TMFB
// Tailor-Made Fuels from Biomass

Status Report 2015-2016

// Cluster of Excellence (EXC 236)
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1 Introduction
The Cluster of Excellence „Tailor-Made Fuels from Biomass“ (TMFB) at RWTH Aachen University has now been working for more than 10 years on the development of sustainable biofuels. The second funding period of the German Excellence Initiative and thus of our Cluster of Excellence started in 2012, and the total funding will last until December 2018, which again provides an exceptional horizon for us to continue and intensify our research activities in the highly motivating and interdisciplinary world of alternative fuels.

From researcher’s perspective, the overall aim and vision of TMFB, namely the description of an integrated Fuel Design Process to describe and derive optimized sustainable biofuels, remained unchanged since the start of the Cluster of Excellence. Some minor adjustments, such as the redefinition of specific project targets, or the establishment of new projects, were undertaken. All these changes were based on the experiences that our researchers had made during their TMFB efforts and helped to refocus our activities in a very efficient way.

Today, we are proud that we were able to make the next big steps towards our final goal. New efficient, catalytic and bio-catalytic pathways from biomass to platform molecules and further onto biofuels could be derived. At the same time, applied and fundamental combustion experiments revealed new potential of TMFB fuel components, which were identified via the Fuel Design Process, to lower emissions and to increase the engine’s efficiency.

For the future, liquid energy carriers will remain of crucial importance not only for individual mobility, but particularly for goods transport and long-distance driving. Within the next years, TMFB is not only focussing on biomass as carbon feedstock, but also CO2. Moreover, electrocatalytic conversion processes are becoming of major interest. Both will not only lead to new molecular structures, but also to completely new fuel synthesis pathways.

With the status report we would like to give you the opportunity to get a close insight into our efforts and results of the last two years. Please, if you have any questions regarding our research program and our recent work, do not hesitate to contact us anytime.
2 Research Targets
Research Targets of TMFB

// Vision of TMFB
Since the beginning in 2007, the vision that is driving our research efforts has remained unchanged: the Cluster of Excellence “Tailor-Made Fuels from Biomass” takes an interdisciplinary approach to investigate new synthetic fuels obtained from biomass feedstock via target-designed production routes, in order to explore new potentials for future combustion engine technologies, while simultaneously reducing the dependence on fossil fuels. The long-term goal is to determine the optimal combination of fuel components and their production processes, which is based on renewable carbon sources and new combustion processes.

// Scientific Activities and Organization
With the beginning of the second phase in 2012, the structure of the overall project was reorganized: today TMFB consists of two Integrated Research Fields (IRF) “From Biomass to Biofuels” and “From Biofuels to Propulsion”, which are strongly linked by the Core Interaction Field (CIF) “Fuel Design”, as illustrated in Figure 2.1

The redefinition of the research structure even further streamlined our research and improved cooperation within different disciplines. Hence, within the recent years we have made big progress to achieve the main goal of TMFB: the definition of the Fuel Design Process as method to describe and produce biofuels which can be characterized as highly efficient, both from a production as well as from a combustion point of view. With continuation of our research and further developing methods and tools, also new fuel components were identified, such as 2-Butanone and 1-Octanol, successfully proving the feasibility of the Fuel Design Process.

Figure 2.1: Scientific Structure: Integrated Research and Core Interaction Fields
Scientific Activities
Integrated Research Field A: From Biomass to Biofuels

// Prof. Dr. rer. nat. Walter Leitner
// Institute for Technical and Macromolecular Chemistry
// leitner@itmc.rwth-aachen.de

// Vision
The conversion of lignocellulosic biomass to tailor-made fuel candidates is based on the development and detailed understanding of the individual (bio)chemical reactions and the integration of these process steps to allow the synthesis of target molecules directly from lignocellulose feedstocks.

The integrated research field IRF-A includes the investigation of novel methods for biomass fractionation (IRF-A1), innovative strategies for the valorization of lignin (IRF-A2), the development of novel catalysts for intermediate and fuel synthesis (IRF-A3/4), as well as the design and analysis of a reference process, combining all reaction steps (IRF-A5/6).

Figure 3.1: Concept and research structure of IRF-A

// Main Results Summary
Regarding the reference process, the conceptual process design and analysis was extended from 2- and 3-MTHF to 2-Methylfuran and butanon. The focus concerning biomass fractionation processes was on solvents (OrganoCat) and electrolyte systems. Besides the two step pretreatment and hydrolysis concept, a new mild and single step approach to glucose applying and electrochemical conversion was developed.
The combination of chemo- and biocatalysis with advanced engineering led to the development of various approaches towards selective lignin degradation. In addition, simultaneous depolymerization of lignin and the separation of the products, using an electrochemical membran reactor, was developed.

The conversion of glucose to levulinic acid as well as the isomerization of glucose to fructose were investigated. Additionally, the combination of glucose fermentation and catalysis as well as fermentative approaches to itaconic acid were demonstrated.

In terms of the hydrogenation of bio-based acids, mechanistic insights allowed the efficient optimization of ruthenium triphos catalysts and the hydrogenation of more challenging substrates. Furthermore, controlling the hydrogenation of furfuralacetone was possible using multifunctional nanoparticle catalysts. Stable supported Re as well as molecular and supported Mo catalysts for the deoxydehydration (DODH) were developed, enabling access to novel fuel structures.
Integrated Research Field A1: Biomass Fractionation

// Prof. Dr.-Ing. Antje Spieß
// Aachen Chemical Engineering – Enzyme Process Technology
// antje.spiess@avt.rwth-aachen.de

// Vision
The mechanistic understanding of different biomass fractionation processes as well as the subsequent enzymatic hydrolysis is the overall vision of project IRF-A1. Thus several analytical techniques are required in order to characterize the content of complex cell wall polymers (cellulose, hemicellulose, and lignin) and their liquefied solutions. Once the biomass is completely characterized, combinations of different fractionation and hydrolysis steps are analyzed to achieve the best mix of fractionation and enzymatic hydrolysis. This knowledge will be provided for further downstream processes in order to produce tailor-made fuels.

// Main Results Summary
The focus of the IRF-A1 during the last two years was on biomass fractionation processes based on solvents and electrolyte systems. As the pretreatment process is still barely understood, interactions of ionic species and water were investigated in order to understand both liquefaction and separation of biomass polymers. Besides the two-step pretreatment and hydrolysis concept, a new mild and single-step approach to glucose applying an electrochemical conversion was developed.

Following the analytical demands to analyze all fractions, a fast and reproducible method for biomass characterization was developed, using a high-performance anion exchange chromatography coupled with pulsed amperometric detection. The simultaneous determination of cellulose-, hemicellulose- and lignin-derived compounds supports the characterization of fractions derived from the investigated pretreatment methods such as acidic, alkaline, deep eutectic solvents (DES), electrochemical ionic liquid (IL) and organosolv pretreatment. These fractionation processes were used for tailoring the composition of cellulose, hemicellulose and lignin in the remaining pulp for subsequent hydrolysis.

// Results
One of the major steps in a biorefinery is the fractionation of biomass in order to obtain cellulose, hemicellulose and lignin fractions suitable for further processing. Simultaneously, the recalcitrance of the polysaccharide fraction against hydrolysis needs to be overcome to obtain high yields for hydrolysis. Thus the various products isolated from the complex cell wall structure require analytical know-how for iden-
tification and quantification according to their differences in both polarity and size.

Therefore, an analytical method meeting these requirements was developed. The degradation pathways of cellulose, hemicellulose and lignin during pretreatment and hydrolysis are complex and lead to numerous compounds (see figure 3.2).

![Figure 3.2: Analysis of lignocellulosic hydrolyzates using HPAEC-PAD. Figure modified based on the published manuscript Anders et al. 2015.](image)

In order to adapt both pretreatment and enzyme cocktail to a specific biomass composition, several plants with varying composition were treated with fractionation processes (see figure 3.3). Pretreatment parameters such as solvent, solvent concentration, temperature, time and catalyst were studied with respect to substrate composition determined by the newly developed HPAEC-PAD method. Following the pretreatment, substrates with various concentrations of cellulose and hemicellulose were hydrolyzed with enzyme cocktails consisting of cellulases and varying activities of mannanases and xylanases. In that sense, an online assay was developed allowing for additional studies on tailoring the enzyme cocktail based on the biomass composition.

Following the pretreatment studies with ionic liquids on a macroscopic scale, a model was set up to characterize effective pretreatment liquids on a molecular scale to determine active species. Since the pretreatment efficiency is drastically reduced above a certain amount of water within the IL - water is inherent to process streams containing biomass - the interaction between ionic components and water was investigated as a function of the water content. Low-field NMR spectroscopy was selected for visualization. The model connects dissociation equilibria and kinetically limited interactions between the individual ionic species to the effects observed from NMR spectra, with the aim of developing universal parameters for the descrip-
tion of various types of pretreatments. The experiments reveal that in the strongly ionic regime the dissociation equilibria change compared to the less effective aqueous regime.

DESs are a cheap alternative to ILs, which have turned out to dissolve lignin and hemicellulose. Additionally, DESs represent a medium for lignin valorization, e.g. as electrolyte for electrochemical conversion. Thus DESs have been applied for fractionation processes followed by lignin depolymerization in an electrochemical reactor.

Electrochemical processes can be an alternative to classical approaches due to the mild reaction conditions. It has been shown that biomass can be depolymerized via electrochemical processes. Anodic and cathodic reactions were studied in this context for the conversion of model compounds into the target compound glucose. While the general technical feasibility was demonstrated, selectivity was rather low. In general, the effect of different electrode catalysts on the efficiency of the electrochemical reaction was studied. Additionally, the effect of reaction parameters such as pH value, reactant concentration and cell potential was investigated with a focus on selectivity towards glucose. To increase selectivity, a strategy for an in-situ product removal based on membrane processes was developed using a tailor-made layer-by-layer polyelectrolyte membrane.

The obtained results show that biomass fractionation is still one of the major challenges. However, due to new analytical approaches, several new pretreatment techniques could be established. Besides the generation of saccharifiable cellulose a better mechanistic understanding of these pretreatments could be achieved. The adaptation to other biomasses will be addressed in the near future.
Integrated Research Field A2: Valorization of Lignin

// Prof. Dr. rer. nat. Carsten Bolm
// Institute for Organic Chemistry
// carsten.bolm@oc.rwth-aachen.de

// Vision
Our goal is to prepare fuels, additives thereof and platform chemicals by selective lignin degradation using chemo- and biocatalysis in combination with advanced engineering. This vision is supplemented by the intention to specifically modify lignin itself, providing valuable products for daily-use applications.

// Main Results Summary
The combination of chemo- and biocatalysis with advanced engineering led to the development of various approaches towards selective lignin degradation. Applying and extending the expertise in modern analytical techniques proved crucial for the transformation of initial results stemming from proof-of-principle studies, involving lignin model compounds, to more practical cleavage strategies with "real" lignin samples.

// Results
The selective degradation of lignin is important for the biorefinery concept. It is generally recognized that this goal is difficult to reach and that even small advances bear the chance of eventually leading to major breakthroughs. Alternatively, specific applications of lignin (or derivatives thereof) as part of high-value products are envisioned, which may also result in significant progress. In the TMFB Cluster of Excellence chemo- and biocatalysis are linked to engineering, and truly impressive results have already been achieved by following this approach. Initially, most studies involved the use of well-defined lignin model compounds with the goal to gain a better understanding of the molecular processes leading to bond cleavage reactions. Those investigations have more and more been followed by attempts to convert lignin itself or lignocellulose present in wood.

Figure 3.4: Cobalt-catalyzed oxidation of a dilignol model compound.
Following the chemocatalytic approach, new redox-neutral ruthenium-based catalysts allowing unprecedented bond fragmentations in lignin model compounds were discovered. The details of such catalytic transformations were investigated by varying the experimental conditions in combination with theoretical studies.

