help of a sensitivity analysis. The thermodynamic data of the C3 sensitive species from our database were replaced using the values from Goos et al. [1] database. The differences established through the comparison of these quantities shows a positive influence on the prediction of the propene and propane ignition delay times. All calculations were performed with the latest version of the DARS program [4] and the current version of the base chemistry from BTU-Cottbus [5], which is based on the work of Hoyermann et. al 2004 [6] was used.

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Oral Contributions WG5

Working Group 5: Experimental and theoretical determination of thermochemical parameters and rate coefficients for elementary steps crucial for successful simulation, but for which important uncertainties remain

Elementary chemical steps in combustion – From biofuels to NO_X formation

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An adequate kinetic parameterization of the elementary chemical steps in combustion mechanisms is a necessary prerequisite for a successful modeling. In the contribution, we will give an overview on experimental and theoretical studies performed in our group at KIT over the last 3 years in collaboration with partners from the COST action.

Examples include initial steps in the pyrolysis of 2,5-dimethylfuran (with J. M. Simmie, NUI Galway, Ireland) [1, 2], the development of a mechanism for 2,5-dimethylfuran pyrolysis (with R. Fournet and B. Sirjean, CNRS and Universite de Lorraine, Nancy, France) [3], the thermal decomposition of the NCN radical (with G. Lendvay, Hungarian Academy of Sciences, Budapest, Hungary) [4, 5], and the global characterization of C_2H_5I pyrolysis as a H atom source in shock tube experiments (with T. Turányi and I. Gy. Zsély, Eötvös University, Budapest, Hungary) [6, 7].

The different experimental and theoretical approaches will be elucidated and consequences for combustion modeling will be discussed.

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Ab initio characterization of the Cresol potential energy surface

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The chemistry of anisole (methoxybenzene), a lignin model compound, has been the subject of kinetic studies for several decades and a detailed mechanism developed by Pecullan and coworkers [1] is able to describe many aspects of their experimental findings. However, the reason for the high yields of cresols and particularly phenol remained unclear and seemed unexplainable. Recent work by Carstensen and Dean [2] suggests that phenoxy radicals are less reactive at low temperatures than previously expected, making them available for recombination with methyl. This led to the current work. The anisole/cresol potential energy surface (C_7H_8O PES) is investigated at the CBS-QB3 level of theory and transition state theory is used to calculate the rate coefficients of reactions that proceed via pronounced barriers. Several rate coefficients for "barrierless" reactions are determined with variational canonical transition state theory. The surface is very complex as it contains in excess of 30 wells (isomers) and more than 100 elementary step reactions. To evaluate the competition of the various reaction channels at 1 atm, we employ QRRK theory coupled with the modified strong collision assumption to calculate apparent pressure-dependent rate coefficients.

Although anisole might directly isomerize to access other parts of the C_7H_8O PES, a more likely scenario is that anisole first decomposes to methyl and phenoxy radicals, which can subsequently recombine to chemically excited C_7H_8O isomers. Low energy barriers allow several of these isomers to interconvert rapidly. Although cresols are energetically the most stable species, their formation requires passing through a tight transition state of relatively high energy. This allows bimolecular product channels such as CO elimination channels as well as re-dissociation to phenoxy plus methyl to compete.

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The work in the US was supported by the National Advanced Biofuels Consortium.

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The chemical kinetics of the reaction $R^{\bullet}$ + HBr(HI) $\rightarrow$ RH + Br(I)$^{\bullet}$ in the range 293-623 K for $R^{\bullet}$ = $C_2H_5^{\bullet}$, i-C_3H_7, n-$C_3H_7^{\bullet}$, and t-$C_4H_9^{\bullet}$

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The goal of the present research is a reinvestigation of the kinetics of free radical-molecule reactions of the type $R^{\bullet}$ + HX (X = I, Br) $\rightarrow$ RH + $X^{\bullet}$ in the range 293 to 623 K. Together with their inverse that have been measured in the past, the present measurements will provide equilibrium constants as a function of temperature enabling the extraction of thermochemical parameters ($\Delta H^0_f(R^{\bullet})$, $S^0(R^{\bullet})$) for the free radicals of interest ($C_2H_5^{\bullet}$, i-$C_3H_7^{\bullet}$, n-$C_3H_7^{\bullet}$, a-$C_3H_5^{\bullet}$, i- or s-$C_4H_9^{\bullet}$, t-$C_4H_9^{\bullet}$ and $C_7H_7^{\bullet}$). Recent studies of the rate parameters of this type of reactions have shown contradictory results, as some researchers reported high rates of reaction associated with a negative activation energy [1-3], while others reported significantly lower rates and positive activation energies [4]. The kinetics of the title reaction is still under debate today, and the solution of this problem is eagerly awaited as previously published "consensus" data were routinely used to determine the thermochemical parameters such as $\Delta H^0_f(R^{\bullet})$ and $S^0(R^{\bullet})$ for prototypical hydrocarbon free radicals. As of late, two sets of significantly different standard enthalpy and absolute entropy values exist in the literature and are discussed, which is an unacceptable situation in view of the key role played by these chemical intermediates important in combustion and atmospheric processes.

In order to achieve the mentioned objective, a new experimental apparatus was constructed (Figure 1). It consists of a Knudsen flow reactor coupled to single-photon (VUV) Photoionization Mass Spectrometry (PIMS) in "line-of-sight" geometry. Hydrocarbon free radicals are generated before their introduction into the Knudsen reactor according to two different chemical schemes: Firstly, a flow of 20% H_2/Ar or 2-5% Cl_2/Ar mixture is established across a tube excited by a 2.45 GHz (λ = 12.2 cm) microwave discharge. When the μ-wave discharge is turned on and powered at 40W, approximately 50% and 80% of H_2 or Cl_2, respectively, undergo bond scission and generate $H^{\bullet}$ and $Cl^{\bullet}$ atoms. This flow of atomic radicals react downstream in a second tube in the presence of a free radical precursor in order to generate the hydrocarbon free radical of interest according to either one of the following reactions: $H^{\bullet}$ + RI $\rightarrow$ $R^{\bullet}$ + HI or $Cl^{\bullet}$ + RH $\rightarrow$ $R^{\bullet}$ + HCl. This system enables a thermal free radical $R^{\bullet}$ generation for essentially two reasons: (i) no direct precursors of $R^{\bullet}$ (RH or RI) interact with the diffuse microwave plasma, and (ii) the numerous collisions of $R^{\bullet}$ with the wall of the second tube will remove a potential excess of internal energy in $R^{\bullet}$. It is therefore expected that all radicals emanating from this second tube and flowing into the Knudsen reactor are thermalized. Artefacts that may perhaps lead to negative values of E_a and the associated abnormally large rate constants are thus minimized or are absent in view of the chemical generation scheme (abstraction of I or H from precursor).

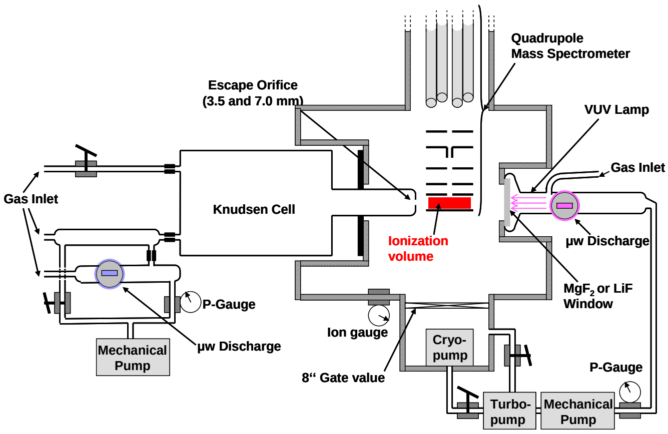

Figure 1: Schematic diagram of PIMS instrument for free radical detection using VUV photoionization

The so produced free radicals flow into the Knudsen reactor via a capillary and react with HX admitted across a separate inlet in an accurately regulated and measured flow. The gases escape from the reactor in an effusive molecular beam across an orifice of 3.5 or 7 mm diameter into the mass spectrometry chamber and are identified and quantitatively analyzed using single-photon VUV-PIMS. An important feature of this experimental device is the close proximity of the beam-forming orifice of the Knudsen reactor to the ionization volume of the quadrupole mass spectrometer. PI was used as it allows a more specific and sensitive detection of $R^{\bullet}$ and selected stable closed shell molecules compared to electron impact MS.

These experiments have so far led to the determination of the rate constants for: $C_2H_5^{\bullet} + HBr \rightarrow C_2H_6 + Br^{\bullet}$, $C_2H_5^{\bullet} + HI \rightarrow C_2H_6 + I^{\bullet}$, $i\text{-}C_3H_7^{\bullet} + HI \rightarrow C_3H_8 + I^{\bullet}$ and $n\text{-}C_3H_7^{\bullet} + HI \rightarrow C_3H_8 + I^{\bullet}$ in the temperature range 293 to 623 K. Results relevant to $t\text{-}C_4H_9^{\bullet}$ will also be discussed. As an example of representative results, Figure 2 shows measurements for the reaction of $C_2H_5^{\bullet}$ + HBr as well as data of previously published results. All results obtained are consistent under all experimental conditions investigated (different reactors, coatings of the Knudsen reactor and radical generation schemes) as well as for both disappearance of $R^{\bullet}$ and formation of closed shell products. The Arrhenius plots in the temperature range 293 to 623 K clearly indicate that these four reactions have low second order rate constants at ambient temperature assorted with a positive temperature dependence of the rate constant. Improvements of the experimental apparatus explain the discrepancies between the present and previous results. The present results suggest a revision of some thermochemical quantities ($\Delta H^0_f(R^{\bullet})$, $S^0(R^{\bullet})$) that are currently widely recommended and used. Table 1 summarizes the rate parameters derived from the obtained Arrhenius plots, as well as a preliminary evaluation of the $\Delta H^0_f(R^{\bullet})$ for $C_2H_5^{\bullet}$, $i\text{-}C_3H_7^{\bullet}$ and $n\text{-}C_3H_7^{\bullet}$ radicals resulting from this work. These have been obtained according to the second and third law method by using currently accepted values of ΔH^0_f of all reaction partners except the free radical in question and of rate constants for the reverse reactions. Currently used ΔH^0_f from [8] are also reported for comparison.

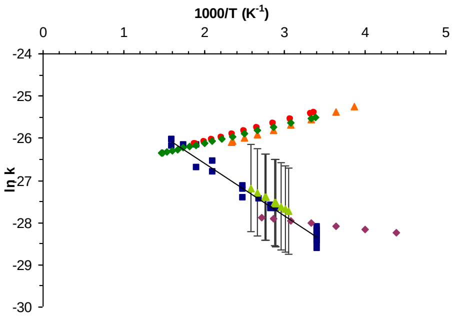

Figure 2: Measured kinetic rate of $C_2H_5^{\bullet} + HBr \rightarrow C_2H_6 + Br^{\bullet}$ and comparison with data previously published. ■ Present work, ▲ Nicovich et al. [1], ● Seakins et al.[2], ♦ Seetula[3], ♦ Dobis and Benson[4], ▲ for Fettis and Trotman-Dickenson [5] in combination with Hunter et al. [6] and Hayes et al.[7]. Uncertainties reflect the disagreement between the studies of Hunter et al. [6] and Hayes et al. [7]

Table 1: Obtained rate parameters and preliminary assessment of $\Delta H^0_f(R^{\bullet})$ for the studied free radicals.