Other chemochemical protocols involved the use of low-cost metals in oxidative lignin degradations. While initially copper- and vanadium-based catalysts were in the focus allowing bond-breakings with dioxygen as terminal oxidant, recent systems involved metals such as iron and cobalt. Whereas the former utilized hydrogen peroxide as oxidant, dioxygen was applied in the latter (Figure 3.4). In each case both the cleavage of stereochemically well-defined β-O-4 lignin model compounds as well as the degradation of native lignin samples were studied and both showed promising results. For all transformations the product analysis proved challenging. Most difficulties could now be overcome, by using 2D-NMR (HSQC) and GPC measurements, in combination with GC-MS identifications of lignin cleavage products, which now belong to the standard repertoire of the TMFB for structure determination and product mixture analysis.

In this context the shift of one project towards the development of analytical methods to be applied on raw, modified and isolated lignin obtained from the various TMFB processes was important. Particular emphasis was put on liquid chromatography methods such as gel permeation chromatography (GPC) to be coupled to mass spectrometry (MS), which allowed gaining comprehensive knowledge of the lignin fragments. Generally, the analytic scheme involved three differently isolated lignins from beech wood. Those were a commercial Kraft lignin (KFL) from the pulp and paper industry, an acid insoluble Klason lignin (KLL), and an Organosolv lignin (OSL) isolated with ethanol. In each case, the results of an aqueous GPC-UV/RI method (H₂O/Na₂HPO₄) were compared with those of an organic GPC-RI method (DMF/LiCl). The analytical toolbox for lignin has then been complemented by a method based on high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) allowing to detect possible chemical changes and degradation products (e.g. aromatic alcohols and aldehydes) due to the alkaline eluent.

Such analytical tools were also relevant for the electrochemical depolymerization of lignin, where an electrochemical membrane reactor (Figure 3.5) has been applied. This method allowed the simultaneous depolymerization of lignin and the separation of the products. For the success of the electrochemical depolymerization process, the electrode geometry proved to be a key factor. Substituting the alkali electrolyte with an innovative Deep Eutectic Solvent represented a green alternative avoiding product over-oxidation.
While all of the aforementioned approaches focused on the search for selective bond-cleavage reactions leading to lignin degradations, an alternative strategy for lignin valorization by molecular modification of the biopolymer core has recently been added. By specifically altering the outer sphere of lignin, the lipophilicity of the readily available biopolymer (or parts thereof) can be increased resulting in intermediates having potential high-value applications in the cosmetic and skin-care industry.

In the biocatalytic approach directed evolution was applied for a semi-rational design focusing on a loop connecting domain two and three of lcc2 from Trametes versicolor to further improve the ionic liquid (IL) resistance. It finally led to a variant carrying four beneficial amino acid positions located showing a 3.4-fold increased activity compared to lcc2 WT in 10% (v/v) EMIM EtSO4. Even in presence of 30% (v/v) EMIM EtSO4 it maintained a 36.2 % activity, while the one of lcc2 WT decreased to 22.3%.

Realizing that in nature peroxidases and laccases are the main enzymes for lignin degradation, various lignocellulose-degrading enzymes of bacterial and fungal origin were heterologously expressed using Escherichia coli and the yeast Kluyveromyces lactis, respectively, depending on the pro- or eukaryotic origin of the enzyme. In screens of such recombinant enzymes with simple and more complex lignin model compounds as well as Kraft lignin bacterial enzymes showed activity towards a phenolic lignin-model compound and Kraft lignin. Three different fungal enzymes from different biomass degrading families were expressed in one K. lactis cell, achieving the first step “in one pot” production system.

Figure 3.5: Ceramic membrane reaction for lignin degradation.
Integrated Research Field A3: Carbohydrates to Intermediates

// Prof. Dr.rer.nat. Ulrich Schwaneberg
// Institute of Biotechnology
// u.schwaneberg@biotec.rwth-aachen.de

// Vision
To achieve sustainable conversion of complex biomass-derived carbohydrate into tailor-made fuel candidates, four research lines are pursued within the sub-IRF-A3: an automated screening system for identifying and improving enzyme variants (Prof. Büchs group, AVT, RWTH Aachen University), the optimization of Ustilago maydis MB215 for xylane degradation and itaconic acid production (Prof. Blank group, iAMB, RWTH Aachen University), the generation of novel biohybrid catalysts for hydrogenation, Hoveyda-Grubbs and Henry type reactions for selective and efficient conversion of carbohydrates to into platform chemicals (Prof. Okuda group, IAC, Prof. Klankermayer group, ITMC, Prof. Schwaneberg group, Biotec, RWTH Aachen University) and the expression and improved recyclability of cellulase cocktails (Prof. Fischer group, MolBioTech RWTH Aachen University).

// Main Results Summary
In order to identify cellulase celA2 variants that can serve as Celluclast additives, the RoboLector platform was used to perform a reliable high-throughput screening of an E. coli library.

To enhance synergistic actions and to improve recyclability, a set of cellulases was expressed in Klyveromyces lactis. The enzyme cocktail yielded 50% and 90% of activity relative to commercial Celluclast (tested against Avicel and PASC, respectively).

In pursuance of identifying novel and superior biocatalysts for efficient carbohydrate conversion to platform chemicals the itaconate production pathway of Ustilago maydis MB215 was characterized and the corresponding gene cluster was identified.

In the interest of generating robust catalysts for the conversion of biomass-derived intermediates the FhuA channel protein was re-engineered to tune the selectivity of the biohybrid catalyst. After establishing the chemistry and analytics of the linking strategy, the range of available biohybrid catalysts was increased to allow transformations of small molecules.
// Results

Cellulose depolymerization is the rate-limiting step for the carbohydrate hydrolysis process. For the identification and characterization of cellulases an efficient screening process is required. Therefore the RoboLector platform was successfully extended by a cooling carrier, a MTP shaker for heat treatment and a vacuum filtration module. A highly parallel biomass growth was obtained and a comparable expression of cellulase celA2 variants was secured via biomass specific induction (Fig. 1). Volumetric activity measurements were performed in triplicates using the 4-MUC cellulase activity assay. The results confirmed the reliability of the system by very small standard deviations. A clone ranking revealed an activity six times higher than the best variant, compared to the wildtype. Induction time, inducer concentration and temperature were further optimized. Optimal IPTG concentration decreases with increasing temperature – at

Figure 3.6: Comparison of induction profiles at different temperatures. Induction of E. coli pRhotHi-2-Tuner EcFbFP with 0 - 0.4 mM IPTG after different times. Black dots indicate individual measurements. Color-gradient depicts the maximum fluorescence intensity of formed EcFbFP. 48-well FlowerPlate sealed with sandwich foil (m2p-labs), 200 µL filling volume, 1400 rpm, 3 mm shaking diameter, measurement of EcFbFP-fluorescence at Ex/Em = 450/492 nm, gain 60, ODstart= 0.1. A) T=28°C, B) T=30°C, C) T=34°C, D) T=37°C.
Summary

Activities 2015-2016

At 37°C the highest expression was achieved for 0.05 mM IPTG, whereas at 28°C the best results were obtained for 0.1 mM IPTG. A new correlation of the first derivative of scattered light, the oxygen transfer rate and the efficiency of enzyme production was identified. With induction conditions having been improved accordingly, a five-fold increase in enzyme production could be achieved (J Biol Eng. 2017, 11:1).

Endoglucanase, Cel5A, two exoglucanases, Cel6A and Cel7A, and a β-glucosidase Bgl1 from Trichoderma reesei were successfully expressed in Kluyveromyces lactis (Cellulose Chem. Technol. 2016, 50(3-4), 385-389). Various amounts and combinations of these enzymes were tested to obtain an optimal mixing ratio. The mixture with a five-fold excess of both exoglucanases compared to Cel5A and - Bgl1 demonstrates the highest activity on cellulose model substrates such as Avicel and PASC. When comparing the optimized mixture derived from K. lactis and the commercially available Celluclast mix, which is the standard enzyme mix used in industrial processes, the activity of the enzyme blend turned out to be half as active as Celluclast is on Avicel, while it shows similar activity on PASC. In order to investigate the recyclability of the enzymes, Cel5A and Bgl1 were successfully immobilized on magnetic beads by the principle of Co2+ mediated binding of 6xHis-tag to epoxy groups to achieve uniform orientation of the enzymes. Immobilized Cel5A retained 50% of its activity after five cycles, while Bgl1 retained 60% of its activity after four cycles. Moreover, the magnetic property of the beads allows for a better separation of the immobilized enzymes from the reaction mixture substrate.

Itaconic acid is an important biomass-derived chemical building block. In order to offer new strategies for biotechnological production the itaconic acid biosynthesis pathway of Ustilago maydis was characterized. 2-hydroxyparaconate (2HP) was identified as a downstream product of itaconic acid. A hyper itaconic acid producer was generated by combinatorial metabolic engineering and together with optimized fermentation conditions the production was greatly improved. Max. titer: 63 g/l itaconate; max. yield: 0.5 g itaconate per g glucose; max. rate: 0.4 g/l/h. This approximately constitutes a 4.5-fold improvement of titer and rate, and a roughly ten-fold increased yield compared to wildtype strain under the same conditions (Metab Eng. 2016, 38, 427-435). Overall a more than 25-fold improved product titer was achieved compared to the starting conditions in 2011. Furthermore a novel CRISPR-Cas9 system was established for efficient genetic engineering and additional production strains for 2HP and malate were generated. Other Ustilago strains which are significantly more pH tolerant than U. maydis were identified.

Biohybrid catalysts combine the structural diversity of biomolecular scaffolds with various types of metal catalysts/organocatalysts. Importantly, the biohybrid cata-
lyst offers great opportunities for genetic optimization. Molecular modeling of a FhuAΔCVFtev-Grubbs-Hoveyda catalyst identified four key residues (Gln505, Ser573, Asp612 and Asn708) in a 5 Å sphere around the Ru catalyst which might influence the stereocontrol of the hybrid catalyst. Sixteen variants with sterically demanding amino acids (Tyr) at four positions were generated to achieve stereoselective polymerization.

**Artificial Diels-Alderase: FhuAΔCVFtev-Cu**

Additionally, three key residues (Phe501, Gln505, Ser573) in a 3 Å sphere around the Ru catalyst were identified to generate a second anchoring through the amino acids methionine or histidine. Chemogenetic engineering of the FhuA CVFtev-Grubbs-Hoveyda hybrid catalyst revealed the influence of a varied linker length on selectivity and activity. A close proximity of the catalyst to the surrounding protein mediated by a shorter linker length promoted activity and selectivity of ring-opening metathesis polymerization. Coupling of copper-terpyridine- (Cu-terpy) and copper-carbene- (Cu-NHC) complexes was achieved.

In the catalyzed Diels-Alder-reaction the use of biohybrid catalyst FhuA CVFtev-Cu allowed endo/exo-discrimination (Fig.2, Beilstein J. Org. Chem. 2016, 12, 1314–1321). The application of insights into Diels-Alder catalysis to bio-based substrates such as furan derivatives is in progress. Cross metathesis of olefinic double bonds derived from lignocellulosic biomass to produce intermediates for fuels showed suppressed side reactions caused by isomerization in presence of the biohybrid catalyst FhuA CVFtev-Ru. These findings will be published soon. The first example of a whole-cell biohybrid catalyst with FhuA CVFtev located in the outer membrane demonstrated the feasibility of metathesis reactions in whole cells.
Integrated Research Field A4: Intermediates to Fuels

Prof. Dr. rer. nat. Regina Palkovits
Institute of Technical Chemistry and Macromolecular Chemistry,
Chair of Nanostructured Catalysis
palkovits@itmc.rwth-aachen.de

Vision

RF-A4 focuses on catalytic transformations of biomass-derived monomers to fuel molecules with major emphasis on the design of efficient homogeneous, heterogeneous and bio(electro) catalysts as well as the development of novel fuel structures. A close integration of the catalytic disciplines, high carbon and/or hydrogen efficiency as well as overall green and sustainable chemical transformations are in the focus of the IRF-A4.

Main Results Summary

Efficient conversion of cellulose and cellulose-derived compounds into fuel molecules was considered. The main focus was laid on adjusting the C/H/O ratios in the molecules to produce potential compounds. In this regard, the catalytic and electrocatalytic transformations, covering decarbonylation, hydrogenation, deoxydehydration, dehydration, and oxidation were investigated. A number of catalysts, including solid materials, such as supported metals/alloys and polymers as well as molecular complexes were uncovered for the processes under discussion.