Reaction	A (cm^3/molec. s)	E_a (kJ/mol)	$\Delta H^0_f(R^{\bullet})$ (kJ/mol)	$\Delta H^0_f(R^{\bullet})$ from [8] (kJ/mol)
$C_2H_5^{\bullet} + HBr \rightarrow C_2H_6 + Br^{\bullet}$	$3.69\ 10^{-11}$	10.62	109.36	120.90
$C_2H_5^{\bullet} + HI \rightarrow C_2H_6 + I^{\bullet}$	$1.20\ 10^{-11}$	7.12	109.76	120.90
$i\text{-}C_3H_7^{\bullet} + HI \rightarrow C_3H_8 + I^{\bullet}$	$1.53\ 10^{-11}$	7.05	75.07	90.00
$n\text{-}C_3H_7^{\bullet} + HI \rightarrow C_3H_8 + I^{\bullet}$	$6.49\ 10^{-11}$	11.08	88.05	100.48

In conclusion, we have reached our main goal, namely obtaining Arrhenius expressions for the T-dependence of the rate constants for the metathesis reactions of the free radicals displayed in Table 1. A fourth free radical, namely $t\text{-}C_4H_9^{\bullet}$ is under active investigation at this time and will be reported at the meeting.Regarding the new experimental methodology used in the present work, we would like to highlight the following features in distinct contrast to previous work:

- External generation of free radicals using a chemical reaction (abstraction of H or I from closed shell radical precursor)
- Complete understanding of the chemical kinetics occurring in the Knudsen flow reactor, including the behavior of the free radical recombination product in the presence of HX
- Direct detection of free radical using single photon PIMS coupled to analog detection techniques
- Use of two Knudsen flow reactors each with a different gas residence time ($\tau_g = 1/k_{esc}$) corresponding to escape orifices of 3.5 and 7 mm (nominal) diameter. Owing to the Teflon or Halocarbon Wax coating the wall loss rate constant for $C_2H_5^{\bullet}$ free radical is a fraction of k_{esc}.

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Reaction dynamics of oxygen atoms with unsaturated hydrocarbons: primary radical and molecular products, branching ratios and role of intersystem crossing

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Small unsaturated hydrocarbons, such as C_2H_2 (acetylene), C_2H_4 (ethylene) and C_3H_4 (allene and methylacetylene), are crucial intermediates in hydrocarbon combustion, where their dominant consumption pathways are reactions with ground-state oxygen atoms, O(^{3}P). These reactions are characterized by a variety of energetically open, competing radical and molecular product channels, some of which can take place only via intersystem crossing (ISC) from triplet to singlet potential energy surfaces (PES). In combustion modelling, among the most important information needed for each of these elementary multichannel reactions of O(^{3}P) are: (*a*) the overall rate constant, (*b*) the identity of the primary products, and (*c*) the branching ratios (BRs) possibly as a function of collision energy E_c (temperature). While kinetics experiments are able to satisfy point (*a*), point (*b*) and (*c*) still represent a challenge for kinetics, although considerable progress has recently been made[1]. The method most suitable to tackle this challenge is the crossed molecular beams (CMB) scattering technique with “universal” mass spectrometric detection based on “soft” ionization by tunable energy electrons[2] or VUV synchrotron radiation[3].

In this presentation we will report on our recent investigations of the reaction dynamics of O(^{3}P) with acetylene[4], ethylene[5], allene[6] and methylacetylene[7] using the CMB method. By exploiting “soft” electron-ionization we have probed all energetically allowed product channels (up to ten in O+C_3H_4) and characterized the dynamics, branching ratios and extent of ISC. The BRs for the five competing channels leading to H+CH_2CHO, H+CH_3CO, H_2+CH_2CO, CH_3+HCO, and CH_2+HCHO from O+C_2H_4 are analyzed together with those obtained from kinetics studies at room temperature[8] ($E_c \approx 0.9$ kcal/mol). The combined kinetics and dynamics results have allowed us to examine the BRs and the extent of ISC in a wide range of E_cs (temperature), from ~1 kcal/mol (300 K) up to ~13 kcal/mol (4300 K). Experimental results are compared with those of available statistical calculations on *ab initio* PESs for all systems and with those of quasiclassical trajectory surface-hopping computations carried out in a synergic fashion by the group of Bowman on coupled *ab initio* triplet and singlet PESs for the benchmark multichannel nonadiabatic reaction O+C_2H_4. ISC is found to increase strongly with molecular complexity (from about 0% in O+C_2H_2 up to about 50% in O+C_2H_4 and more than 90% in O+CH_2CCH_2) and to depend on molecular structure (about 80% in O+CH_3CCH).

Acknowledgments: Support from MIUR (PRIN 2010-2011) and EC COST Action CM0901 “Detailed Chemical Models for Cleaner Combustion” is gratefully acknowledged.

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Reaction kinetics, photochemistry and CI-engine study of *γ*-valerolactone

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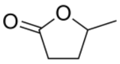
In recent years, very efficient catalytic methods have been developed for the production of γ-valerolactone (GVL) from carbohydrates and even directly from biomass feedstock. GVL has been widely considered as a potential biofuel and a renewable platform molecule for the chemical industry. In contrast with this, apart from our own preliminary reports, no reaction kinetics, photochemistry and engine study with GVL has been published so far.



γ-valerolactone (GVL)

We have used the complementary experimental methods of pulsed laser photolysis and low pressure discharge flow to determine rate constants for the reaction of GVL with OH using resonance fluorescence detection. This reaction is important both in the atmospheric chemistry and combustion of GVL. GVL has been found to react in fast reaction with OH radicals implying a favourable short lifetime (~10 days) for its atmospheric depletion. The reaction does not depend on pressure, displays positive temperature dependence and a non-Arrhenius kinetic behaviour. The experimental results are supported by results of quantum chemical computations.

Exciplex laser photolysis (at 193 and 248 nm) coupled with GC analysis was applied to study the photochemistry of GVL. The overall photolysis quantum yield has been found significantly less than unity indicating the importance of photophysical processes. Products are formed via ring-opening and subsequent intermolecular rearrangements, elimination of CO and CO_2 is less important. Since GVL absorbs light in a significant extent only below ~260 nm, its photochemical degradation can not be significant in the troposphere.

Comparative investigations of engine performance and exhaust emission were performed with fossil diesel (D), D + biodiesel (BD) and D + BD + GVL blends. A four cylinder, turbocharged direct injection diesel engine was used for the tests. The engine was coupled to a dynamometer to vary the load. CO, NO_x, unburned fuel and smoke emissions were measured by using a multi-channel gas analyser. Compared with D, and D + BD blends, addition of GVL had relatively little effect on engine performance and NO_x emissions, but reduced the concentration of CO and smoke significantly.

Ketene formation from P_2O_3/P_2O_5 -catalyzed pyrolysis of acetic acid

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Ketene and its dimer, diketene are of commercial and industrial importance. Because of their multiple functionality, they find application in a number of industrial processes. They serve as starting material for many intermediates used for the production of pigments, drugs and agrochemicals, intermediates for the paper industry or as powerful bactericidal agent. The use of ketene for the production of acetic anhydride has often been used for "recycling" acetic acid. Acetoacetic esters or diketene are utilized for the production of various heterocyclic intermediates. Long chain (C_{12} - C_{20}) alkyl derivatives have been used as paper sizing agents.

Ketene is formed by thermal elimination of H_2O from acetic acid at temperatures above 650°C. In industry this process is catalyzed by P_2O_3/P_2O_5 which is introduced via organic phosphorous compounds. In this work a detailed chemical kinetic mechanism the P_2O_3/P_2O_5-catalyzed formation of ketene (CH_2=C=O) in the 923 K – 1123 K temperature range has been developed. For this, thermochemical properties of intermediates, transition states and products were estimated with the help of Quantum Chemistry methods (DFT at B3LYP/6-311g(d,p)) and ab-initio G3MP2B3 calculations. Application of the transition state theory permitted the evaluation of the rate constants of reactions. A model describing the high temperature $CH_3C(=O)OH/P_2O_3/P_2O_5$ system has been developed and combined with the modified mechanism from Mackie and Doolan [1] which describes the thermal decomposition reactions of acetic acid. It results that the P_2O_3/P_2O_5 mixture accelerates the formation of ketene substantially. The conversion of acetic acid increases with increasing temperature and with higher content of P_2O_5. The mechanism allows the design of temperature profiles for the ketene synthesis with optimal conversion of acetic acid. The mechanism developed for the $CH_3C(=O)OH/P_2O_3/P_2O_5$ system was validated against experimental data [2].

Investigation of methylfuran pyrolysis at Swiss Light Source

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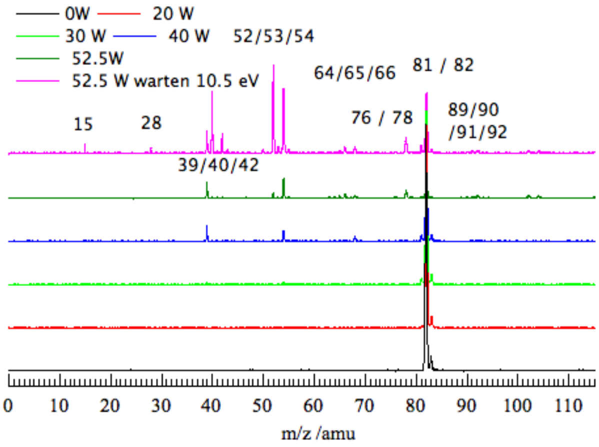
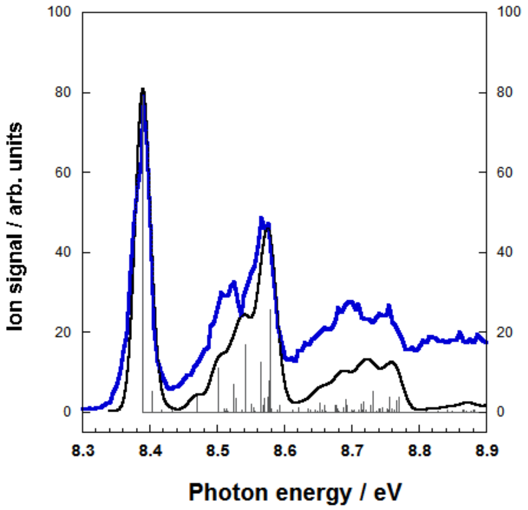
Thermal decomposition of 2-methylfuran under pyrolysis conditions was investigated at the VUV beam line of the Swiss Light Source at Paul Scherrer Institute, Villigen, Switzerland.

A small heated SIC reactor was used to decompose the oxygenated fuel, which was flowing in a buffer gas stream through it. Residual fuel and the resulting reaction products were detected and identified with photoionisation photoelectron technique.

Methylfuran pyrolysis products



A threshold photoelectron spectrum of unpyrolysed fuel was measured (blue line).

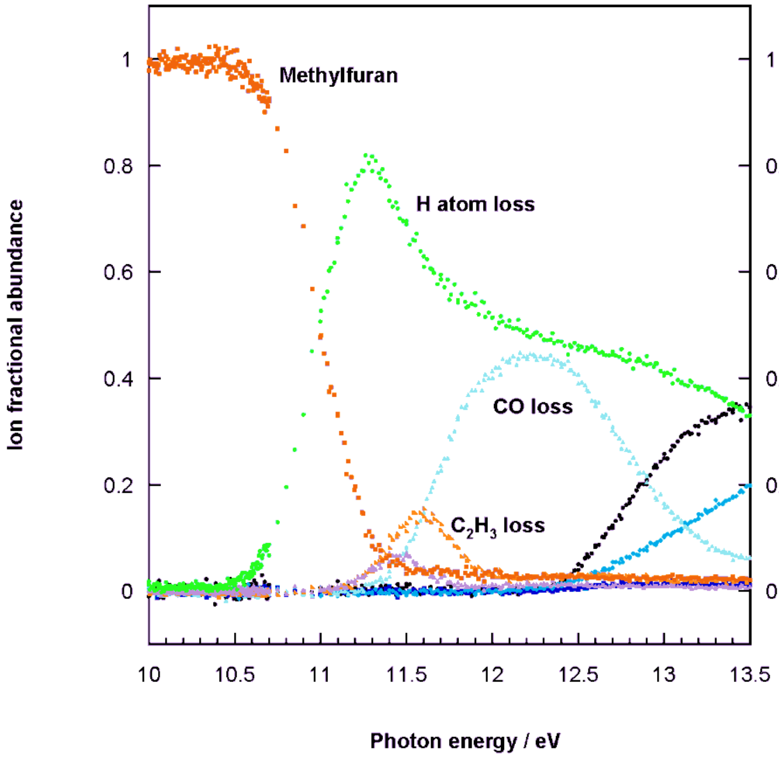


Molecular properties of neutral and ionic fuel molecule in its ground states were calculated with quantum chemical methods and good agreement between measured and calculated ionisation potentials was found.

A photoelectron spectrum in the harmonic approximation of the vibrational modes was calculated (for ideal conditions, especially at a temperature of 0 K). As the measured spectrum was obtained at room temperature, the calculated stick spectrum was convoluted with a gauss function to consider the rotational broadening through the higher temperature (black curve).

Considering the used approximations, such as ignoring anharmonicity and hot bands, the resulting spectrum reproduces the shape of the measured threshold photoelectron spectrum well.

Additionally dissociation of methylfuran ion was observed. The break down diagram shows hydrogen atom, ethenyl and carbon monoxide loss.



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Molecular dynamics investigations on Xylenes and dimethlfurane at the VUV beamline at Swiss Light Source

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Coincident photo-electron- (PES) and Photo-ionization-mass-spectrometry (PIMS) is performed with tunable monochromatic light in the vacuum ultraviolet (VUV) spectral range at the Swiss Light source (SLS). The SLS/VUV beamline, dedicated to molecular dynamics, incorporates a PEPICO (Photo Electron Photo Ion Coincidence) endstation that allows the detection of intermediate short-lived species isomer specifically and the determination of molecule/radical enthalpies via a positive ion cycle. In cooperation with external groups the speciation of pyrolized xylyl and dimethylfuran was investigated using an effusive pyrolytical radical source. It was found the m-xylyl does not convert after H-loss to m-xylylene but to p-Xylylene.

With PEPICO (Photo Electron Photo Ion Coincidence) measurements at the SLS/VUV beamline (Fig 1) the formation enthalpy of molecules and their fragments can be inferred. PEPICO experiments directly yield the formation enthalpy of fragment ions. With additional knowledge of their ionization energies, binding energies in the neutral species can be derived. The registration of ions coincident with zero kinetic energy electrons provides in addition to mass spectrometric information also information about the ionization potential and the vibrational spectrum of an addressed species. This data set enables the disambiguation of isomers of the same compound.

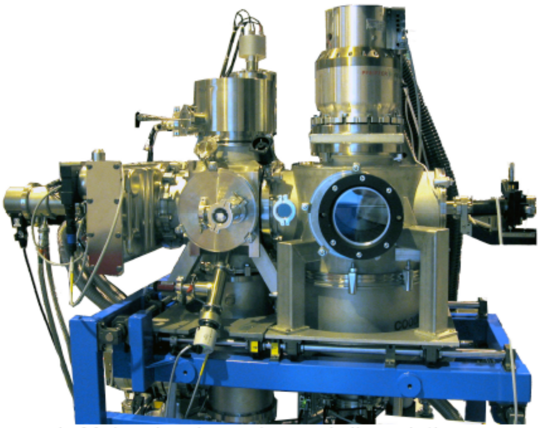

Figure 1: Molecular dynamics and dissociation processes can be measured by PEPICO in a velocity map imaging PES/PIMS apparatus.

The challenge now is to apply the well proven experimental techniques to combustion kinetics. In cooperation with Prof. T. Kasper from the university of Duisburg a flat flame burner was installed in the SLS/VUV iPEPICO end station. From flames up to a pressure of a few 10 mbar intermediates can be skimmed and transferred to the interaction region of the photo-electron, photo-ion time of flight apparatus. Profiles of the radical pool in a flame can be measured by skimming at different heights along the 1-D flame. A first run of experiments with alkene fuels were performed and will be published end of 2013.

Alternatively pyrolytic radical sources can be installed to produce radicals in a molecular beam. Recently the isomerization of m-xylyl to p-xylyl at different pyrolysis temperatures was measured[1].

The speciation of 2,5-dimethylfuran was monitored as a function of temperature (Fig.2). A compilation of the results is currently prepared by Dr. Elke Goos from DLR, Stuttgart.

A new i^{2}PEPICO (imaging Photoelectron-imaging Photoion Coincidence) setup allows

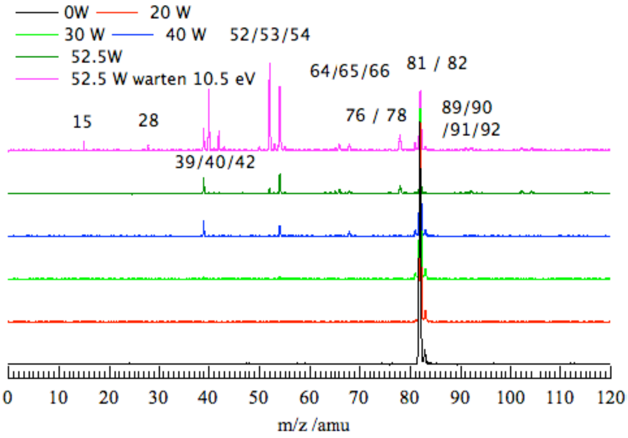

Figure 2: Major pyrolysis products of 2,5-dimethylfurane. The 6 traces correspond to mass spectra acquired at different temperatures (T=uncalibrated. The highest heating power of 52.5 W corresponds to about 1300K).

in addition to mass, electron momentum (zero kinetic energy) and ionization potential, also measurements of fragment ion kinetic energy. Dissociation reactions with a reverse barrier can thus be assessed. This feature is essential for working out thermochemical data for molecules that isomerize prior to a dissociation.

In the fs-laser lab molecular dynamics and dissociation processes are investigated with a recently commissioned ARPES/PIMS apparatus basing on a time of flight (TOF)/velocity map imaging (VMI) detection scheme. Electron and ions leaving the interaction volume can be imaged simultaneously. Molecular systems are probe on the < 100 fs scale with tunable fs-laser pulses. Delayed dissociation/ionization following the probe pulse can be observed with a 20 ps resolution. The new instrument comprises most features of the i2PEPICO instrument at the SLS/VUV beamline.

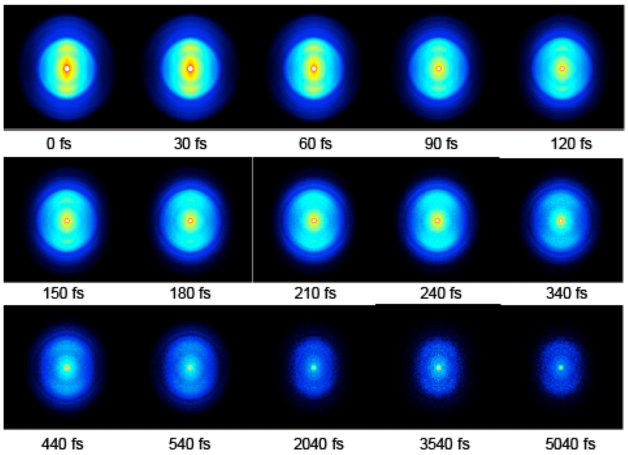
0 fs 30 fs 60 fs 90 fs 120 fs
150 fs 180 fs 210 fs 240 fs 340 fs
440 fs 540 fs 2040 fs 3540 fs 5040 fs

Figure 3: A series of time-resolved raw photoelectron images of o-xylene registered at a pump laser wavelength of 400 nm and a probe wavelength of 800 nm. The linear polarizations of the pump and probe lasers are aligned vertical in the plane of the figure.

We investigated the internal conversion processes in ethylbenzene[2] and o-xylenes[3,4] as an example of a system with strongly reduced symmetry. The non-degeneracy of states in substituted benzenes leads to a higher density of vibrational levels and to a higher number of symmetry-allowed interactions, thus fast transition rates are expected. By two-photon absorption at 400 nm, the S_2 state of ethylbenzene or o-xylene is excited. Ionization by a probe pulse yields photoelectrons with different energies according to their provenience from an S_2 or S_1 state, and in the case of o-xylene also from a T_3 state after an intrersystem crossing (ISC). The photoelectron energies and their angular distribution are monitored by Velocity Map Imaging[5]. The lifetime of excited ethylbenzene S_2 states relaxing to the S_1 manifold could be evaluated to be in the order of60 fs. In o-xylene $S_1 \leftarrow S_2$ inter system crossing (IC) and $T_3 \leftarrow S_2$ ISC proceeds on a comparable 60 fs time scale.

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The decomposition kinetics of xylyl radicals

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Toluene and xylenes are often used as surrogates to model the reactivity of alkylated aromatics, which are among the major constituents of many fuels. Recently, we have investigated theoretically (Cavallotti et al., 2009; Derudi et al., 2011) and experimentally (Sivaramakrishnan and Michael, 2011; Sivaramakrishnan et al. 2011) the decomposition kinetics of benzyl, finding that the key reaction pathway involves the formation of fulvenallene and benzyne as decomposition intermediates. In the present work, we extend our investigation to the study of the pyrolysis of xylyl radicals. Experimentally, the decomposition of the o-xylyl radical was studied using the ANL flash photolysis shock tube. Br-ARAS experiments using o-xylylbromide as the o-xylyl precursor indicated that a near-instantaneous pulse of Br-atoms were generated at T>1200 K. The subsequent decomposition of o-xylyl radicals was then characterized using H-atom ARAS over the 1267-1597 K and 0.3-1.0 atm temperature and pressure ranges. The experimental rate coefficients have been subsequently compared with the results of a computational investigation in which the xylyl potential energy surface has been analyzed at the DFT and CBS-QB3 levels, while channel specific rate coefficients were determined as a function of temperature and pressure integrating the 1D master equation over the relevant portion of the PES. It was found that the main reaction channels include H loss to form o-xylylene and decomposition to phenyl and ethylene. The theoretical analysis also considered the decomposition kinetics of the o-xylylbromide precursor. Finally, the pyrolysis of the meta and para xylyl isomers were theoretically studied combining ab initio calculations with the master equation simulations.

Acknowledgements
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A theoretical study on the O +O_2 isotope exchange reaction

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The reaction of O atoms and molecular oxygen can take place under every environment where both species are present. The reaction generally has no observable consequences concerning the chemistry of the system but may induce changes in the energy of the reactants, for example, vibrationally excited O_2 can be formed. At higher energies, nonadiabatic transition to one of the low-lying electronic states is also possible. Because the reactants and products of the reaction can not be distinguished, the reaction can be experimentally only with isotope labeling. Isotope effects in this reaction were found to be extremely large, in spite of the small relative mass difference (at most 2:16), large isotope effects have been observed in the reaction. The enhancement of the rate due to the increase of the heavy isotopes with regular O_2 is though to be responsible for the much larger heavy O isotope abundance in tropospheric ozone with respect to the normal abundance.

The dynamics of the isotope exchange reaction has been studied by J. Lin and coworkers and by T. Minton and coworkers. The theoretical work reported here is intended to interpret the experimental results.