Figure 3.8 Carbon based hollow sphere catalysts with embedded PtCo nanoparticles for HMF hydrogenolysis to 2,5-DMF (G.-H. Wang et al, Nat. Mater., 2014, 13, 293-300)
Results

Preliminary results have shown that a hydrogen-free access of fuel candidate 2-MTHF from cellulose is possible with a hydrogen free decarboxylation strategy. In the next steps, the reaction will be optimized in cooperation with the chemical engineering department. It was also shown that fructose, another molecule available based on cellulose, can be converted into HMF in the presence of novel N-alkyl-4-vinylpyridinium-base polymers. In turn, catalysts for further transformations of HMF were uncovered: it can be highly selectively hydrogenated into 2,5-DMF with > 95% yield in the presence of PtCo catalysts and synthesized utilizing a core-shell catalyst design. Alternatively, an oxidation of HMF to a di-acid, catalyzed by Ru, supported on amine functionalized silica, is possible, overcoming challenges of product adsorption and decomposition. In addition, hydrogenation of bio-based acids and related substrates was addressed. Mechanistic insights concerning the hydrogenation of bio-based acids lead to the development of a new set of ruthenium triphos catalysts able to promote the reduction of even more challenging substrates. Electrochemical reduction using a lead catalyst was proposed as an alternative. Promising lead candidates for a bioelectrochemical reduction of biogenic acids were identified, facilitating future directed optimization. Molecular and supported catalysts were proposed for efficient deoxydehydration (DODH) of biomass-based substances to yield alkenes. Stable supported Re catalysts for deoxydehydration could be developed exhibiting high performance in DODH and high stability even in a continuous flow reactor. DODH provides an access to novel fuel structures.

Figure 3.9: Lab-scale demonstrator for the preparation of 3-MTFH using Ru(triphos) as catalyst (J. Klankermayer, W. Leitner, M. Meuresch, PCT/EP2015/052881; M. Meuresch, S. Westhues, W. Leitner, J. Klankermayer, Angew. Chem. Int. Ed. 2016, 55, 1392-1395)
Integrated Research Field A5: Multiphase Reaction Integration

// Prof. Dr.-Ing. Matthias Wessling
// Aachen Chemical Engineering - Chemical Process Engineering
// matthias.wessling@avt.rwth-aachen.de

// Vision
The IRF-A5 focuses on the development and investigation of chemo- and bio-catalytic processes for the valorization of biomass as well as the production and recovery of biomass-based compounds. This involves the conversion of plant biomass to itaconic acid using co-cultures of two microorganisms in one reactor (consolidated bioprocess), model-based experimental analysis in multiphasic conditions and new extraction processes for high-value products.

// Main Results Summary
A new analytical tool was developed to evaluate the digestibility of different cellulose substrates. This is particularly important for the consolidated bioprocess to produce itaconic acid. Furthermore, new methodologies for the recovery of itaconic acid have been developed: a chemo-catalytic approach, based on adsorption, and an in-situ reactive extraction, including a final crystallization step, were presented. Since fructose is also an attractive substrate in biorefineries, a new chemo-catalytic reaction was developed.

// Results
The group of Prof. Palkovits (ITMC) developed a chemo-catalytic three-step approach, combining the isomerization of glucose into fructose with recovery of the product. Fructose presents a highly attractive substrate for future biorefineries. The first step of the process covers isomerization of glucose into fructose, using water as a solvent and soluble Na2HPO4 + NaH2PO4 as a catalyst.

The second step relates to the recovery of fructose by selective anionic extraction. Furthermore, itaconic acid was separated and purified from aqueous solutions by a selective liquid phase adsorption for the first time (Fig. 3.10).

The surface polarity and the textural properties of the adsorbent were identified to be critical parameters for the process efficiency. Adsorption from mixed solutions of itaconic acid and glucose exhibited extraordinary high selectivities for adsorbents with highly hydrophobic surfaces, especially certain activated carbons and hyper-cross-linked polymers. This demonstrates a model system for an alternative technology to conventional separation strategies in biorefinery concepts.
In the previous project phase of TMFB, the group of Prof. Büchs (AVT-BioVT) demonstrated a consolidated bioprocess that integrates cellulase production, cellulose hydrolysis and fermentative conversion of produced sugars into itaconic acid. However, the digestibility of the substrate cellulose depends on the applied raw material and pretreatment methods. Therefore, a new method was developed that measures the sugar consumption of Trichoderma reesei Rut-C30, by monitoring the oxygen uptake rate, to evaluate the digestibility of cellulose (Fig. 3.11). The impact of the biomass pretreatment methods OrganoCat and OrganoSolv could already be tested on beech wood and saw dust. Moreover, known (cellulobiose, sophorose, urea, tween 80, peptone) and new (miscanthus steepwater) compounds enhancing cellulase production were evaluated. Furthermore, new concepts (freeze assay) were set up to screen cellulase producers for consolidated bioprocessing applications. Additionally, fluorescence-tagged T. reesei and A. terreus strains were designed that help to establish a mixed-culture system by assessing the mixed-culture population dynamics.

The group of Prof. Jupke (AVT-FVT) developed a novel downstream process for itaconic acid via in-situ reactive extraction, back extraction and final pH-shift crystallization. The aim was to increase space-time yield and minimize energy demand. Additionally, a liquid-liquid separation in a centrifugal force field was investigated by single-drop as well as droplet-swarm sedimentation and coalescence behavior experiments. For this purpose, new laboratory equipment was successfully developed.
The group of Prof. Mitsos (AVT-SVT) is working on the identification of kinetics in biphasic chemical reactions relevant to the Cluster of Excellence. They successfully modeled the hydrogenation of methyl benzoate, allowing the comparison between experimental and theoretical parameter values. First steps on the integration of model identification and conceptual process design were addressed. Information from process optimization is integrated into optimal experimental design for parameter precision via the formulation of a tri-level optimization problem.

Figure 3.11: Process scheme of cellulose digestion by T. reesei.
Integrated Research Field A6: Reference Process

// Prof. Dr.-Ing. Jochen Büchs
// Aachen Chemical Engineering - Biochemical Engineering
// jochen.buechs@avt.rwth-aachen.de

// Vision
One goal of the TMFB cluster is to identify scientific principles and to provide tools that are needed for the development of biorefinery processes. In the Integrated Research Field IRF-A6, these tools and principles are applied to a reference process in order to investigate and demonstrate their feasibility in a realistic case study, rather than focusing on single process steps. This allows the identification of critical unit operations and realistic assessment of process conditions.

// Main Results Summary
A reference process, including biomass pretreatment, biotechnological itaconic acid production and subsequent purification as well as transformation to the promising future fuel candidate methyltetrahydrofuran (MTHF) was investigated. Different computational and experimental methods were developed to optimize the process under realistic conditions, integrate process steps and minimize the overall energy consumption. Itaconic acid fermentation with integrated in-situ reactive extraction, followed by back-extraction and crystallization, yielded biotechnologically produced itaconic acid crystals and thereby experimentally demonstrated the feasibility of an integrated process concept.

// Results
To define a suitable reference process, different production routes for the promising fuel candidate methyltetrahydrofuran (MTHF) were evaluated. After biomass pretreatment, itaconic acid is produced as intermediate in a fermentation followed by purification and transformation to MTHF. In this evaluation, special focus was put on the interaction between different process steps like biomass pretreatment, fermentation and purification.

The first step for biorefinery processes is biomass pretreatment and especially the fractionation of lignocellulose. In the developed, completely bio-based biphasic OrganoCat process, oxalic acid is used as catalyst to selectively hydrolyze hemicellulose. Additionally, an organic MTHF phase is used for in-situ extraction of lignin. The OrganoCat process was optimized regarding the diversity of the utilized plant material as well as downstreaming. Thereby, generally applicable correlations of cell wall structure and degradability of the biomass were found.
For itaconic acid production, fermentations of Aspergillus terreus and Ustilago maydis were investigated. Applying low-field NMR, a non-invasive online monitoring system for itaconic acid production during the cultivation was established. Additionally, a computational tool was developed to minimize the power consumption of the fermentation. A significant part of the cost of biotechnological processes arises from downstream processing. Therefore, the recovery of itaconic acid from the fermentation broth was investigated. A software framework was developed to validate electromembrane processes for the separation of itaconic acid. Thereby, steady-state and dynamic processes can be investigated to improve the understanding of basic physical principles in electromembrane processes and to simulate complex separation tasks.

Furthermore, in-situ reactive extraction of itaconic acid was integrated in the fermentation of Aspergillus terreus. Thereby, product inhibition could be overcome and the final itaconic acid concentration was increased. Additionally, a link between the fermentation and further downstream processes was established. In-situ reactive extraction was followed by alkaline back-extraction and pH-shift crystallization. Thus, the feasibility of an integrated process concept was demonstrated experimentally, yielding pure itaconic acid crystals from a real fermentation broth. Based on these results, a process scheme for itaconic acid recovery was proposed (Figure 3.13). Development of shortcut methods for separation models allowed for automated process evaluation, also for large-scale processes, to minimize the overall energy demand. In this context, a new solvent selection methodology was developed to screen for suitable solvent systems. Furthermore, this methodology also enables the evaluation of novel designer solvents by predicting the process performance, based on thermodynamically accurate shortcut models.

In addition to the biotechnological itaconic acid production, chemical valorization strategies were investigated. The transformation of furfuryl alcohol to hydroxycyclopentenone was used as representative biomass valorization reaction. Automatically processed self-optimization of the reaction was performed in a continuously operated reaction. Furthermore, conversion of glucose to levulinic acid and furanic sugars was studied. Isomerization of glucose and extraction of the produced methylfructosides with MTHF was demonstrated.

Figure 3.12: Possible downstream route based on crystallization.
List of Projects IRF-A

**Project**  
IRF-A1-2 “Design and Application of Electrolyte Solutions as Solvents for Cellulose”  
Max-Planck-Institut für Kohlenforschung (Dr. Roberto Rinaldi)

**Aim**  
The main goal of the project is to understand the molecular and thermodynamic properties related to the solvation power of electrolytes for dissolution and depolymerization of cellulosics.

**Results**  
A calorimetric description of the solvation power of electrolytes for dissolution of cellulose was accomplished, publications are pending. Solvent effects on the hydrolysis of cellulose and cellobiose were identified (publications are also pending).

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**Project**  
IRF-A1-1 “Systematic Experimental Analysis of Pretreatment in Strong Electrolytic Media”  
Aachen Chemical Engineering – Process Systems Engineering (Prof. Alexander Mitsos)

**Aim**  
The project aims at understanding the conversion of lignocellulosic biomass in pretreatment liquids of high ionic strength with the aid of spectroscopy. This includes the quantification of pretreatment as well as modeling of the ionic interaction. Eventually, this shall aid in the design of new solvent mixtures for efficient pretreatment and simple recycling.

**Results**  
After the assessment of pretreatment with ionic liquids on process level, a model has been set up to correlate spectral information with the interaction between species of the pretreatment liquids on molecular level. In correlation with composition of the pretreatment mixtures, the active species shall now be determined and this information be transferred to equally efficient but cheap electrolyte solutions.
### Project
**IRF-A1-3 “Mechanochemical Hydrolysis of Lignocellulose to Water Soluble Products and Conversion of the Hydrolysate”**
Max-Planck-Institut für Kohlenforschung (Dr. Roberto Rinaldi, Prof. Ferdi Schüth)

**Aim**
The upscaling of mechanocatalytic depolymerization of cellulose to water soluble oligosaccharides is investigated. The aim is to improve the energy efficiency of the process and make it feasible from the economic point of view.

**Results**
A remarkable reduction of energy demand for depolymerization was achieved by upscaling the depolymerization process of acid impregnated cellulose and different types of wood from g to kg scale in a simulation mill. In a side project, a PtCo based catalyst supported on nitrogen-doped ordered mesoporous carbon for the upgrading of phenolic streams was derived from "real-world" wood by a hydrodeoxygenation reaction was developed.

### Project
**IRF-A1-4 “Simulation Toolbox for the Multi-Enzyme-Catalyzed Degradation of Biomass Derived Lignocellulose”**
Aachen Chemical Engineering – Enzyme Process Engineering (Prof. Antje Spieß)

**Aim**
The reduction of enzyme costs is the main leverage to increase the overall economy of the biorefinery process. Thus, an adjustment of both pretreatment method and enzyme cocktail to the particular lignocellulosic biomass by mechanistic modeling is a powerful tool to make biorefinery processes more competitive.