The potential energy surface of the lowest electronic state of the O_3 system has a deep potential well corresponding to ozone. There is a shallow van der Waals attractive region at relatively large distances which is separated by a submerged (lower than the reactant level) potential well from the ozone well. The quasiclassical trajectory calculations address the angular distribution of the products as well as the translational, vibrational and rotational product energy distributions. Comparisons with experiments will also be presented.

Poster Contributions

Production and characterization of oxygenated soot surrogates from carbon black and comparison with real diesel soot

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Soot represents one of the most important pollutants in the exhaust gases emitted from combustion processes. The combustion conditions determine to a large extent soot micro- and nanostructure (i.e. primary particle dimension, length and arrangement of the graphene layers) and soot surface chemistry (i.e. number and typology of functional groups). Soot chemico-physical features have a direct influence on its reactivity towards the combustion gases [1]. One of the most meaningful parameters that have a direct influence on the soot reactivity is the oxygenation degree. In this work soot surrogates of uniform size bearing different kind of oxygenated functionalities have been produced through wet oxidations of a commercial carbon black (CB). The selected CB presents morphological and chemico-physical characteristics close to soot generated in combustion environments (flames [2], engines). CB microstructure consists of chain-like aggregates of spherical primary particles with an average diameter in the range of 15-20 nm. The CB organization at a nanoscale level is typical of a disordered carbon exhibiting a concentric organization of the stacked graphitic layers throughout each primary particle, in the better organized areas. Two different oxidation strategies were performed in order to vary the typologies of oxygenated functionalities introduced. Nitric acid [3] (67 wt.%, at 100 °C) and a mixture of concentrated sulphuric acid/hydrogen peroxide in ratio 70:30 v/v (piranha mixture) in accordance with the procedure reported for carbon nanotubes (CNT) [4] were used. The reaction time ranged from 4 to 24 hours with the aim to modulate the number of oxygenated functionalities. The CB-derived soot were gathered in two groups according with the oxidation procedure adopted (nitric acid: SN, piranha mixture: SP) and with the reaction time (SN4, SN15, SN24, SP4, SP15, SP24). Following purification, the soot surrogates were fully characterized by applying a large array of analytical techniques (TEM microscopy, infrared and UV-Visible spectroscopy, thermogravimetry, BET specific surface area, elemental analysis, dynamic light scattering). The evaluation of surface acid site content has been performed by a fluorimetric test with thionine acetate.

Results showed that both the oxidative treatments leave the CB microstructure untouched while a variable number of oxygenated functionalities are introduced. The oxidation with HNO_3 leads to the introduction on the CB surface of both carboxylic and carbonyl functionalities whereas the H_2SO_4/H_2O_2 treatment leads to the formation of carbonyl groups (Figure 1).

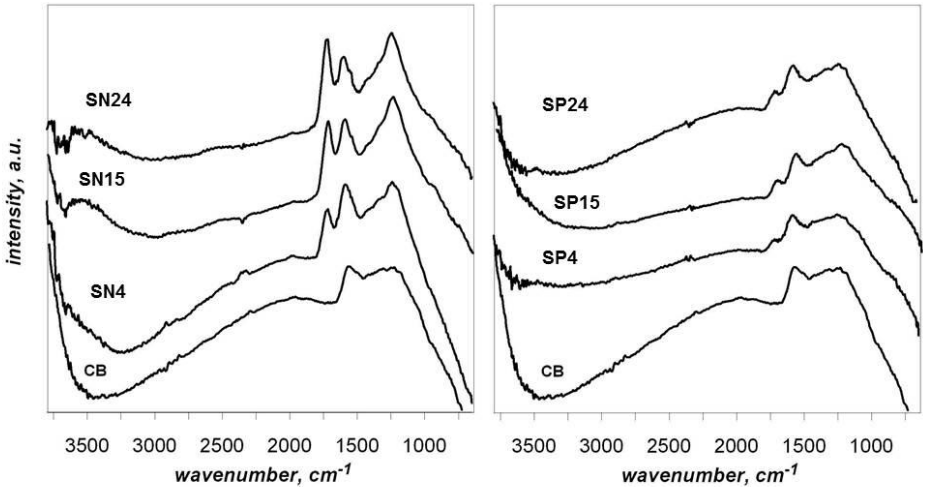

Figure 1 - ATR-IR spectra (600-3800 cm-1) of raw CB, SN-4,24 (left) and SP-4,24 (right).

The surface area and porosity distribution of the soot surrogates were evaluated by BET analysis. All of the materials show a pore size distribution with the maximum centered between 20 and 50 Å. The treatments with HNO_3 lead to a significant increase on both microporosity and mesoporosity while the H_2SO_4/H_2O_2 treatments enhance only the mesoporosity of the raw CB. The samples were subjected to a moderate heating (450 °C) under inert atmosphere aimed to study the effect of the decomposition of the oxygenated functional groups on soot porosity. Thermal treatment at 450 °C of the raw CB produces the formation of new mesopores, while the formation of micropores is negligible. The heating at 450°C enhance the microporosity of the CB treated with HNO_3 (SN samples) while it does not provide a significant increase of porosity on the SP samples.

The chemico-physical properties of the oxygenated soot surrogates were compared with the properties of a standard diesel particulate matter (SRM1650b: SRM), provided from the National Institute of Standards and Technology, and with two different types of soot sampled from diesel engine exhausts (DS). DS were obtained from exhaust gas recirculation (EGR) heat exchangers working at different experimental conditions (engine bench and vehicle).

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Reactivity of two different carbonaceous materials with NO

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Reducing diesel pollution has become nowadays a public priority. Some of the main pollutants of the exhaust gases from these engines are particulate matter (or soot) and nitrogen oxides (NO_x) [1]. Since NO_x emissions are of general concern, the research of the different possibilities for NO reduction is of great interest. Carbon materials are known to be active in the reduction of NO under appropriate conditions. In this way, soot and NO_x may react *in situ* with each other and reduce their emissions at the same time [2,3]. Many studies on the reaction between different carbonaceous materials and NO can be found in literature, but in the soot case these are scarce. In this context, the objective of this work is to analyze the reactivity of soot towards NO under different conditions. Two materials were employed in this study: one commercial surrogate for soot, called Printex-U, which was found in literature [4] to be a representative model compound for diesel soot, and a Standard Reference Material called 1650b (SRM1650b), which is described as a diesel particulate matter. Therefore, a specific study of the interaction with NO of Printex-U and SRM1650b has been developed and both the influence of temperature and inlet NO concentration have been analyzed.

The experiments were carried out in an experimental installation that consists of a gas feeding system, a reaction system and an analyzing system. Gases are fed and dosed through mass flow controllers. The reacting gas is NO in N_2 and the gas used to complete the balance to reach a total flow rate of 1000 (STP) mL/min is N_2. The reaction takes place within a quartz tubular reactor. The amount of soot weighed is around 10 mg per batch. The sample is heated up to the reaction temperature at 10 K per minute in an inert atmosphere of nitrogen. Once the desired temperature is reached, a fraction of the nitrogen is replaced by the reactant gases which are fed into the reactor. The reaction products are measured using two continuous infrared gas analyzers Uras14/IR for NO and CO/CO_2.

As mentioned before, the effect of temperature and NO concentration were studied. The experiments were carried out with different inlet NO concentrations ranging from 200 to 2000 ppm at 1273 K. The influence of temperature was evaluated in the 1173-1373 K range for 2000 ppm NO. A systematic working procedure was established to ensure the experimental results to be repetitive.

Soot properties usually have a direct influence on its reactivity towards NO. Therefore, the characterization of the commercial soot and the SRM1650b has been performed by using different techniques such as: Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and Raman spectroscopy, which have been chosen due to their demonstrated suitability for carbonaceous materials. The results obtained will allow us to know the composition, morphology and structure of carbon materials considered in this study and to relate those with its reactivity towards NO.

To be able to compare the reactivity of the different materials, the parameter τ was used in this study and successfully employed before [2,3]. The parameter τ is defined as the time needed for the complete carbon conversion, hence, the lower the value, the higher the reactivity. It was calculated from the shrinking core model with decreasing particle size and chemical reaction control equations. The model applied was already used in similar studies on soot interaction with NO at high temperature [3].

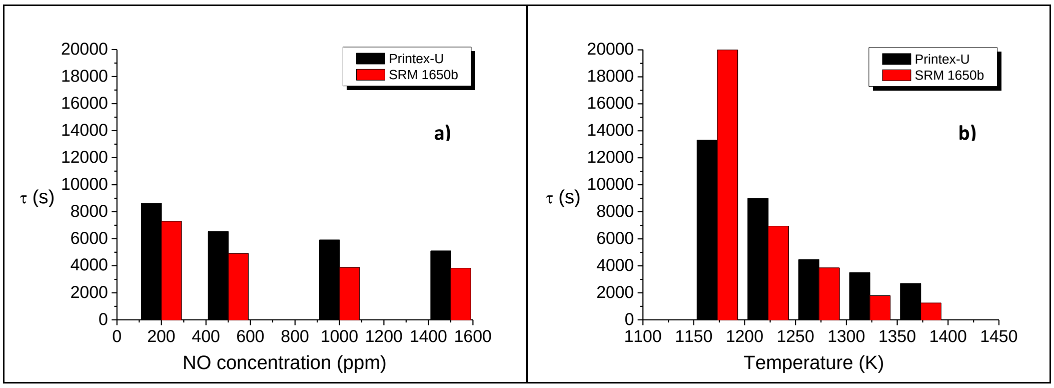

Figure 1. Comparison of the time needed for the complete carbon conversion in the reactivity experiments with NO for the different soot samples: a) as function of inlet NO concentration and b) as function of reaction temperature.

In Figure 1a, it can be observed from the experimental results obtained at a fixed temperature of 1273 K, the parameter τ is always lower for SRM1650b, indicating a higher reactivity for this material, for all the different inlet NO concentrations. Regarding temperature dependence, Figure 1b, it may be noticed that, except for the case of the lowest temperature at 1173 K, the carbon sample SRM1650b is the most reactive material. These findings, where SRM1650b is the most reactive material, are in agreement with the results obtained from the characterization of both samples. From the different techniques employed, it was obtained that SRM1650b is more disordered than Printex-U (XRD and Raman spectroscopy), as well as it presents particles with smaller mean diameter of the primary particles (FESEM and TEM).

The exception case, at 1173 K, could be explained through the activation energy value of the process, E_a (the procedure followed to obtain this value is not shown in this work). The activation energy for Printex-U and SRM1650b was equal to 107 and 190 kJ/mol, respectively. As E_a value for SRM1650b is higher than for Printex-U, the interaction SRM1650b-NO is more sensitive to temperature changes. Therefore, it is possible that at lower temperatures, the reactivity of SRM1650b is lower than for Printex-U.

Acknowledgements

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Crossed molecular beam study of the radical + radical reaction N + OH

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The N+OH→NO+H reaction and related HNO/HON radicals play an important role in many gas-phase processes, from combustion of N-containing fuels to atmospheric nitrogen-cycle. Several reactions [H+NO, O+NH], sample the three lowest HNO/HON potential energy surfaces (PESs) (X^1A', a^3A'' and A^1A''), while $N(^4S)$+OH samples only the triplet PES. From a fundamental point of view, N+OH is a prototypical 3-atom radical-radical reaction which has attracted a large theoretical attention over the past decades, and especially in recent years, both at the level of electronic structure calculations of the three lowest PESs and of dynamical calculations (both quasiclassical and quantum) of reactive integral and differential cross sections as well as rate constants on the relevant *ab initio* PESs[1,2,3]. The PESs are dominated by deep wells and barrierless reaction pathways. Experimentally, kinetics studies also down to very low (56K) temperatures have been reported recently for $N(^4S)$+OH and the determined rate constants compared with theoretical predictions[4]. The NO vibrational distribution was determined early on in a flow system by LIF[5]. However, no experimental scattering studies under single-collision conditions have been reported on this reaction up to date, because of difficulties in generating beams of OH and N radicals sufficiently intense and no scattering calculations have been performed so far on the singlet PESs for the $N(^2D)$+OH reaction.

Here, we report on the first determination of the differential cross section for the reaction of both ground state ^4S and excited state ^2D N-atoms with OH, leading to NO+H. We exploit the capability of generating intense supersonic beams of OH radicals and $N(^4S, ^2D)$ atoms by radiofrequency discharge in dilute mixtures of H_2O and N_2 in He, respectively, and a sensitive crossed-beams apparatus with "universal" mass-spectrometric detection and TOF analysis. To overcome interferences from elastically scattered $^{14}N^{16}O$ impurities (in the reactant beams) we have resorted to using ^{18}OH and ^{15}N, which has allowed us to detect the $^{15}N^{18}O$ product at *m/z*=33, a "clean" mass. Product angular distributions have been measured at a collision energy of about 11 kcal/mol. Product velocity distribution measurements are currently under way. The reaction dynamics of the two electronic states of N atoms appear to be distinct. The results are expected to provide a sensitive benchmark for quantum scattering calculations on *ab initio* triplet and singlet PESs for these "simple", prototypical radical-radical reactions.

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Hexadecane Mechanisms:
Comparison of hand-generated and automatically generated with pathways

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Abstract

In contrast to other systems for automatic generation, the REACTION system uses pathways to organize the application of reaction classes. A pathway is a sequence of reaction classes where only those species produced by the previous step of the pathway are used in the current step of the pathway. This "controlled" generation process not only mimics what is done during hand-generation of the reaction mechanisms, but also helps limit the size of the generated mechanisms. In this paper, the automatically generated mechanism using pathways of hexadecane with both high and low temperature chemistry included is compared to a systematically generated mechanism by hand for hexadecane. Both systematic reaction by reaction comparisons and numerical simulation (zero-dimensional constant pressure) comparisons were done and the mechanisms were found to have minor differences. Both mechanisms used the same set of reaction classes to model the high and low temperature combustion chemistry of all the n-alkanes up to hexadecane. In addition, a sensitivity analysis of all the reaction classes was performed. The generated mechanism has 2176 species and 7269 (reversible) reaction.

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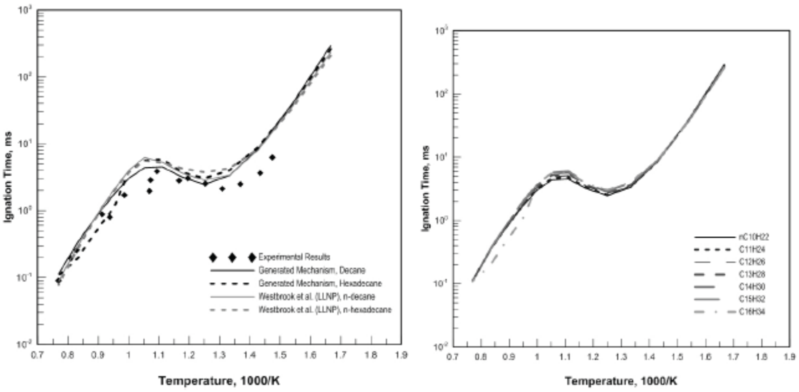

Figure 1: : Ignition delay times for the oxidation in shock tube of for at 13 bar for equivalence ratio=1, a) n-decane and n-hexadecane results are plotted for the Westbrook et al. mechanism and Generated mechanism. b) Ignition delay times using the generated mechanism for fuels from n-decane to hexadecane.

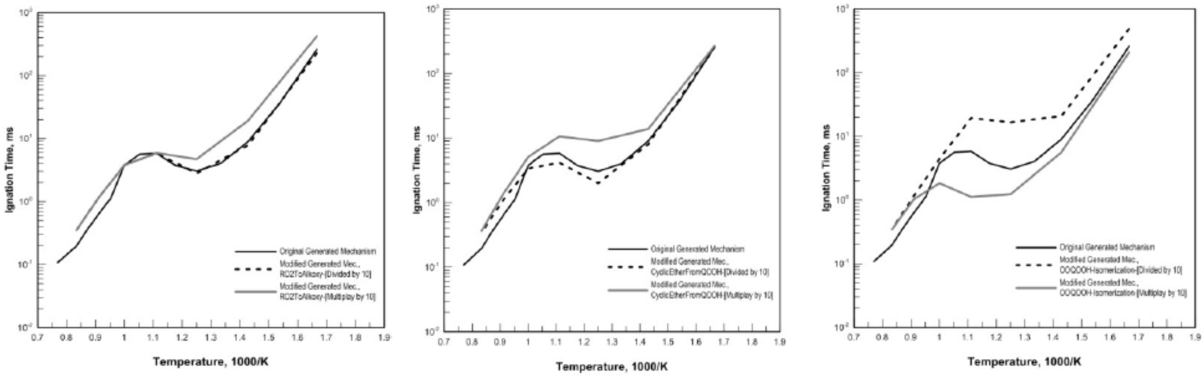

Figure 2: For the work of this paper, the sensitivity of each reaction class was analyzed by multiplying and dividing the original Arrhenius constant by a factor of ten. The three graphs show some classes which yielded a signifigant change.

Effects of water vapor on a methane and hydrogen flame

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In hydrocarbon combustion, lean combustion is frequently used as a way to reduce pollutant formation [1]. Lean combustion scenarios present some challenges, as there is a risk of flame extinction due to heat loss and stretch effects. This will lead to increased emissions of hydrocarbons and carbon monoxide. To circumvent these unwanted effects the temperature of the unburned mixture can be raised, but this will subsequently lead to a higher production of NOx. A way to stabilize the flame is by enriching it with hydrogen, the laminar burning velocity will then be increased [2]. Another factor affecting the combustion stability is the presence of water vapor in the combustion air, which result in lowering of the temperature and burning velocity [2].

To investigate how the hydrogen enrichment and water dilution will affect the combustion of methane the burning velocity of methane-hydrogen-steam-air flames was measured using the heat flux method. The hydrogen content in the fuel was varied between 0-35 molar percent. The steam concentration in the mixture was varied between 0-15 molar percent at temperatures of 298-358 K. All measurements were performed at ambient pressure. To the best of our knowledge, this is the first determination of the laminar burning velocity of methane-hydrogen-steam-air flames.

The heat flux method [3] is used to measure the adiabatic laminar burning velocity. The perforated burner plate generates a flat, stretch free flame. The temperature distribution that arises in the burner plate represents the net heat loss from the flame to the burner and by adjusting the unburned gas velocity, the point at which zero heat loss is observed can be found. This characterizes the adiabatic state and the burning velocity can be obtained directly.

Figure 1 shows the dependence of the laminar burning velocity on steam concentration of a methane-hydrogen-steam-air flame at 330 K. Results for hydrogen enrichment of 35% and 25% as well as pure methane are shown. All three cases show a linear decreasing trend of the burning velocity with increasing steam dilution. The decreasing trend of the burning velocity is independent of hydrogen enrichment (up to 35 molar percent). Previous studies [2, 4] have shown that the steam dilution effect on the burning velocity was less pronounced when the flame temperature was increased to from approximately 2200K to 3000K. An enrichment of 35% hydrogen will introduce a temperature increase of roughly 20 K [2], not enough for the decrease of the burning velocity to be affected as seen in Figure 1.

Present measurements are further analyzed using detailed kinetic modeling. Both chemical and thermal effects of steam dilution are isolated and discussed. The role of hydrogen enrichment in the chemical effect of steam is also elucidated.

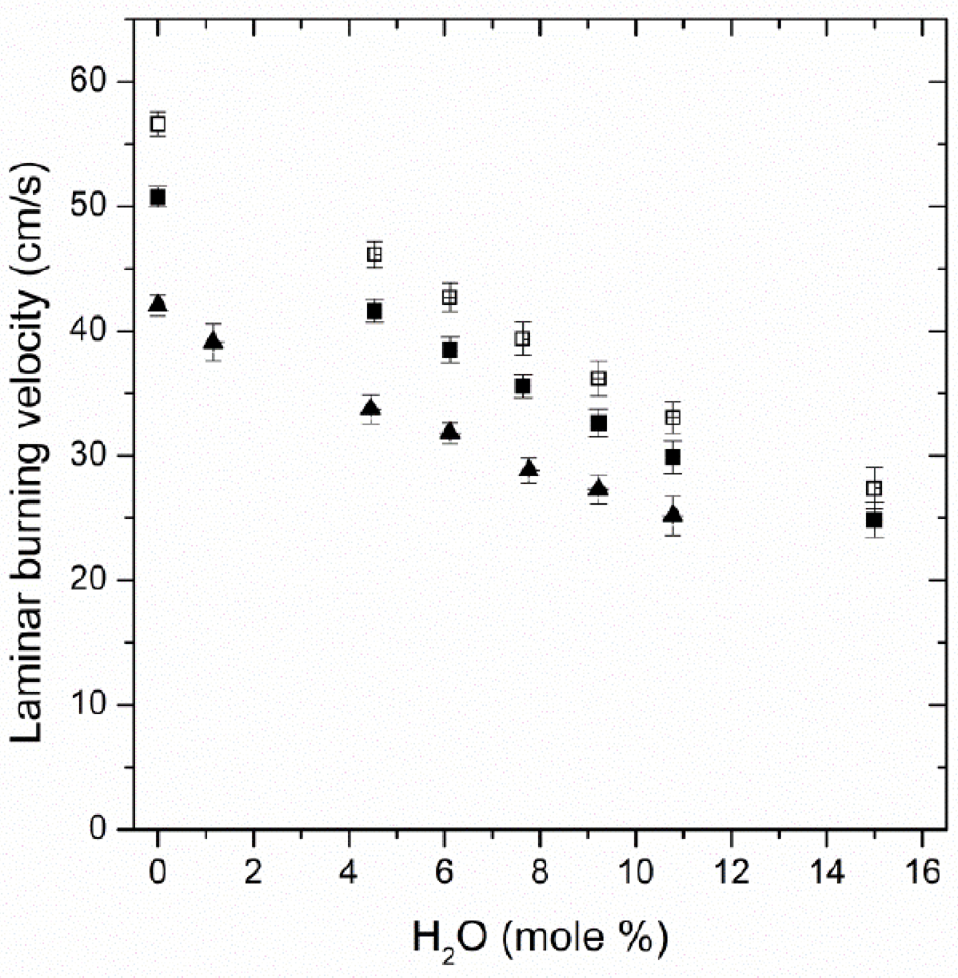

Figure 1. The laminar burning velocities of a methane-air flame enriched with 0-35% hydrogen and diluted with 0-15% steam at 330 K and stoichiometric conditions. 35 % enrichment (open squares), 25% enrichment (solid squares), 0% enrichment (triangles).

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Validation of chemical mechanisms in rich methane flame using laser absorption spectroscopy diagnostics

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The growing demand for energy production is a strong motivation behind research concerning more efficient and less emissive ways of fuel combustion. One of these new developing techniques is the conversion of natural gas to syngas. Syngas production from natural gas can be established as a first stage of the so-called Gas-to-Liquid process (GTL). Usually, the GTL process involves two stages: the first is the conversion of methane to syngas (a mixture of CO, H2 and H_2O) and the second is the so-called Fischer-Tropsch process or similar, where syngas is converted to liquid hydrocarbons. There are several methods to carry out the first stage of GTL, the most advantageous of which seems to be partial oxidation, as it does not require additional energy sources and results in a H_2 to CO ratio, favorable for the subsequent Fischer-Tropsch process.