**Results**
One important result is the examination of the influence of biomass type and pretreatment parameters on the substrate composition and hydrolysis by varying enzyme cocktails containing cellulases, xylanases and mannanases. The second major achievement lies in the development of a chromatographic online activity assay based on xylanases as tool for data acquisition for mechanistic modeling of biomass hydrolysis.
IRF-A1-5 “Coarse Grained Simulation of Biomass for Process-Scale Models”
Aachen Chemical Engineering – Molecular Simulations and Transformations (Prof. Ahmed Ismail)

Aim
Molecular dynamics simulations were used to study the dissolution of cellulose in ionic liquids and the organic solvent NMMO. This included a detailed analysis of the occurring dynamic changes in hydrogen bonding, an estimation of the free energy of dissolution as a function of water concentration, and the role that water plays in disrupting the dissolution process.

Results
It was determined that water primarily interferes with cellulose dissolution in ILs through crowding of the IL anion’s basic sites, preventing its strong interaction with cellulose. Thermodynamic quantities obtained from the simulations cellulose in aqueous NMMO agreed incredibly well the experimental trend in solubility and showed that NMMO’s good solvent properties can be attributed to the presence of strongly basic sites and hydrophobic domains that interact with and complement the amphiphilic nature of cellulose.

IRF-A1-6 “Electrochemical Cellulose Depolymerization”
Aachen Chemical Engineering – Chemical Process Engineering (Prof. Matthias Wessling)

Aim
Electrochemical processes can be utilized to pretreat and even depolymerize cellulose. In this project, different electrochemical reactions, reactors and operating conditions are investigated to learn more about the technical feasibility of biomass conversion.

Results
Depolymerization of the model compound cellobiose has been studied and the target molecule glucose has successfully been formed. To increase selectivity, groundwork for an in-situ extraction via membrane processes has been laid.
Project  
IRF-A1-7 “Reactive Molecular Dynamics Studies on the Inner Structure of Crystalline Cellulose and Its Dissolution by Alkaline/Urea Aqueous Solution”  
Aachen Chemical Engineering – Enzyme Process Engineering (Prof. Antje Spieß), Institute of Biotechnology (Prof. Ulrich Schwaneberg)

Aim  
Computational methods are used in order to quantify the energy contribution of a hydrogen bonding network to the stability of crystal structure of cellulose and to explore the dissolution mechanism of cellulose in NaOH/urea solution.

Results  
Alternative hydrogen bonding network of cellulose was found and challenged the current experimentally established one. Urea, as a co-solvent that better and rapidly dissolves cellulose in pre-cooled NaOH solutions, was found to directly adsorb on cellulose surface, which is driven by the maximization of solvent entropy. These findings will guide the development of new solvents for cellulose dissolution.

Project  
IRF-A2-1 “Reaction Engineering and Laccase Re-Engineering for Lignin Degradation From Lignocellulosic Substrates”  
Aachen Chemical Engineering - Enzyme Process Engineering (Prof. Antje Spieß), Institute of Biotechnology (Prof. Ulrich Schwaneberg)

Aim  
The aim is the protein engineering of laccases such as lcc2 from T. versicolor for increased resistance to ionic liquids/organic solvents and the improvement of expression level by expressing lcc2 variants in P. pastoris. Chromatographic techniques for lignin molecular weight determination and detection of degradation products are developed to evaluate lignin degradation and oxidation in homogeneous catalysis with ionic liquid/organic solvent tolerant laccases.

Results  
A three-step semi-rational design of lcc2 from T. versicolor was performed with OM1 as best variant. In the second part of this project a gel permeation chromatography method (GPC-UV/RI) with reduced non-size exclusion effects as well as up to 50 % decreased lignin association was developed and applied.
| Project | IRF-A2-2 “Catalyzed Lignin degradation”  
Institute of Organic Chemistry (Prof. Carsten Bolm) |
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<tr>
<td>Aim</td>
<td>This project is focused on the catalyzed cleavage of the lignin polymer to value added products and their subsequent synthetic utilization. Furthermore, oxidative cleavage pathways based on lignin model compound studies are investigated.</td>
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<tr>
<td>Results</td>
<td>Transition metals (Fe, Cu/V, Co) in combination with different oxidanting agents were successfully employed as homogeneous or heterogeneous catalysts for lignin model compounds. Furthermore, representative bonds in Organosolv- and Kraft lignin samples were cleaved and confirmed by a variety of established analysis tools (NMR, GPC, GC-MS).</td>
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| Project | IRF-A2-3 “Knowledge-Based Identification of Lignin-Degrading Enzymes From Non-Conventional Sources”  
Institute for Molecular Biotechnology (Prof. Rainer Fischer) |
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<tr>
<td>Aim</td>
<td>To be able to generate tailor-made enzyme cocktails that are active on different biomass sources, individual lignocellulose-degrading enzymes of bacterial and fungal origin were selected and heterologously expressed using various bacterial hosts and the yeast Kluyveromyces lactis, depending on the pro- or eukaryotic origin of the enzyme, respectively.</td>
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<tr>
<td>Results</td>
<td>A set of different bacterial lignin-degrading enzymes were expressed in different host organisms reaching high expression yields, and the activity of those recombinant enzymes on lignin-model compounds and Kraft lignin was shown. Moreover, various lignocellulose-modifying enzymes from fungal sources were expressed in a single Kluyveromyces lactis cell achieving the production of multiple enzymes “in one pot.”</td>
</tr>
</tbody>
</table>
### Aim

**THE ELECTROCHEMICAL MEMBRANE REACTORS (ECMR) FOR CONVERSION OF BIO-RENEWABLES**

Aachen Chemical Engineering – Chemical Process Engineering (Prof. Matthias Wessling)

The electrochemical depolymerization of lignin is a green and sustainable process to valorize lignin coming from biorefinery processes. Different reactor setups, innovative electrolytes, electrode materials and geometry are used to investigate the technical feasibility of lignin utilization.

#### Results

The electrochemical depolymerization for producing monomers has been achieved in a continuous electrochemical membrane reactor with a particular focus on electrode geometry. Innovative deep eutectic solvents have been used as a novel electrolyte for electrochemical depolymerization.

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### Aim

**THE DEVELOPMENT OF METAL ALLOY CATALYSTS FOR THE HYDROGENOLYSIS OF LIGNIN**

Max-Planck-Institut für Kohlenforschung (Dr. Roberto Rinaldi)

The electrochemical cleavage of technical lignin to produce value-added compounds is investigated in lab-scale batch reactors. The results will be transferred to a continuous process to investigate the technical feasibility of lignin utilization.

#### Results

The influence of several process parameters on the electrochemical degradation of technical lignin has been intensively investigated and characterized. The addition of filtration processes to alleviate certain drawbacks of the degradation process is underway.
**Project**  
IRF-A2-6 “Catalytic de-functionalisation of lignin”  
Institute of Technical and Macromolecular Chemistry (Prof. Jürgen Klankermayer)

**Aim**  
Development of homogeneous catalysts for the disintegration of lignin linkages via transfer hydrogenolysis.

**Results**  
Novel Ruthenium-phenolate-complexes could be developed and efficiently used in the selective cleavage of lignin model compounds. Successful development of a family of catalysts for selective C-O and C-C bond cleavage of the β-O-4 linkage model compounds was achieved. Furthermore application of these catalyst candidates on real lignin samples showed promising selective depolymerization activity.

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**Project**  
IRF-A2-7 “Bio-Cracking: Enzymes for Tailor-Made Lignin Fractionation”  
Institute of Biotechnology - Biocatalysis (Prof. Anett Schallmey), Institute of Technical Chemistry and Macromolecular Chemistry (Dr. Pablo Dominguez de Maria)

**Aim**  
Within the project, novel bacterial b-etherases and glutathione lyases have been exploited for their potential application in selective lignin depolymerization.

**Results**  
A three-enzymatic process for the selective depolymerization of OrganoCat lignin has been developed resulting in a stream of low molecular weight aromatics. Additionally, a thermostable glutathione lyase for application in lignin bio-cracking has been identified and the utility of synthetic lignin for the identification of novel microbial lignin-degrading enzymes has been demonstrated.
Project: IRF-A2-8 “Oxidative Cleavage and Synthetic Use of Lignin Degradation Products”
Institute of Organic Chemistry (Prof. Carsten Bolm)

Aim: Initial attempts focused on the cleavage of the arene portion of lignin. Currently, lignin is converted through the (trans)esterification of its hydroxyl groups with long-chain fatty acids and esters.

Results: Oxidative cleavage of the arene portion of lignin model compounds can lead to cyclic products with relevance for supramolecular chemistry. A mechanochemical approach has been developed leading to lipophilic lignin-based products with potential relevance in the cosmetic industry.

Aachen Chemical Engineering - Biochemical Engineering (Prof. Jochen Büchs)

Aim: For effective hydrolysis of cellulolytic precursors, it is of great importance to select the most suitable enzymes and convenient process conditions. Thus a customized high-throughput screening is necessary to overcome the experimental effort.

Results: An automated cellulase clone bank screening was developed on the RoboLector platform to overcome common screening problems and was successfully applied to an E.coli library. Afterwards, the best variant was used to further improve the yield by finding optimal induction conditions in an automated induction profiling.
Institute of Technical Chemistry and Macromolecular Chemistry (Prof. Walter Leitner), Institute of Biotechnology (Prof. Ulrich Schwaneberg)

Aim: The aim is the development of hybrid catalysts for catalytic cascade transformations. Artificial metalloenzymes are synthesized via the incorporation of transition metal complexes into FhuA channel protein.

Results: A hybrid catalyst [Rh(Triphos)(DMAD)BF4-FhuAΔCVFtev] has been developed. This novel hybrid catalyst shows activity in the hydrogenation reaction of dimethylacetylenedicarboxylate and butylacrylate which were investigated with parahydrogen-induced polarization (PHIP).

Project: IRF-A3-3 “Hybrid Catalyst for Selective Transformation of Biomass-Derived Intermediates”
Institute of Biotechnology (Prof. Ulrich Schwaneberg), Institute for Organic Chemistry (Prof. Jun Okuda)

Aim: The project is focused on the development of biohybrid catalyst systems (composed of protein backbone FhuA and a metal catalyst) for catalyzing TMFB relevant reactions from biomass-derived intermediates. The FhuA channel is re-engineered to tune the selectivity of the biohybrid catalyst.

Results: Variants with sterically demanding amino acids at four positions and second anchoring points for defined catalyst position were generated to achieve stereoselective polymerization. Diels-Alder reactions with a copper catalyst attached to FhuAΔCVFtev were investigated and published. First attempts of FhuAΔCVFtev-Ru metathesis with HAAs and cross-metathesis of olefinic double bonds derived from lignocellulosic biomass to produce intermediates for fuel production were performed.
Project  IRF-A3-4 “Rational Strain Engineering – Constructing a Hyper-Itaconic Acid Producer”
Institute of Applied Microbiology (Prof. Lars Blank)

Aim  The aim of this project is the characterization of the genetic background of itaconic acid biosynthesis in Ustilago maydis as well as the construction of an U. maydis strain for the enhanced production of itaconic acid by metabolic engineering based on characterization results.

Results  One recent achievement lies in the characterization of probable P450 monooxygenase Cyp3 and the identification of 2-hydroxyparaconate formation from itaconate catalyzed by this enzyme. Deletion of the/a? cyp3 gene led to enhanced itaconate production up to 60 g/L itaconate.

Project  IRF-A3-5 “Production of Alternative Intermediates by Microbial Whole-Cell Catalysts”
Institute of Applied Microbiology (Prof. Lars Blank)

Aim  The objective of this project is the microbial production of novel intermediates for the chemical conversion to fuels. This is achieved by modifying microorganisms using synthetic biology.