However, the kinetic mechanisms of methane oxidation under very fuel-rich conditions are still not well-developed. Therefore, the goal of the present work was to acquire the information about flame structure valuable for the kinetic model development. Specifically, the objective of the present work was to study HCO radical in low pressure flames with equivalence ratios up to $\phi = 4$, both experimentally and by detailed kinetic modeling. In the experimental part, Intracavity Laser Absorption Spectroscopy (ICLAS) technique was utilized for the flames stabilized on the McKenna burner with a central jet. The objective of the modeling part was to investigate the possibility to approximate the complex two-dimensional geometry of the experimental flame configuration with one dimensional reaction model for stretched flames.

The HCO radical was not studied extensively in flames, although it is a good flame front and heat release marker [1]. ICLAS technique was chosen for the present measurements, since it provides a very high spectral sensitivity [2]. In this technique, the absorbing medium is placed inside a laser cavity, forcing the laser light to pass the sample many times, and the laser gain compensates broadband cavity losses, e.g. mirror transmission. If the duration of laser generation, t, is selected to be much shorter than the spectral saturation time, t_s, the effective absorption path length is determined by the laser pulse duration:

$$L_{eff} = c \cdot t \cdot \frac{l}{L} \ll c \cdot t_s \cdot \frac{l}{L}$$

where l/L is the filling factor of the cavity, with l being the optical length of a sample and L – the optical length of the cavity. The value of L_{eff} can be readily set to about 1 km [3].

The ICLAS spectrometer is based on a dye laser and is similar to the one used in [3]. The setup was built around the low pressure chamber with a McKenna burner. The light from continuous Nd-YAG laser is chopped over 30-100 µs pulses by using an acousto-optic modulator (AOM), and that pulse length defines the dye laser generation time t. The pumping beam is focused into the dye jet. The cavity of the dye laser is organized in a three mirror scheme: two high reflectivity spherical mirrors and the partially reflective plane output mirror, wedged in order to avoid interference fringes. The flame is placed between two last mirrors inside the low pressure chamber (30 Torr). The laser beam enters the chamber through two 1^0 wedged windows mounted at the Brewster angle. After the output coupler, the second AOM is placed in order to select a short fraction (about 5 µs) of the generated laser pulse (30-100 µs) delayed by the time *t*, which corresponds to a certain value of L_{eff}. The spectral data were obtained with 1 m spectrograph (SPEX 1000 M) and 3000 pixel CCD array (Ames LARRY-3000). The exposure time of the CCD was typically set to about 300 ms, corresponding to the recording of about 1000-10000 pulses at one exposure. Later the data were averaged over 10 images in the computer.

The experimental flame conditions were the following. Two separated mixtures of $CH_4/O_2/N_2$ were fed into the porous plug and the central tube of the burner respectively, resulting in the occurrence of two flames: a flat pilot flame and a bulb-shaped central flame. The role of the pilot flame was to provide stabilization of the central flame. Therefore, the central flame can have equivalence ratios in the range where the corresponding flat flame would have been impossible to stabilize. In the present experiments, a flame with the equivalence ratio of 4 was obtained, which is beyond the flammability limit under normal conditions. In the present experiments this configuration can exist due to heat conduction and radical diffusion to the central flame from the pilot flame. However, since the central flame is narrower than the pilot flame, then L_{eff}, i.e. the spectral sensitivity, in the central flame was several times lower than in the pilot flame and it lead to some experimental difficulties regarding the interpretation of the signal due to increased signal-to-noise ratio. The experimental spectra of the HCO were recorded as a function of height above the burner for different equivalence ratios. The interpretation of the spectral data is presented and its potential for the model development is discussed.

The experimental flame configuration described in the previous paragraph is substantially not one-dimensional, therefore, ideally it should be simulated as a two-dimensional problem in cylindrical coordinates. However, in order to have reasonable computational time and effort, and at the same time, to focus on the flame chemistry, it was chosen to utilize the one-dimensional premixed opposed-flow reactor model. In this configuration, the composition of the flow from one side corresponded to the reactants for the flat flame and the other side simulated the reactant flow in the central flame. In the simulations, HCO concentration was found to be weakly dependent on the set value of flame stretch. Hence, this approach can be applicable for the simulation of the experimental flames. The applicability aspects as well as the comparison between the modeling and the experiments are further discussed.

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Shock tube studies and modeling of the pyrolysis of 2,5-dimethylfuran

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2,5-dimethylfuran (25DMF), which can be produced from fructose or glucose [1], is a promising candidate as a second-generation biofuel. It is a cyclic unsaturated ether, which is chemically stable and insoluble in water. It has properties similar to gasoline [2]. Compared to ethanol it has a higher energy density (by 40 per cent) and a higher boiling point (by 20 K) [1].

To understand the ignition process of fuels in engines, detailed kinetic mechanisms are necessary. In these mechanisms, pyrolytic reactions of the fuel molecule represent a very important part at higher temperatures.

In 1985 Grela et al. [3] studied very low pressure pyrolysis of furan, 2-methylfuran and 2,5-dimethylfuran to characterize the stability of furan rings. In 1998 Lifshitz et al. [4] published a pyrolysis mechanism containing 181 reaction steps and 49 different species. Since 2009 detailed information on crucial steps was obtained by Simmie et al. [5,6] and Sirjean et al. [7-9] from quantum chemical calculations. In addition a wide range of experiments was performed, including a study of the thermal decomposition of DMF with gas chromatography as detection method [10]. Very recently, Sirjean et al. published a shock tube and chemical kinetic modeling study of the oxidation of 25DMF [11]. The mechanism consists of 1459 elementary chemical steps with 294 different species. It was validated in terms of shock tube ignition delay time measurements of 25DMF ($T = 1300 - 1831$ K, $P = 1$ and 4 bar) and single-pulse shock tube measurements by Lifshitz et al. [4].

Our group at KIT studied the pyrolysis of 25DMF behind reflected shock waves with time-of-flight mass spectrometry (TOF-MS) and hydrogen atom resonance absorption spectroscopy (H-ARAS) as detection methods. Overall rate coefficients for the H atom production from 25DMF pyrolysis as well as for the 25DMF + H reaction [12] were obtained from H-ARAS experiments ($T = 950 - 1500$ K, $P = 1.6$ and 4.8 bar). In our time resolved TOF-MS experiments ($T = 1100 - 1500$ K, $P = 1.0$ bar), we were able to observe concentration-time profiles of 25DMF itself and several products.

Initialized by a short term scientific mission within this COST action, the 25DMF pyrolysis mechanism by Sirjean et al. [11] was used to model the concentration-time profiles measured in our shock tube experiments at KIT. A very good agreement was found for hydrogen atoms and 25DMF, and a reasonable agreement for CH_4, C_2H_n ($n = 2, 4, 6$) and C_4H_4O. Possible assignments of observed peaks to specific compounds will be discussed and consequences for the mechanism will be elucidated.

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Experimental and theoretical study of $O(^3P) + C_2H_4$ multichannel reaction dynamics

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Small unsaturated hydrocarbons, such as C_2H_2 (acetylene), C_2H_4 (ethylene) and C_3H_4 (allene and methylacetylene), are crucial intermediates in hydrocarbon combustion, where their dominant consumption pathways are their reactions with ground-state oxygen atoms, $O(^3P)$. The reactions of $O(^3P)$ with unsaturated hydrocarbons are characterized by a variety of energetically open, competing reaction channels, some of which can take place only via intersystem crossing (ISC) from triplet to singlet potential energy surfaces (PES). In fact, a peculiarity of these multichannel $O(^3P)$ reactions is that the reactants approach on a triplet PES which intersects a singlet PES usually supporting a stable intermediate; ISC is then possible from the triplet to the singlet PES, making the dynamics which involve motion on the underlying singlet PES different from those involving motion only over the triplet PES. In combustion modelling, among the most important information needed for each of these elementary polyatomic multichannel reactions of $O(^3P)$ atoms with unsaturated hydrocarbons are: (*a*) the overall rate constant, (*b*) the identity of the primary products, and (*c*) the branching ratios (BRs) possibly as a function of collision energy E_c (temperature). While kinetics experiments are able to satisfy point (*a*), point (*b*) and (*c*) still represent a challenge for kinetics, although considerable progress has recently been made [1]. The method most suitable to tackle this challenge is the crossed molecular beams (CMB) scattering technique with "universal" mass spectrometric detection and time-of-flight analysis, based on "soft" ionization by tunable low energy electrons [2, 3] or vacuum-ultraviolet (VUV) synchrotron radiation [4].

Here, we report on a combined experimental and theoretical study of the reaction $O(^3P)+C_2H_4$ as a function of collision energy. Experimentally, we have investigated this reaction at the two E_cs of 8.4 and 13.7 kcal/mol, by characterizing the product angular and translational energy distributions in the center-of-mass system, and deriving BRs for the five competing channels leading to $H + CH_2CHO$, $H + CH_3CO$, $H_2 + CH_2CO$, $CH_3 + HCO$, and $CH_2 + HCHO$ [5]. Some of these channels can only be formed via ISC. The derived BRs are analyzed together with those obtained previously from kinetics studies at room temperature ($E_c \approx 0.9$ kcal/mol) [6]. The combined kinetics and dynamics results allow us to examine the BRs and the extent of ISC in a wide range of E_c (temperature), from about 1 kcal/mol (300 K) up to about 13 kcal/mol (4300 K). Notably, it is found that about 50% of the overall reaction occurs via ISC, and that the extent of ISC has a weak collision energy (temperature) dependence, decreasing slightly with increasing E_c. Theoretically, full dimensional potential energy surfaces for the triplet and singlet states as well as spin-orbit couplings between them have been calculated and half a million of surface hopping quasiclassical trajectories have been run on the coupled singlet-triplet PESs to compare with the experimental BRs and differential cross sections at the different E_cs [5,7]. Good agreement is observed between detailed theoretical and experimental results; from this we can conclude that QCT surface-hopping calculations, using reliable coupled multidimensional PESs, can yield reliable dynamical information for polyatomic multichannel reactions in which ISC plays an important role.

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New improvements in the direction of analyzing more detailed mechanisms with the package **`ReactionKinetics`**

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In the previous COST Action conferences we introduced a program package, which is based on the language of *Mathematica*, named **`ReactionKinetics`**, serving as a general framework to compute several characteristics in chemical kinetics, involving symbolic and numeric treatments of mechanisms as well [1]. The package is especially useful when the number of species and reaction steps is larger than to allow manual investigations, i.e. if one has hundreds or even thousands of species and reaction steps as well.

We made the package capable of reading CHEMKIN files by **`CHEMKINImport`**, and also to export mechanisms to CHEMKIN format by **`CHEMKINExport`**, which is especially useful when one intends to create mechanisms from old ones, or to build up a completely new mechanism. Along this way we added filtering options and functions (see **`FilterReactions`**) for mechanism manipulations. Also we extended the package with several functions to extract important subgraphs of the Feinberg--Horn--Jackson graph such as:

- **`MaxFHJWeaklyConnectedComponents`**,
- **`MinFHJWeaklyConnectedComponents`**,
- **`MaxFHJStronglyConnectedComponents`**, and
- **`MinFHJStronglyConnectedComponents`**,

to mention just a few (see Figure 1).

As a continuation we are planning to add some new functionalities such as visualizing further important graphs (e. g. SCR-graph, etc.), to find and show the atomic fluxes and to give approximate clustering of the graphs.

So far we investigated dozens of detailed models for combustion of hydrogen, carbon monoxide and methanol [2]. Essential characteristics are extracted, and similarities and differences of the mechanisms are highlighted. These results will be the main topic of Prof. Tóth's lecture. The preceding studies can be used before or parallel with usual numerical investigations, such as parameter estimation, sensitivity analysis or simulation.