Results  Production of the two intermediates (HAA and 2,3-butandiol) was successfully carried out using recombinant Pseudomonas putida and Lactococcus lactis, respectively. In the case of HAAs, an efficient purification procedure was established. Sample material was handed over to the chemists for further conversion.
Project

IRF-A3-6 “Enzyme Engineering in Adaption to the Conditions of the Reference Process”
Institute of Technical and Macromolecular Chemistry (Prof. Regina Palkovits)

Aim

The aim of the project is the expression and immobilization of a minimal set of cellulases to enhance synergistic actions and improve recyclability of these enzymes. Our strategy also includes the production of chimeric cellulosomes by incorporation not only of different cellulases, but also of non-cellulolytic enzymes into a multicomponent complex, using high-affinity dockerin and cohesion interactions.

Results

We successfully expressed an endoglucanase, Cel5A, two exoglucanases, Cel6A and Cel7A, and a β-glucosidase Bgl1 from Trichoderma reesei in Kluyveromyces lactis. In the second approach, cellulosomal components, a chimeric tetravalent scaffold composed of modular cohesins from Clostridium spp. and dockerin-fused variants of Cel5A have been successfully expressed in Escherichia coli.
3
Summary
Activities 2015-2016

Project IRF-A4-1: “Conversion of Glucose to Methyl-THF over Polymeric Catalysts”
Institute of Technical and Macromolecular Chemistry (Prof. Walter Leitner, Prof. Jürgen Klankermayer)

Aim The synthesis of 2,5-dimethylfuran (DMF) from 5-hydroxymethylfurfural (HMF) is a highly attractive route to a renewable fuel. However, achieving high yields in this reaction is a substantial challenge. In this project, it is described how PtCo bimetallic nanoparticles with diameters of 3.6 ± 0.7 nm can solve this problem.

Results Over PtCo catalysts the conversion of HMF was 100% within 10 min and the yield to DMF reached 98% after 2 h, which substantially exceeds the best results reported in the literature. Moreover, the synthetic method can be generalized to other bimetallic nanoparticles encapsulated in hollow carbon spheres.

Project IRF-A4-2: “Computational Investigation of Hydrogen Transfer Processes”
Institute of Technical and Macromolecular Chemistry (Prof. Walter Leitner, Dr. Markus Hölscher)

Aim The focus of our investigations is on the density functional theory (DFT) guided studies of the mechanisms of hydrogen transfer reaction relevant for TMFB. Those include the hydrogenation of methyl benzoate and the conversion of CO2 to methanol.

Results In the course of our studies, a coherent understanding of the hydrogenation of CO2 to methanol was established. Based on these findings computationally new catalysts are being developed in further computational studies which – in case of the identification of more active catalysts – will subsequently be examined experimentally.
Project: IRF-A4-3 “Efficient Catalytic Processing of Hemicellulose to Sugar Alcohols and Furan-Based Commodities over Multifunctional Catalyst Systems”
Institute of Technical and Macromolecular Chemistry (Prof. Regina Palkovits)

Aim: This project focuses on the development of heterogeneous catalysts for the deoxydehydration (DODH) of biomass-based diols to valuable products.

Results: The first stable rhenium- and molybdenum-based heterogeneous DODH-catalysts were developed. The system was further improved by a broad catalyst screening and tested for different biomass-based substrates.

Project: IRF-A4-4 “Catalytic Transformation of Biomass-derived Furanics to Fuel Components”
Institute for Organic Chemistry (Prof. Jun Okuda)

Aim: The focus of the project is on the development of catalytic systems for the removal of oxygen from biomass-derived intermediates. These catalysts are based on earth-abundant and non-toxic metals to identify substitutes for rare and expensive elements used in catalytic transformations.

Results: Molybdenum complexes were developed as catalyst precursors for deoxydehydration (DODH) of vicinal diols. The insights gained were transferred to the design of molybdenum-based heterogeneous catalysts for DODH in cooperation with project IRF-A4-3.
Project: IRF-A4-5: “Heterogeneously Catalyzed Production of Biomass-Derived HMF and Its Transformations to Biofuels and Fine Chemicals”
Institute of Applied Microbiology (Prof. Miriam Agler-Rosenbaum)

Aim: Two utilizations of fructose-derived 5-hydroxymethylfurfural (HMF) are studied: Synthesis of 2,5-Dimethylfuran (DMF) as a promising biofuel and Furandicarboxylic Acid (FDCA), a monomer that can be used in polymer industry. DMF is synthesized in gasoline to yield a readily usable fuel blend, while FDCA is gained in green solvents of cyclopentyl-methyl ether or water.

Results: Quantitative hydrogenation of HMF and 98% yield of DMF were achieved in Super 95 over PtCo-bimetallic nanoparticles supported on graphitic or activated carbonaceous materials. Selective and quantitative oxidation of HMF to FDCA is shown.

Project: IRF-A4-6 “Microbially-Catalyzed Reduction of Biomass Intermediates to Tailor-Made Fuels”
Institute of Applied Microbiology (Prof. Miriam Agler-Rosenbaum)

Aim: The overall goal of this project is to identify new biocatalysts and explore the microbial reduction of the platform chemicals itaconic and levulinic acid to target compounds, with electrons or hydrogen produced at the cathode providing the necessary reducing equivalents for the microbial reaction.

Results: The uptake of the two platform chemicals was tested and four of the bacterial strains were able to metabolize itaconic acid while three of them were able to use levulinic acid. Our reactor experiments were used to identify one promising candidate that was growing while taking up the energy provided by the cathode. In a last step we want to bring both parts together and characterize the growth of our candidate in a bioreactor with the platform chemical itaconic acid as cosubstrate.
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<tr>
<th>Project</th>
<th>Aim</th>
<th>Results</th>
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<tr>
<td>IRF-A4-8 “Genetic Manipulation of Clostridium ljungdahlii for the</td>
<td>This project explores the genetic manipulation of a microbial bio-</td>
<td>The finding that Clostridium ljungdahlii needs hydrogen produced at the cathode and further improvements of the reactor set-up led to an increased overall productivity. A low pH tolerant strain produced with the new rapid whole-cell evolution tool as well as new screening methods and enzyme assays were used to identify strains that can produce target compounds out of the platform chemical itaconic acid.</td>
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<tr>
<td>Reduction of Biomass Intermediates to Tailor-made Fuels”</td>
<td>catalyst for the microbial reduction of precursor chemicals (e.g.</td>
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<tr>
<td>Institute for Applied Microbiology (Prof. Miriam Agler-Rosenbaum)</td>
<td>itaconic acid, levulinic acid) to target compounds (reduced alcohols and lactones (e.g. γ-butyrolactones and -valerolactones) with a cathode as the source for the necessary reducing equivalents for the microbial reaction.</td>
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<td>IRF-A4-9 &quot; Homogeneous Catalysts for the Selective Reduction of</td>
<td>The focus of the project is the development, understanding and</td>
<td>The development of new catalysts for the reduction of various carbonyl functionalities has been successfully accomplished. Moreover the reaction system has been further optimized based on comprehensive mechanistic investigations.</td>
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<tr>
<td>Biogenic Starting Materials.”</td>
<td>optimization of new homogeneous catalysts for the selective</td>
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<td>Institute of Technical Chemistry and Macromolecular Chemistry</td>
<td>reduction of biogenic compounds.</td>
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<td>(Prof. Jürgen Klankermayer)</td>
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Project IRF-A5-1 “Efficient recovery of key platform chemicals for production of lignocellulose-based biofuels”
Institute of Technical and Macromolecular Chemistry, Max Planck Institut für Kohlenforschung (Prof. Regina Palkovits, Prof. Marcel Liauw)

Aim The project aims at the elaboration of catalytic processes for production of biomass-based compounds. The main focus is placed on process design to enable chemo- and bio-catalytic valorization of biomass associated with the efficient recovery of the products.

Results Methods for recovery of HMF and itaconic acid out of aqueous solutions by means of liquid-liquid extraction and adsorption, respectively, were proposed. A process for isomerization of glucose into fructose combining chemo-catalysis and product recovery using an anionic extraction was developed.

Project IRF-A5-2 “Identification of Reaction Kinetics for Process Design”
Aachen Chemical Engineering – Process Systems Engineering (Prof. Alexander Mitsos), Institute of Technical and Macromolecular Chemistry (Prof. Walter Leitner)

Aim The project aims at identifying kinetics of biphasic chemical reactions relevant to the TMFB cluster using Model-based Experimental Analysis methodology. Due to the challenges in identifying reliable reaction kinetics, the development of a new methodology that links reaction identification with conceptual design could result in a more precise reactor design.

Results The hydrogenation of methyl benzoate was successfully modeled allowing the comparison between experimental and theoretical parameter values. First steps on the integration of model identification and conceptual process design were addressed, in which information from process optimization is integrated into optimal experimental design for parameter precision via the formulation of a tri-level optimization problem.
Project: IRF-A5-3 "One Reactor Approach for Direct Platform Chemical Production from Cellulose Combining Mixed-culture Fermentation and Product Extraction"
Aachen Chemical Engineering – Biochemical Engineering (Prof. Jochen Büchs), Chemical Process Engineering (Prof. Matthias Wessling), Microbial Electrocatalysis (Prof. Miriam Agler-Rosenbaum)

Aim
The main goal of the project is the conversion of plant biomass to itaconic acid using a co-culture of two organisms in one reactor approach. The first organism produces cellulolytic enzymes and degrades cellulose to glucose, the second one converts the monosaccharides to itaconic acid.

Results
A new method has been developed that allows an online evaluation of cellulose digestibility by T. reesei Rut-C30 in complex and non-complex fermentation media. Furthermore, new concepts (freeze assay) were set up to screen cellulase producers for consolidated bioprocessing applications. Additionally, fluorescence-tagged T. reesei and A. terreus strains were designed that help to establish a mixed-culture system by assessing the mixed-culture population dynamics.

Aachen Chemical Engineering – Fluid Process Engineering (Prof. Andreas Jupke)

Aim
Objective of this project is the development and investigation of new extraction processes for biotechnologically-produced fuel intermediates. A new method for model-based design of centrifugal extractors is to be developed, supported by experimental investigations of liquid-liquid separation in the centrifugal force field.

Results
A novel downstream process for the biotechnological production of itaconic acid by fermentation via in-situ reactive extraction, back extraction and final pH-shift crystallization was investigated in detail to increase space-time yield and minimize energy demand. Liquid-liquid separation in the centrifugal force field was investigated by single-drop as well as droplet-swarm sedimentation and coalescence behavior experiments. For this purpose, new laboratory equipment was successfully developed.
Project

IRF-A6-3 “Continuous SSF (Simultaneous Saccharification and Fermentation) Process with in-situ Downstream Processing”
Aachen Chemical Engineering – Biochemical Engineering (Prof. Jochen Büchs)

Aim
The aim of the project is the biochemical production of platform chemicals. To integrate the fermentation processes in the fuel production chain, utilization of wood hydrolysates as substrates and in-situ product recovery are investigated.

Results
In-situ reactive extraction of itaconic acid was realized and used to design an integrated process of itaconic acid production, isolation and crystallization. Using low field NMR spectroscopy, online monitoring of itaconic acid production has been established and a computational tool has been developed to minimize the energy demand of fermentation.
Project IRF-A6-5 “Organic Acid-Catalyzed Fractionation of Lignocellulose”
Institute of Technical and Macromolecular Chemistry (Prof. Walter Leitner),

Aim Lignocellulosic biomass is pulped and fractionated with the completely biobased biphasic OrganoCat process. In this process, the lower aqueous reaction phase selectively hydrolyzes hemicellulose, using oxalic acid as catalyst while lignin is extracted in-situ into the upper 2-MTHF phase. The process is designed and optimized by use of a holistic approach, including diversity of plants, fractionation, and downstreaming.

Results The OrganoCat process was successfully adapted to different perennial plant biomasses, showing correlations between cell-wall composition and recalcitrance, caused by different composition of the cell-wall structure. Process conditions have been further optimized to enhance downstreaming and the process was scaled up to 20 L reactor volume.

Project IRF-A6-6 “Catalysts for Dehydration of D-Glucose”
Institute of Technical and Macromolecular Chemistry (Prof. Walter Leitner), Max-Planck-Institut für Kohlenforschung (Dr. Nils Theyssen),

Aim One objective is the evaluation of the performance of sulfonated graphene oxide in the dehydration of glucose to levulinic acid (investigated by Nesrine Said). Another focus is on obtaining furanic sugars from glucose via zeolite-catalyzed glucose isomerization and on their conversion to biogenic platform chemicals (investigated by Fabian Pienkoß).

Results It has been proved that the application of solid catalysts functionalized with sulfonic acid entities is – contrary to the results reported in literature – not a promising alternative to sulfuric acid which is applied in the biofine process. Moreover, isomerization of glucose into methylfructosides has been shown to be possible. These can be extracted from unreacted glucose by 2-Me-THF and further transformed into HMF.
Project: IRF-A6-7 “Catalytic Systems for the Selective Transformation of Levulinic Acid to MTHF”
Institute of Technical and Macromolecular Chemistry
(Prof. Walter Leitner, Prof. Marcel Liauw)

Aim: The Piancatelli rearrangement of furfuryl alcohol to 4-hydroxycyclopent-2-enone was investigated as a representative biomass valorization reaction. Two different methodologies were tested for the continuously operated reaction, the self-optimization of the reaction with a simplex algorithm and integrated kinetic investigation of sample points as well as an automated reactor set-up for sampling to generate additional kinetic data.

Results: An automatically processed self-optimization of the Piancatelli rearrangement of furfuryl alcohol was performed in a continuously operated reactor. Subsequently, the kinetics of the reaction was investigated thoroughly and the reactor system was scaled up.

Project: IRF-A6-8 “Integrated Organic Acid Recovery From Fermentation Broth by Means of Electrochemical Membrane Processes”
Aachen Chemical Engineering – Chemical Process Engineering
(Prof. Matthias Wessling)

Aim: Electromembrane processes can be used to downstream process fermentation broths with ionic components. The project aims to understand the basic physical principles of electromembrane separation tasks driven by pressure gradients or electric field gradients.

Results: A complete software framework called EnPEn was developed and validated with regard to steady-state and dynamic processes in reactive, multilayered systems under direct current and alternating current. Unprecedented possibilities were demonstrated by simulating complex layered systems and impedance spectroscopy in multi-ionic solutions.
### Summary

#### Activities 2015-2016

**Project**

IRF-A6-9  "Holistic Design of Biofuel Separations"
Institute of Technical Thermodynamics (Prof. André Bardow)

**Aim**

This project is aimed at developing a fast and reliable method for the integrated design of solvents and processes leading to the efficient production of biofuels. The key challenge is to establish a close link between sound predictive thermodynamics and fast and robust process models.

**Results**

An integrated solvent and process design tool has been developed that allows to evaluate several thousands of designer solvents based on their process performance. With this tool, novel extraction solvents have been designed, e.g. for the production of the bio-based platform chemical γ-valerolactone.

**Project**

IRF-A6-10  "Investigation on Mechanisms of 2-methylfuran Synthesis as Basis for Equipment and Process Design"
Institute of Technical and Macromolecular Chemistry (Prof. Marcel Liauw)
Aachen Chemical Engineering - Fluid Process Engineering (Prof. Jürgen Klankermayer)
Aachen Chemical Engineering - Process Systems Engineering (Prof. Andreas Jupke, Prof. Alexander Mitsos)

**Aim**

In this project, an enhanced overall process strategy should be developed to maximize the yield of 2-methylfuran (2-MF), which, for the current process configuration, is about just 60%. This includes development of advanced process analytics based on in-situ Raman- and infrared spectroscopy, rigorous process modeling and model-based design of process equipment, such as tailored multiphase reactors.

**Results**

The new lab-scale reactor has been commissioned and experiments with HI catalyzed fructose dehydration were successfully conducted. Further experiments focus on determination of biphasic reaction kinetics and humin characterization.
 Integrated Research Field B: From Biofuels to Propulsion

// Prof. Dr.-Ing. Heinz Pitsch
// Institute for Combustion Technology
// h.pitsch@itv.rwth-aachen.de

// Vision
Custom-made bio-derived fuels can be tailored to specific engine needs and allow more opportunities in the design of new combustion systems. Therefore, fuel structure and combustion systems have to be jointly optimized with respect to chemical kinetics, mixture preparation, and the integrated system. To facilitate this optimization process, IRF-B is divided into three subgroups. In the chemical kinetics subgroup IRF-B1, fundamental combustion parameters of new biofuels are characterized. Detailed kinetic models for ignition, flame speed, and emission chemistry are developed. IRF-B2 focuses on the aspects of fuel injection, mixing, and their effect on the combustion process. In IRF-B3, specific fuel candidates are evaluated from a system perspective in system scale facilities and test engines regarding their emission behavior, their tribology properties, and effects on exhaust gas aftertreatment.

Figure 3.13: Structure of IRF-B “From Biofuels to Propulsion”
// Main Results
Ketones have been identified as promising SI engine fuel candidates within the first part of the second TMFB funding period due to their high knock-resistance. Within the second part, a principal focus has been on 2-butanone. Reaction chemistry has been investigated experimentally and numerically, highlighting the importance of low-temperature oxidation for correctly predicting ignition events. Spray chamber and full engine experiments showed better mixture formation and pre-ignition resistance compared to ethanol and thus proving the suitability of 2-butanone as gasoline fuel. While previous studies of n-octanol and DnBE already indicated their potential as diesel fuels, greater emphasis was placed on combining the individual advantages via blending these two components. Different blending ratios have been investigated, showing non-linear behavior in efficiency and soot emissions. In fact, the overall performance could be improved significantly, with the 50/50 blend showing the best trade-off.
Vision
The combustion kinetics research domain IRF-B1 is concerned with two major tasks. The first is to establish detailed descriptions of the chemical kinetic processes and to investigate the impact of the fuel structure on combustion behavior and pollutant formation. One focus is on studying large numbers of biofuels containing the functional groups of interest, especially with relevance to new, including lignin-derived fuel compounds and fuel blends. The second task is the development of detailed and reduced chemical kinetic schemes that will be used in computational fluid dynamic (CFD) simulations, especially needed for combustion system design within the Fuel Injection and Combustion System research domain (IRF-B3).

Main Results Summary
Accurate detailed chemical mechanisms were developed for the oxidation of a set of novel biofuels including butanone and 2-butyltetrahydrofuran (2-BTHF), assisted by computational ab-initio calculations of bond-dissociation energy and chemical kinetic rate data of elementary reactions. Experimental investigations of these fuels were performed in a shock tube, a rapid compression machine, and a spherical combustion vessel. The derived chemical models were validated successfully against the obtained experimental data. In addition, a comparison of the novel biofuels, 2-butyltetrahydrofuran (2BTHF), di-n-butylether (DnBE), and n-octanol, which have the same elementary composition (C8H18O) but different molecular structures, was conducted to analyze the impact of fuel structure and functional groups on fuel combustion behavior.

Results
The main objectives of the research domain IRF-B1 are to provide experimental and numerical data and the theory of chemical processes of auto-ignition, fuel oxidation, and pollutant formation with respect to novel biofuels and biofuel blends. Further, within IRF-B1, appropriate detailed and reduced chemical kinetic mechanisms are developed, which are required for CFD simulations.

Butanone
Experimental data for butanone have been reported. The ignition-delay times were determined by using a shock tube and a rapid compression machine and the laminar burning velocities were measured in a spherical constant-volume combustion vessel. These
experiments form the foundation for the validation of the newly developed detailed chemical kinetic model for butanone and importantly, span conditions akin to practical combustors. What is unique to this butanone model is the inclusion of detailed reaction pathways for the low-temperature oxidation of butanone and the incorporation of quantum calculations for the thermodynamic properties of butanone and its related low-temperature oxidation species. Butanone shows no evidence of negative temperature coefficient behavior. However, inclusion of the low-temperature oxidation pathways is shown to be important to accurately predict the low-temperature ignition-delay times of butanone. Of particular importance are the radical β-scission and HO2-elimination reactions, which are essential in accurately predicting the ignition-delay times.

Figure 3.14: Experimental (symbols) and numerical (lines) laminar burning velocities of butanone

// 2-Butyltetrahydrofuran

The novel lignocellulosic biofuel 2-butyltetrahydrofuran was investigated experimentally and numerically. Laminar burning velocities were measured in a combustion vessel. Ignition-delay times were experimentally determined in a rapid compression machine and in a shock tube at high pressures covering a wide temperature range. A detailed chemical kinetic mechanism is proposed to describe the oxidation of 2-BTHF at both low and high temperatures. It could be demonstrated that the model gives satisfactory results for the various experimental configurations. A comparison of ignition-delay times between 2-BTHF and other C8 fuels including n-octane, n-octanol, and DnBE was conducted. The linear ether functional group strongly enhances the fuel ig-
nition propensity over the entire temperature range, while the existence of an alcohol functional group in the molecular structure inhibits the oxidation reactivity compared to the normal alkane with identical carbon number. For 2-BTHF, the lower C-H BDEs of ring carbons lead to quick H-atom abstractions from the fuel and consequently to an enhanced ignition propensity at high temperatures compared with n-octane. In the low temperature range, the lower energy barriers promote the ring-opening reactions for α-fuel radicals and thus inhibit the chain-branching channels as well as the fuel reactivity.

![Figure 3.15: Numerical ignition delay times of C8 fuels at 20 bar and φ = 1.0](image)

// Soot measurements
After the successful construction and validation of the counterflow burner setup in the last research period, this configuration has been further extended. Laser measurement techniques were applied to measure soot volume fraction (SVF) quantitatively. As soot formation is a rate limited process, detailed studies of the dependence of soot emission on strain rate, as a measure for molecule residence time, have been performed for gaseous as well as conventional petroleum fuels and their blends with bio-fuels. While the computed SVF are in good agreement with the experimental results for ethylene flames, the differences between experimental and computed data for all liquid fuels indicate a high need for further soot model development.
// CFD application
In the previous research period, detailed models for n-octanol and DnBE were derived. In this research phase, the detailed models were successfully reduced and further applied in CFD engine simulations to study the behavior of these fuels in diesel engine combustion.
Integrated Research Field B2: Fuel Spray, Flow and Mixing

// Prof. Dr.-Ing. Wolfgang Schröder
// Institute of Aerodynamics
// office@aia.rwth-aachen.de

// Vision
The impact of the composition of novel biofuels on spray penetration, evaporation, mixing and the overall effect on ignition delay and pollutant formation under engine conditions is being analyzed in detail in the fuel, spray, flow and mixing research domains. Furthermore, a quantitative description of fuel structure and fuel performance with respect to the aforementioned processes will be given. In order to thoroughly understand the flow physics of the novel biofuels, highly resolved experimental and numerical analyses are a must. Besides an analysis of local flow phenomena, the results of the investigations will be used to determine the complete highly intricate three-dimensional flow structure.

// Main Results Summary
The comparison of the experimental findings in a constant pressure vessel and in a combustion chamber showed the impact of the outer flow field on the vertical penetration and the half-cone angle of the injected fuel. Furthermore, 2-butanone has been proven to have superior spray propagation properties. Transmitted light microscopy resulted in an almost fuel-blend independent jet angle. The jet cross section and surface geometry depend on the fuel properties. The numerical analysis of the influence of the fuel properties on droplet size yielded smaller droplets at higher Reynolds numbers and show the impact of cavitation on the nozzle exit velocity distribution. A newly developed vapor-liquid equilibrium apparatus allows lowering the measurement time. TMFB-related data were collected for various mixtures. Using spectroscopic laser measurements showed for several operating conditions of, e.g. di-n-butylether, that unlike the expected flame-surface concentrated distribution the NO-profile over the flame is nearly flat.

// Results
High-speed stereoscopic particle-image velocimetry (PIV) measurements were performed in IRF-B2-1 to show the interaction between directly injected ethanol and the flow in the combustion chamber. Fuel injection has a stabilizing effect on the flow field and influences the large-scale flow structures, e.g. the out-of-plane vorticity and the trajectory of the tumble vortex. Furthermore, Mie-scattering imaging measurements were conducted to analyze the influence of the engine flow field on the spray propagation of hollow-cone sprays. In collaboration with IRF-B2-5, the measurements illustrated in Fig.
3.16 were compared to spray measurements inside a constant-flow pressure vessel with negligible air flow to further evaluate the impact of the flow field and to determine the suitability of tailor-made fuels. The experimental results evidenced that for spray mixing 2-butanone is a superior surrogate for ethanol and gasoline.