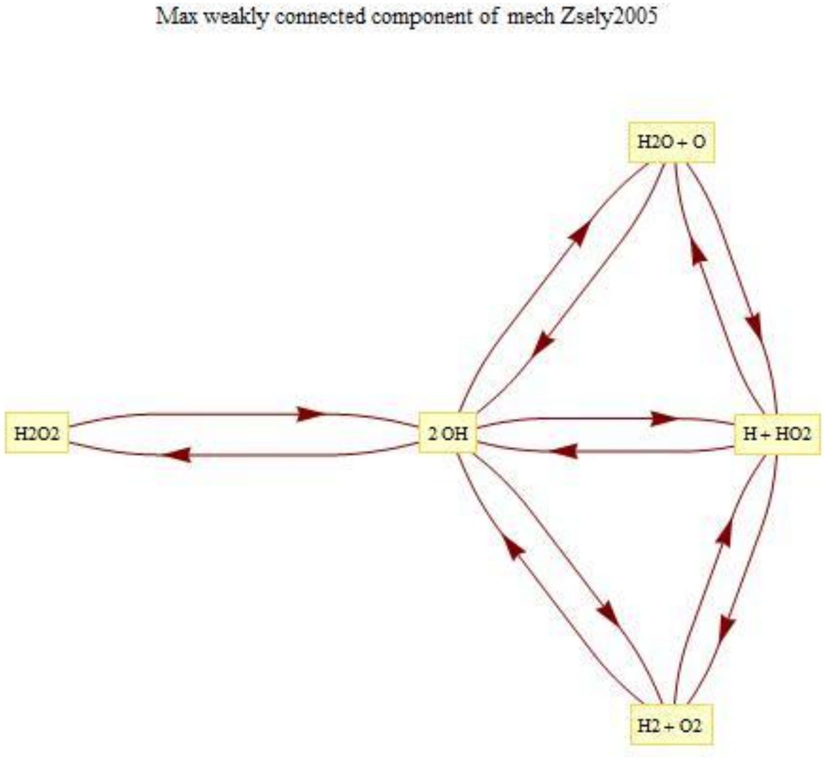

Figure 1: Maximum weakly connected component of the hydrogen mechanism by Zsely (2005)

We are planning to apply the program package to other, even larger and more complex, mechanisms.

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The role of combustion intermediates in soot precursor's formation chemistry

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A semi-empirical model was previously developed for modeling the soot formation characteristics, typically measured during hydrocarbon pyrolysis and oxidation in shock tube experiments [1]. The model with its latest modifications was calibrated with experimentally measured soot yield, recalculated as particle volume fraction in conditions typical for isothermal flow reactor [2]. Then it was applied for soot formation modeling of selected flow reactor experiments using different detailed chemical kinetic schemes.

This simple soot model revealed a significant dependence on the calibration procedure and on the gas phase chemistry with its characteristic reaction paths of aromatics formation together with the kinetic and thermodynamic parameters of the relevant combustion intermediates. Their role is often neglected, but might be important for minimizing the mechanism's uncertainties. Another important feature is the opportunity to model the complex phenomenon of soot formation without neglecting the detailed chemistry, running both sub-models simultaneously.

The semi-empirical model was preferably applied in spatially homogenous systems but the development of soot models relevant to combustion systems with complex geometry is of considerable importance for industrial applications. It requires sophisticated strategies to incorporate the detailed chemistry with the turbulent combustion models. Nevertheless, appropriate procedures for dealing with such obstacles exist and might be an interesting issue for the future improvements of the complex-model's representation.

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Crossed molecular beam study of the O(^{3}P) + propene reaction: Primary products and branching ratios

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The O(^{3}P) + C_3H_6 (propene) system belongs to the wider family of reactions between ground state oxygen atoms and unsaturated hydrocarbons, which is hugely involved in the formation and consumption of combustion intermediates [1]. Due to the larger structural complexity of propene molecule compared to the systems studied previously (e.g. O(^{3}P) + C_2H_4, O(^{3}P) + C_3H_4), this reaction can serve as a gateway to the richer chemical pathways available in larger hydrocarbons as pointed out by Savee et al. [2]. Therefore the O(^{3}P) + propene reaction has been of significant interest for both experimentalists and theoreticians during the past decades (see references in [2]).

According to the so-called Cvetanovic rule [3], addition of the oxygen atom to the lesser substituted terminal carbon atom (from -CH_2 group of propene) should be favored as an initial step of all possible reaction pathways. However, recently available information from theoretical calculations [4,5] as well as experimental kinetics data [2] also indicate the importance of the central (C2) carbon attack by O(^{3}P). Moreover, considerable tendency of both possible isomers of the C_3H_6O triplet biradical to undergo intersystem crossing (ISC) followed by the production of various species on the singlet potential energy surfaces implies an even more complex set of possible reaction channels.

In order to identify individual reaction channels and to quantify their relative branching ratios for collision energies (temperatures) relevant to combustion environments, crossed molecular beam (CMB) experiments were performed on the title reaction by using mass spectrometric (MS) detection and time of flight (TOF) analysis, and exploiting soft electron ionization [6]. Combination of product angular and TOF distributions at different product mass-to-charge ratios enables to conclusively distinguish the various products and assign them to appropriate reaction channels. Preliminary results allow to conclude that the following exoergic reaction channels (with the enthalpy of formation at 0 K relative to reactants as adopted from [2,4,7]) are of major importance at the collision energy of about 10 kcal/mol:

$$O(^3P) + CH_3CHCH_2 \rightarrow H + CH_3CHCHO \qquad \Delta H_{f,0} = -18.7 \text{ kcal/mol}$$
$$O(^3P) + CH_3CHCH_2 \rightarrow H + CH_3COCH_2 \qquad \Delta H_{f,0} = -20 \text{ kcal/mol}$$
$$O(^3P) + CH_3CHCH_2 \rightarrow HCO + CH_3CH_2 \qquad \Delta H_{f,0} = -26.6 \text{ kcal/mol}$$

$O(^3P) + CH_3CHCH_2 \rightarrow CH_3 + CH_2CHO \qquad \Delta H_{f,0} = -27.5$ kcal/mol

Other channels (not explicitly specified here), such as those leading to formation of formaldehyde+ethylene and H_2+methylketene were also identified but the proper interpretation of spectral features observed by TOF-MS requires detailed analysis, which is currently in progress.

Based on the "best-fit" procedure of the laboratory data, total branching fractions relevant to the $O(^3P)$ + propene reaction will be derived from the measured TOF data and angular distributions of the products. Results of CMB experiments in such form provide valuable quantitative information for validation of chemical kinetic data, as previously done for $O(^3P)+C_2H_4$ [8], $O(^3P)+CH_2CCH_2$ (allene) [9] and $O(^3P)+CH_3CCH$ (propyne) [10]. Furthermore, results of these measurements are also expected to give unambiguous answer to still open questions concerning the importance of ISC and central carbon attack in the case of this system.

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Optimization and uncertainty quantification of a wet CO combustion mechanism

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In recent years, there has been an increased interest in studying the combustion of wet CO fuel mixtures. These fuels are considered to be a promising option towards cleaner combustion technologies for power generation from coal or biogenic feedstock in IGCC-CCS plants. Also, wet CO combustion forms the basis of the combustion of hydrocarbons and oxygenates. Predictive CFD models used in combustor design require accurate kinetic mechanisms to describe the chemistry of wet CO oxidation particularly at operating conditions predominant in gas turbines.

For the present work, a large amount of experimental data was collected from 34 publications: 976 ignition delay time data points (532 in shock tubes, 444 in rapid compression machines), 1711 flame velocity measurement points and 54 concentration profile data points. Wide regions of operating conditions are covered by these data (T_{ign} = 933–2870 K for ignition delay times, $T_{cold\ side}$ = 293–700 K for flames, p = 0.5–49.35 atm Φ = 0.1–6.83, CO/H_2 = 0.05–243.4). The experiments were carried out in various diluent systems containing species N_2, Ar, He, CO_2 and H_2O. CHEMKIN simulations were performed with 15 reaction mechanisms, which had been published between 1999 and 2013.

Typically, the agreement between the measurements and the simulations is characterized qualitatively by figures, in which the experimental data and the simulation results are plotted together. By using a sum-of-square normalized deviation-based error function [1], this characterization can be quantified. A comprehensive mechanism comparison was carried out to provide users of detailed kinetic mechanisms with a guideline for choosing the most appropriate wet CO mechanism. Mechanism-specific strengths and weaknesses were identified with respect to variations of T, p, Φ, CO/H_2 ratio and the diluent system. Another aim was to select a base mechanism for the subsequent optimization.

Starting from a slightly modified version of the Kéromnès 2013 [2] mechanism, 32 rate coefficients (Arrhenius parameters A, n, E and 3rd body collision efficiencies) of the 11 most influential reactions were optimized based on ignition delay time data and reaction rate coefficient measurements. Thereby, the optimization methodology of Turányi et al. [1] was applied. The joint uncertainty domain of all optimized parameters was determined.

Driven by a large improvement for RCM simulations, the average error function value of the optimized mechanism is 19% lower in comparison to the second best mechanism. Due to its good performance at turbine-relevant conditions, robustness and size (14 species, 33 reactions), it can be recommended for a wide range of possible applications.

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Crossed molecular beam study of the O(^{3}P) + CH_3CCH reaction

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Reactions of unsaturated hydrocarbons with ^{3}P oxygen atoms are important elementary steps of detailed combustion mechanisms. These reactions are characterized by a variety of energetically open, competing product channels, some of which can take place only via intersystem crossing (ISC) from triplet to singlet potential energy surfaces (PESs). While there have been extensive studies on the overall kinetics of many of these reactions, much less is known about the identity of the primary products and the branching ratios (BRs), especially at combustion temperatures. Although modern kinetics investigations employing mass spectrometric photoionization detection by synchrotron radiation are starting to provide information on the nature of primary products and branching ratios at room temperature, the most suitable technique to unravel the detailed dynamics of these class of reactions, which are polyatomic multichannel nonadiabatic reactions, is the "crossed molecular beams" (CMB) scattering technique with "universal" mass spectrometric detection and time-of-flight analysis, based on "soft" ionization by tunable low energy electrons [1-3] or vacuum-ultraviolet (VUV) synchrotron radiation [4].

In our laboratory we have undertaken a systematic investigation of the dynamics of O(^{3}P) reactions with unsaturated hydrocarbons [1-3], as well as with hydrocarbon radicals, such as allyl [5] and methyl [5]. Recently, in order to explore how the reaction dynamics varies with molecular complexity, we have extended our studies also to the reaction with the simples diene, namely O(^{3}P)+allene (C_3H_4) [7]. In this contribution we report the results of a CMB study of the reaction O(^{3}P)+propyne (methylacetylene, C_3H_4). By comparing the results with those obtained for the isomeric reaction O(^{3}P)+allene and with the simpler reaction O(^{3}P)+acetylene we explore how the reaction dynamics varies with molecular structure and with molecular complexity, respectively.

The only previous experimental investigation of the possible reaction channels in the O(^{3}P)+propyne reaction is the pioneering study of Gutman and coworkers [8], using room temperature crossed molecular beams and photoionization mass spectrometry detection (on axis with the oxygen beam). In that study branching ratios were not derived. Later on, Bersohn and coworkers [9] looked in some detail at the CO release and H atom release channels using VUV laser-induced-fluorescence (LIF) in a flow system at room temperature. Surprisingly, the CO product was found to be rotationally and vibrationally very cold. In 2009, the product channels and mechanisms of the title reaction were investigated further by Su and coworkers [10]. Theoretically, high level *ab initio* calculations were performed for both triplet and singlet PESs and the minimum energy crossing between the two surfaces was located. Experimentally, the CO from the CO+C_2H_4 channel was investigated with time-resolved-FTIR emission spectroscopy in a flow chamber. CO was found to be vibrationally excited up to v=5, and this was noted to be consistent with the statistical partition of the singlet C_2H_4+CO channel, but not with the triplet CH_3CH+CO channel. It was concluded that nonadiabaticity (ISC) should play an important role in this reaction.