In the unstructured hierarchical cut-cell method multiphase flows in IRF-B2-2, primary and secondary break-up models are implemented. The primary break-up is modeled either by a Rosin-Rammler distribution or a blob method. The secondary break-up is modeled either by the Kelvin-Helmholtz-Rayleigh-Taylor (KHRT) or the TAB method. The KHRT method combines the Rayleigh-Taylor break-up and the Kelvin-Helmholtz break-up. In the TAB method, break-up occurs by definition as soon as a critical distortion is reached.

![Figure 3.16: Vertical penetration (row 1) and half cone angle (row 2) of Ethanol and 2-Butanone at varying ambient pressure.](image)

A high-fidelity simulation method for predictive injector simulations with a focus on penetration length and droplet size distributions was developed in IRF-B2-3. Multi-scale coupling was investigated to reduce computing cost and to capture effects such as cavitation, hydraulic flip, or turbulence considering real injector geometries. New models for cavitation and hydraulic flip were derived and efficient coupling methods for transfer-
ring information between Eulerian and Lagrangian description have been implemented. This framework was applied to TMFB fuels and validated by experiments (see Figure 3.17). The influence of fuel properties on the formation of ligaments and droplets on the one hand and resulting droplet size distributions on the other was studied. It was found that smaller droplet sizes occurred with increasing Reynolds numbers, and that cavitation and hydraulic flip significantly influence the velocity profile close to the nozzle exit. Most recent computations of 1-octanol, DnBE and 2-butanone showed similar trends in spray characteristics.

The in-cylinder mixture formation was experimentally investigated in IFR-B2-4. Fuel influences were studied using transmitted light microscopy (TLM) and laser correlation velocimetry (LCV). Promising fuel blends of DnBE/1-octanol were investigated in detail. The TLM-results show a jet core angle that is almost independent of the fuel blend, a star-like cross-section area of the jet and periodic ripple structures on the jet surface that are caused by the nozzle flow and thus depend on fuel properties. LCV measurements revealed a fuel-dependent nozzle flow with higher velocity for lower fuel viscosity.

Figure 3.17: Comparison of computational and experimental results.
In IRF-B2-5, spray propagation and mixture formation of TMFB fuels on a macroscopic scale as well as droplet evaporation on a microscopic scale are measured. On a macroscopic scale, blends of DnBE and 1-octanol were studied under diesel-like conditions. Spray characteristics were found to linearly scale with blending. Moreover, spray characteristics of 2-butanone were found to outperform those of ethanol under gasoline conditions. The smaller 2-butanone droplets are more easily transported by ambient gas flow and thus contribute to an enhanced in-cylinder mixture formation. For micro-droplet investigations, a new “pulsed 2-color laser-induced-fluorescence with MDR-enhanced energy transfer” method was developed.

Vapor-liquid equilibrium (VLE) data are important to assess novel biofuels for combustion. To overcome the limits of commercial equipment, a novel VLE measurement apparatus was designed and validated in IRF-B2-6. Due to its smaller system size, equilibration is accelerated, which leads to faster experiments. Phase compositions are analyzed non-invasively by Raman spectroscopy, resulting in significantly shorter analysis times. VLE data were collected for mixtures of interest such as 1-octanol/DNBE for cooperating TMFB projects studying process design and combustion behavior.

In IRF-B2-7 spectroscopic laser measurements were simultaneously performed with shadowgraphy and OH*-chemiluminescence measurements in a high pressure and temperature vessel. The measurements were conducted for n-heptane, di-n-butylether, n-dodecane and various fuel blends. The postprocessing of the NO-signals was performed for di-n-butylether. The distribution of NO through the flame is nearly a flat profile for all operating conditions. This is the first time that this distribution is observed for diesel flames.
Vision
The work of this research domain is dedicated to the energy conversion from chemical to mechanical energy on the system scale with a main focus on efficiency and emission characteristics. The vision of IRF-B3 is to develop a combustion system consisting of both the engine hardware and the fuel. Besides focusing on completely new combustion systems as Reactivity Controlled Compression Ignition (RCCI) with in-cylinder fuel blending, a further goal lies in the advancement of the conventional combustion system which includes adjusting the injection strategy and piston bowl design. Since the engine hardware for the optimal combustion process is highly dependent on fuel characteristics, this is an iterative optimization process that requires high interaction with the CIF in order to feed back the fuel characteristics desired for the optimal combustion system. Overall, the combustion system is to feature very high fuel efficiency with lowest engine-out emissions. However, to ensure an almost zero-emission vehicle, the exhaust gas aftertreatment system has to be optimized for the newly derived fuels as well.

Main Results Summary
The major work since the last status report was the deeper investigation of the new fuel candidates 1-octanol and 2-butanone. On the spark ignition side the compression ratio could be further increased to 14.7, which led to an indicated efficiency of 42.6 % for 2-butanone without any knock limitations. Additionally, pre-ignition measurements were conducted since abnormal combustion phenomena will be of utmost importance for future highly boosted gasoline engines. Here 2-butanone shows the highest resistance to glow plug induced pre-ignitions as well as free pre-ignitions of all investigated fuels. For the compression ignition engine, blends of 1-octanol with diesel were investigated and a strongly non-linear soot-reduction potential was observed where small quantities of 1-octanol led to a great soot reduction. To take the investigations a step further towards application, vehicle tests on a dynamometer were performed with the blends. Here a high soot reduction was observed alongside an engine-out soot reduction of over 90 % during NEDC with a 50 % 1-octanol blend.
Results

IRF-B3 focuses on the application of newly derived fuels in engines. For this purpose, the combustion in engines as well as the fuel injection system and the exhaust gas composition and its aftertreatment are investigated. Within IRF-B3, the main focus has been on 1-octanol, di-n-butyl ether and diesel-blends for compression ignition (CI) engines, and 2-butanone and 2-methylfuran for spark-ignited (SI) engines.

Regarding the fuel injection system, the tribological contacts of high-pressure pumps have been optimized for low-viscosity biofuels by elasto-hydrodynamic simulations and it was found that a hollow cone piston design led to lowest friction and leakage losses. Additionally, the high-pressure test-rig was redesigned to enable measurements of rheological characteristics of fluids at pressure levels up to 7500 bar in a temperature range from -20 to +120 °C. An increase in pressure and temperature range resulted in a wider range of viscosity values. In order to measure the extended range, a new falling body viscometer was designed and optimized by CFD simulations.

Figure 3.18: Equivalence ratio image sequence of gas phase in N2 of 1-octanol + 1.5 % TMPD for part load operation point.

For the spark ignition engine 2-methylfuran and 2-butanone were compared to RON95 E10 and ethanol as benchmark. The compression ratio was further increased from 13.5 to 14.7 for the thermodynamic measurements enabled by an increased engine stroke.
For ethanol and 2-butanone no knock restriction was observed even at highest loads and the efficiency was increased by more than 20% compared to RON95 E10. Maximum indicated efficiency was found to be 43.2% in case of ethanol, followed by 2-butanone with 42.6% and 42% for 2-methylfuran. Additionally, pre-ignition measurements were conducted at a compression ratio of 11. The engine was equipped with a glow plug to create a defined hot spot and ethanol was found to be less resistant to glow ignition than regular RON95 E10 and to lead to a drop of 25 °C of the critical glow plug temperature. The highest glow ignition resistance by far was measured with 2-butanone with a glow plug temperature of 910 °C, which is 40 °C higher compared to RON95 E10. This resistance is predominantly caused by the remarkably low chemical reactivity of 2-butanone.

With regard to diesel type fuels, an alternative low temperature combustion mode was assessed after the promising results of pure 1-octanol and DnBE in normal combustion mode. With Reactivity-Controlled Compression Ignition (RCCI), a low-reactivity and high-reactivity fuel are blended within the cylinder to achieve high efficiency and low emissions. DnBE was chosen as high reactivity fuel and 2-butanone as low-reactivity fuel. The engine results showed that indicated efficiencies of more than 45% with nearly zero NOX emissions could be achieved while virtually no soot emission could be detected. The indicated efficiency of RCCI is on average one percent higher than normal diesel combustion.

On the optical diesel engine tracer, planar laser-induced fluorescence (PLIF) measurements were performed for 1-octanol and DnBE. These measurements visualized the heavy fuel impingement of 1-octanol in part load operation. After being impinged on the wall, the fuel slowly evaporates before building quite a homogenous near-stoichiometric mixture in the peripheral regions of the bowl. For DnBE slight wall impingement was observed as well. Planar laser-induced incandescence (PLII) measurements confirmed the previous OH* chemiluminescence and soot luminosity measurement for 1-octanol. Within the measurement plane, no PLII signal can be seen for 1-octanol. DnBE in comparison to diesel fuel shows a PLII signal earlier in the cycle. For both fuels the...
PLII signal starts in the outer parts of the piston bowl and moves towards the inside and is therefore in accordance with the previous soot luminosity measurements. Unlike for DnBE, a PLII signal for diesel fuel can even be detected late in the cycle.

In order to simulate the combustion of TMFB fuels in engines, the Large-Eddy Simulation (LES) framework has been extended towards full engine simulations. The immersed boundary method, which imposes the boundary conditions of complex shaped walls on structured grids more accurately, has been integrated and validated. Additionally, ignition models for both SI and CI engines have been implemented and validated against experimental results. The dodecane spray flame configuration "Spray A" from the Engine Combustion Network (ECN) has been used for validating the spray combustion model. By using the detailed primary breakup results of IRF-B2 as initial droplet conditions, the LES model was able to predict the spray characteristics without parameter tuning in terms of spray and combustion characteristics. The spray evaporation model has been extended towards discrete multicomponent fuel blends and the fuel decomposition of DnBE and 1-octanol blends has been studied in a single-hole injector spray. The results showed strong fuel decomposition in the vicinity of the nozzle, yielding high concentrations of the more volatile di-n-butyl ether. However, further downstream, decomposition decreases rapidly due to strong turbulent mixing.
List of Projects IRF-B

| Project | IRF-B1-1 “Development of Detailed Kinetic Models for Novel Fuels Derived from Biomass”  
  | Physico-Chemical Fundamentals of Combustion (Prof. Alexander Heufer) |
|---------|------------------------------------------------------------------|
| Aim     | This project is aimed at developing detailed chemical kinetic models and computational kinetic studies on biofuel combustion using ab-initio methods to provide insight into their elementary reaction kinetics. |
| Results | A validated comprehensive detailed chemical kinetic model for 2-butanone has been published. Furthermore, rate constants for the intramolecular H-shift reactions in 3-MTHF and 2-MTHF are computed using ab-intio methods. Focusing on ketones, rate constants are determined for the hydrogen atom abstraction reactions from 2-butanone by methy hyperoxy radicals and also theoretical investigations are performed to understand kinetics of acetone combustion reactions. |

| Project | IRF-B1-2 “Experimental Determination of Ignition Delay Times in a Rapid Compression Machine”  
  | Physico-Chemical Fundamentals of Combustion (Prof. Alexander Heufer) |
|---------|------------------------------------------------------------------|
| Aim     | To assist the validation and hierarchical development of reliable chemical kinetic mechanisms of possible bio-fuel candidates/groups, a rapid compression machine (RCM) is used to provide experimental ignition delay time measurements. For further in-depth understanding of the kinetics involved in the reactions, intermediate species measurement using RCM coupled with gas chromatography and mass spectrometry is under investigation. |
| Results | Ignition delay time measurements of various fuel candidates from different bio-fuel groups such as furans, tetrahydrofurans, ketones, alcohols and ethers have been screened and studied with respect to the dependency of the ignition behavior on the molecular structure of the fuel. Ignition delay times and kinetics of 2-BTHF and 2-butanone have been studied extensively in co-operation with other groups within the IRF-B. |
Project

IRF-B1-3 “Experimental Investigation of Ignition Delay Times in a High-pressure Shock Tube”
Physico-Chemical Fundamentals of Combustion (Prof. Alexander Heufer)

Aim

The reflection of the shock wave at the closed end-wall of the shock tube led to a nearly instantaneous, homogeneous compression and temperature distribution of gaseous fuel mixtures, which makes it possible to measure ignition delay times and species time histories of novel (bio-)fuels without evaporation or flow effects. This makes the shock tube results valuable for the validation of detailed chemical kinetic models.