We have investigated the O(^{3}P)+propyne reaction by the CMB method at the collision energy, E_c, of 9.4 kcal/mol by exploiting soft electron ionization. From product angular and velocity distribution measurements in the lab frame at different *m/z* ratios we have identified the following primary product channels: H+C_3H_3O, CH_3+HCCO, C_2H_4+CO, C_2H_3+HCO and C_2H_2+H_2CO, derived the product angular and translational energy distributions in the center-of-mass frame, and determined the BRs (these vary from less than 1% for the CH_3 channel to about 70% for the CO channel). Four of the five characterized channels are the same observed in the related O(^{3}P)+allene reaction studied at the same E_c [6], while the CH_3+HCCO (ketenyl) channel has as counterpart in the case of the allene reaction the CH_2+CH_2CO (ketene) channel. As in the O(^{3}P)+allene reaction many of the observed products can be only rationalized by invoking ISC from the triplet to the singles PES. In the case of O(^{3}P)+propyne the extent of ISC is smaller than in O(^{3}P)+allene, as shown by a significantly smaller ratio (molecular C_2H_4+CO channel)/(radical H+C_3H_3O channel). Qualitative analysis of singlet and triplet PESs available from the literature for O(^{3}P)+propyne [11] and O(^{3}P)+allene rationalizes this behaviour. It can be concluded that the reactions of O(^{3}P) with the two C_3H_4 isomers, allene and propyne, are obviously different, in spite of the apparent similarities.

It is interesting to note, however, that while ISC is very important for the reaction O+CH_3CCH, it is minor for O+HCCH. Any kind of extrapolation along the series O(^{3}P)+acetylene, methylacetylene, ethylacetylene and so on cannot be done. Only detailed studies of the same kind as those reported here will permit to characterize the extent of ISC and the branching ratios for the reactions involving oxygen atoms and small hydrocarbons.

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Development of a hydrogen combustion mechanism using an optimization approach

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The reaction steps of hydrogen combustion form a central part of the high temperature combustion of all hydrocarbons and oxygenates. Also, hydrogen is an important fuel itself in areas like carbon-free economy, safety issues, and rocket propulsion. In accordance with its high significance, several new hydrogen combustion mechanisms were published even in the last decade. Despite the extensive research, a generally accepted hydrogen combustion mechanism that performs well at a wide range of experimental conditions does not exist.

An optimization approach was recently proposed [1] that was extended in this work with the response surface methodology [2]. A large set of experimental data was collected for hydrogen combustion: ignition measurements in shock tubes and rapid compression machines, flame velocity measurements and concentration–time profiles in jet-stirred reactors, covering wide ranges of temperature, pressure and equivalence ratio. Using sensitivity analysis, the influential reactions at the conditions of each experiment were identified. For each influential reaction, the temperature dependent uncertainty of the rate coefficient was determined from direct measurements and theoretical rate calculations. The uncertainty of ln k was then converted to the uncertainty of the corresponding Arrhenius parameters using the approach of Nagy and Turányi [3].

Response surface was calculated for each experimental data point. First, quasi-random samples of the influential Arrhenius parameters were generated within their respective uncertainty ranges. Simulations of the experiments were performed with each quasi-random Arrhenius parameter set using the appropriate program of CHEMKIN-II package [4]. Finally, the relation between the influential Arrhenius parameters and the results of the simulations was described by fitting a 2nd to 6th order polynomial. These response surfaces were used during the optimization, instead of using the CHEMKIN simulation code directly, which greatly reduced the computational costs. Optimization of the mechanism was performed using a combination of global and local methods. The least-squares difference between the experimental and simulation results was minimized. The optimization also provided the uncertainty domain of the influential Arrhenius parameters.

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Experimental and modeling study of the structure of laminar premixed flames of tetrahydrofuran/Oxygen/Argon

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As traditional fossil fuels are considered to be largely responsible for causing important atmospheric degradations, there is an increasing interest to shift from petroleum-based fuels to bio-fuels. The use of bio-fuels allows a reduction of the dependence on fossil fuels. Moreover burning this renewable fuel should not lead to an increase of the total amount of greenhouse gases in the atmosphere. Several strategies are being developed to transform biomass, which contains a variety of substituted five- and six-membered cyclic ethers, into suitable transportation fuels or fuel additives. The cyclic ethers of furan family: 2-methylfuran (MF), 2,5-dimethylfuran (DMF), and tetrahydrofuran family: 2-methyltetrahydrofuran (MTHF), 2,5-dimethyltetrahydrofuran (DMTHF), have been recently considered as potential additives to gasoline or diesel fuel. In addition, these cyclic ethers have been identified among the emissions produced during the combustion and auto-ignition of alkanes and alkenes by isomerization of alkylhydroperoxy radicals. The subsequent reaction of these cyclic ethers may then influence the overall chemical kinetics mechanisms of alkanes and alkenes combustion. For these reasons, a detailed chemical kinetic model for the high-temperature combustion of Tetrahydrofuran (THF) has been developed. The new mechanism was generated using the automatic generator software EXGAS [1,2]. Several key kinetic parameters were updated to take into account the specificity of cyclic ethers combustion chemistry. In particular, Evans-Polanyi correlation of Dean and Bozelli [3] and electronic structure calculations, coupled to canonical transition state theory, have been employed to estimate the rate constants for this set of reactions. The thermochemical properties of the species involved in the updated sub-mechanism have been also recalculated to ensure consistency with the kinetic data.

Simulations were performed using PREMIX software from CHEMKIN [4] and mole fraction profiles for reactants (THF, O_2, Ar), mains products (CO, CO_2, H_2, H_2O), and C_1-C_6 hydrocarbons and oxygenated intermediates have been compared to our experimental data.

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Automatic generation of kinetic models for the oxidation of large alkylbenzenes

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Among automotive fuels, diesel fuel is a complex mixture consisting of alkanes, alkylcyclohexanes, alkyldecalines, alkylbenzenes (approximately 10%) and polycyclic naphthenoaromatic compounds, which contain from 10 to 20 carbon atoms. As it is difficult to consider the chemistry of all diesel fuel components due to the complexity of these mixtures, surrogate fuels have been suggested: e.g. a mixture of *n*-hexadecane, heptamethylnonane, 1-methylnaphthalene and *n*-decylbenzene [1]. However, while some kinetic models are available for the three first proposed surrogate compounds, no model has been yet proposed for alkylbenzenes larger than butylbenzene [2].

In the present study, an new version of software EXGAS (EXGAS-alkylbenzenes) has been developed in order to automatically generate model for the oxidation of large alkylbenzenes.

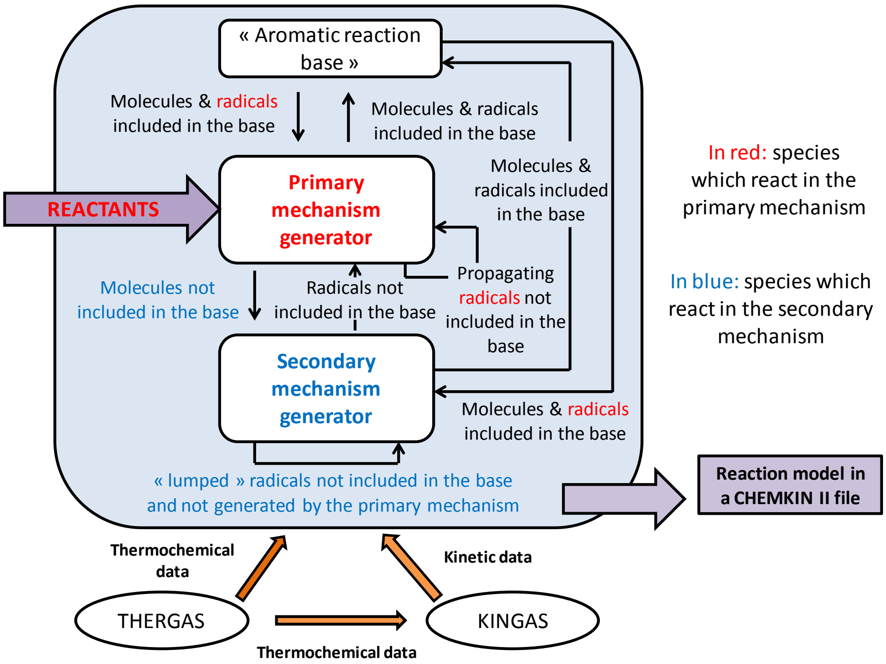

Figure 1: General structure of EXGAS-alkylbenzenes.

The generated models all contain the toluene-ethylbenzene mechanism proposed by Husson et al. [3] which is used as an aromatic reaction base. For alkylbenzenes with an alkylic chain containing more than 2 atoms of carbons, a primary and a lumped secondary mechanisms are generated based on generic reactions which have been defined following our previous modelling work on butylbenzene [2]. The algorithm of generation of the primary mechanism is displayed in figure 2. Most of the generic reactions are similar to those used for alkanes, only the ipso-additions are specific to aromatic compounds.

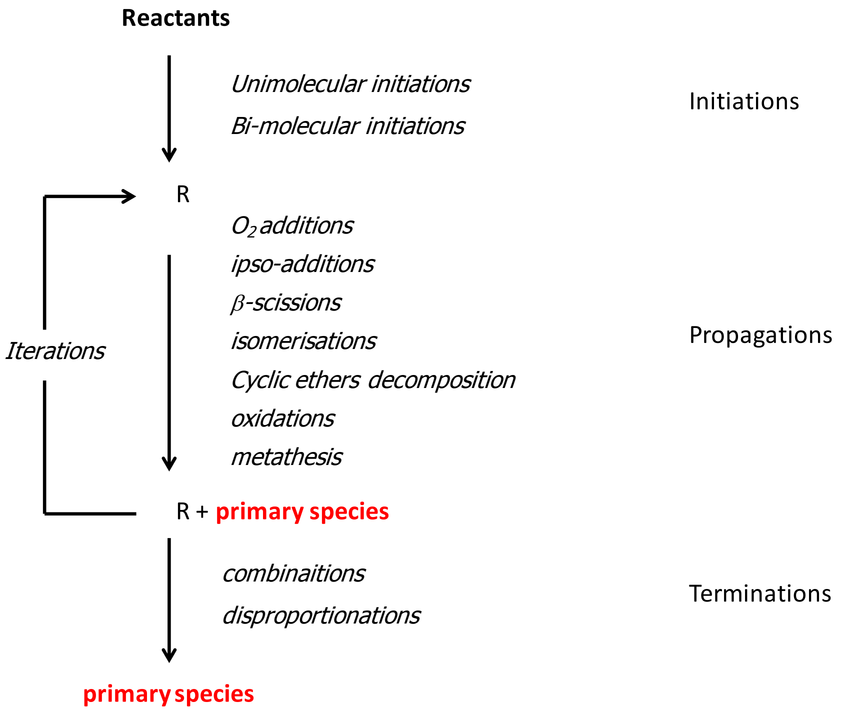

Figure 2: algorithm of generation of the primary mechanism.

The generated models have been validated by simulating experimental results obtained in a jet-stirred reactor for butylbenzene [2] and hexylbenzene and an *a priori* prediction of the reactivity of decylbenzene has been given.

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