Results

Ignition delay times were taken for linear C3-C5 ketones, 2-butyltetrahydrofuran, 3-methyltetrahydrofuran, γ-valerolactone (GVL) and n-heptane under engine-relevant conditions. The results were used to understand the reaction networks of the considered fuels, highlighting e.g. the impact of hot β-scission to GVL combustion. Furthermore, it was found that acetone kinetics is not yet understood completely although it is widely used.

Project

IRF-B1-4 “Laminar Burning Velocities and Fundamental Exhaust Emissions of Tailor-Made Fuels – Numerical and Experimental Approach”
Institute for Combustion Technology (Prof. Heinz Pitsch)

Aim

The main objectives are to measure burning velocities and pollutant emissions, in particular the formation of nitrogen oxides, of bio-derived fuels with very little fuel in contrast to steady flame burners. In addition, chemical mechanisms representing high-temperature chemistry are validated with the results presented within this project, and 1D-modeling is used for chemical mechanism improvement.

Results

Laminar burning velocities of promising alternative fuels, e.g. 2-BTHF and butanone, were investigated experimentally under a wide range of initial conditions and in various equivalence ratios. A fundamental assessment of driving parameters related to burning velocities has been performed. Detailed models for the combustion of bio-derived fuels, such as 2-BTHF, have been developed.
### Project IRF-B1-5 “Detailed Characterization of Soot Formation Pathways of Tailor-Made Fuels Using a Counterflow Burner”

**Institute for Combustion Technology (Prof. Heinz Pitsch)**

**Aim**
The soot formation of bio-derived fuels is known to differ significantly from crude oil-based fuels, and so far the question of how bio-fuels affect the structure and chemical properties of soot has been unresolved. Therefore, experimental data of a new laminar counterflow burner are used to develop new multi-variant soot models.

**Results**
Dependence of soot formation on the strain rate has been investigated in a well-defined counterflow setup by means of laser measurement techniques for a gasoline surrogate and its blends with bio-fuels. The overall soot emission is reduced with bio-fuel addition, moreover bio-fuel blends indicate a stronger soot reduction with increasing strain rate.

### Project IRF-B1-6 “Ab-initio Elementary Reaction Kinetics”

**Institute of Technical Thermodynamics, Model-Based Fuel Design (Prof. Kai Leonhard)**

**Aim**
To obtain rate constants for reactions proven to be significant by our cooperation partners or known to be important from the literature, this project combines quantum chemical ab-initio methods with transition state theory. With reactive molecular dynamics simulations, it has even become possible to identify unknown reaction pathways.

**Results**
A tool for the automatic mechanism derivation from reactive molecular dynamics simulations has been developed and tested for methane. For the bio-fuel candidate 2-butanone, hydrogen abstraction and beta-scission rate constants have been calculated quantum mechanically.
### Project IRF-B2-1 “Experimental Analysis of Turbulent Mixing of Tailor-Made Fuels in Internal Combustion Engines”
Institute of Aerodynamics (Prof. Wolfgang Schröder)

**Aim**
Experimental investigation of the in-cylinder flow field of a four-valve internal combustion engine is conducted to estimate the suitability of novel tailor-made fuels for low-temperature combustion. The knowledge of the characteristic structures of the flow field is used to analyze the mixing process during the intake and compression stroke.

**Results**
Investigation of the interaction between direct fuel injection and the engine flow field displays an influence of the injection on the large-scale flow structures and a stabilizing effect on the flow field. A comparison of the macroscopic spray behavior inside the combustion chamber and a pressure chamber has revealed, from a mixture point of view, 2-butanone to be a superior fuel compared to ethanol and gasoline.

### Project IRF-B2-2 “Simulation of Spray Formation and Turbulent Mixing of Tailor-Made Fuels in Internal Combustion Engines”
Institute of Aerodynamics (Prof. Wolfgang Schröder)

**Aim**
This project is aimed at the thorough numerical investigation of the turbulent in-cylinder flow and mixing behavior of tailor-made fuels from biomass using large-eddy simulation. To achieve this goal, the Cartesian cut-cell based flow solver for large-eddy simulation of compressible flows is extended by a spray model.

**Results**
The flow solver has successfully been extended with a Lagrangian-based spray model and extended to handle multiple species. Furthermore, the multiple level set method has been improved to allow for higher accuracy.
### Project

**IRF-B2-3 “DNS of Primary Atomization and Evaporation of Multi-Component Liquid Jets”**  
Institute for Combustion Technology (Prof. Heinz Pitsch)

**Aim**  
The objective of this project is to use direct numerical simulation to further investigate the fundamental physics of the primary breakup of liquid jets into sprays, in order to develop a detailed atomization model for the large-eddy simulation of spray-combustion.

**Results**  
Multi-scale coupling has been investigated to reduce computing costs and capture all relevant physical effects such as cavitation, hydraulic flip or turbulence, considering real injector geometries. Consequently, new models for cavitation and hydraulic flip have been derived and efficient coupling methods for transferring information between Eulerian and Lagrangian description have been implemented. The resulting framework has been used to compute the spray characteristics of TMFB fuels.

### Project

**IRF-B2-4 “Fundamental Investigation of Fuel Spray Atomization”**  
Institute of Heat and Mass Transfer (Prof. Reinhold Kneer)

**Aim**  
This subproject investigates the influence of fuel on primary breakup, which is responsible for spray formation, and thus, overall mixture formation. New measurement techniques are developed or improved with regard to the region of interest close to the nozzle outlet, such as double-pulsed transmitted light microscopy (TLM) and laser correlation velocimetry (LCV).

**Results**  
After the optimization of the developed measurement techniques and the installation of a new constant-pressure flow microscopy chamber, different fuel-blends were investigated with regard to the primary spray breakup. Several findings were made: the spray’s jet core angle is independent of the fuel; the jet core cross-sectional area has a star-like shape and furthermore, periodic ripples develop on the jet surface as a function of fuel-dependent nozzle flow.
Institute of Heat and Mass Transfer (Prof. Reinhold Kneer)

Aim
This subproject deals with the influence of TMFB-fuels on spray propagation and mixture formation under engine-relevant conditions, whereas the focus of work lies on the field of evaporation. Microscopic and macroscopic investigations are carried out using various methods, such as high-speed visualization, Schlieren, PDA and 2cLIF-EET.

Results
Spray propagation and mixture formation of DnBE and 1-octanol fuel blends were found to be excellent for application in diesel engines, whereas 2-butane spray breakup outmatches ethanol under gasoline-like conditions. Moreover, a new temperature measurement technique for microscopic droplets and sprays has finally been established, called "pulsed 2D-2-color laser-induced fluorescence with MDR-enhanced energy transfer" (pulsed 2D-2cLIF-EET).

Institute of Technical Thermodynamics (Prof. André Bardow)

Aim
The objective of this project is to support spray and combustion modeling by providing deeper and quantitative knowledge of the evaporation of novel multi-component biofuel blends. Furthermore, vapor-liquid equilibrium data are collected for process-design purposes.

Results
A milliliter-scale setup for the efficient characterization of isothermal vapor-liquid equilibria using Raman spectroscopy was designed and validated. This novel setup allows the use of small amounts of substance and accelerates phase equilibrium measurements to enable the screening of novel biofuel blends within TMFB.
### Project
**IRF-B2-7 “Steady-State Investigation of TMFB Fuel Mixture Formation and Combustion Processes”**  
Institute for Combustion Engines (Prof. Stefan Pischinger)

#### Aim
The major aim of this project is the optical characterization of fuel-dependent properties like liquid-spray penetration, evaporation, mixture formation, physio-chemical ignition delay, combustion behavior and initial pollutant formation at part- and full-load-related boundary conditions. The investigations take place in a continuously scavenged high-pressure chamber up to Ta=1000K and pa=145bar.

#### Results
The quantitative NO measurements in the core of diesel-like jets were done by means of NO laser-induced fluorescence (LIF). The required quantification made measurements of temperature, CO mole fraction and light attenuation necessary, which were done by spontaneous Raman scattering (SRS) measurements.

### Project
**IRF-B3-1 “Tribological Contact Analysis in Injection Systems Focusing on Low-Viscosity Biofuels and Blends”**  
Institute for Fluid Power Drives and Controls (Prof. Hubertus Murrenhoff)

#### Aim
The focus of this project lies on investigating the tribological contacts inside a common-rail pump and optimizing them in order to achieve higher pump efficiency. Additionally, high-pressure rheology is further developed with a newly designed high-performance viscometer.

#### Results
Adaptions of tribological contacts have been completed by simulating various geometries, showing promising reductions in solid friction and leakage. Additionally, the efficiency of TMFBs has been investigated and measured on a pump test rig, and relevant fluid characteristics have been determined on a corresponding test rig.
Project IRF-B3-2 “Large-Eddy Simulation of Internal Combustion Engines Based on Fine-Scale Mixing and Detailed Combustion Chemistry of Novel Fuels” Institute for Combustion Technology (Prof. Heinz Pitsch)

Aim The aim of this project is the development of an accurate and efficient simulation framework based on the large-eddy simulation (LES) approach using high-order numerical methods. The model is used for analyzing and understanding the in-cylinder combustion process of novel fuel candidates and their blends.

Results Combustion models for both CI and SI engine combustion modes have been developed and validated against combustion vessel experiments. Additionally, the effect of different fuel evaporation properties have been studied for high-pressure di- n-butyl ether / n-octanol sprays using a multicomponent evaporation model. At constant primary break-up conditions, the liquid penetration length was only affected marginally and strong fuel decomposition has been observed for the fuel blends in the vicinity of the nozzle orifice.

Project IRF-B3-3 “Cycle-Resolved Multi-Parameter Laser Diagnostics Under Real-Engine Conditions for TMFs” Institute of Technical Thermodynamics (Prof. André Bardow), Research Group Laser Diagnostics in Thermofluidodynamics (Prof. Gerd Grünefeld)

Aim In this project, the structure of diesel-like combusting TMF jets is investigated experimentally by using optical diagnostics under engine-like conditions in the high-pressure vessel at the Fuel Design Center (FDC). In particular, spatially resolved temperature and multi-species measurements are conducted by spontaneous Raman scattering and LIF.

Results The feasibility of quantitative temperature, CO mole fraction, and light attenuation measurements by Raman scattering has been demonstrated in non-sooting TMF jets. This leads to quantification of LIF from NO and a new conceptual model of TMF combustion under diesel-like conditions.
| Project | IRF-B3-4 “Optical Investigation of TMFB Fuel Mixture Formation and Combustion Processes Under Motored and Fired Operation Conditions”  
Institute for Combustion Engines (Prof. Stefan Pischinger) |
<table>
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<tbody>
<tr>
<td>Aim</td>
<td>The optical investigations at the transparent single-cylinder diesel engine are the experimental link between the steady-state high-pressure chamber (IRF-B2-7) and the thermodynamic single-cylinder diesel engine (IRF-B3-5) experiments. The purpose of this project is the understanding and optimization of fuel-dependent in-cylinder processes like mixture formation, ignition, combustion, and soot formation at transient boundary conditions and application-relevant operation points.</td>
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<tr>
<td>Results</td>
<td>Analysis of the mixture formation with PLIF showed significant spray wall impingement for 1-octanol, which explains higher HC emissions compared to e.g. DNBE observed in the SCE investigation (IRF-B3-5). Studies of the hot and cold soot formation for DNBE showed less soot being formed during combustion compared to diesel fuel, pointing at soot formation being inhibited by a bound oxygen atom.</td>
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Project IRF-B3-5 “Advanced Combustion Systems for Tailor-Made Biofuels”
Institute for Combustion Engines (Prof. Stefan Pischinger)

Aim The aim of the project is to assess the thermodynamic potential of the novel biofuels and biofuel blends. Furthermore, new combustion processes are explored and the combustion system will be optimized for these fuels.

Results In previous investigations using 2-butanone, a remarkable efficiency increase had been observed compared to RON95 fuel. Pre-ignition measurements were conducted and it was found that the critical glow plug temperature of 2-butanone at 2% pre-ignition probability is 40°C higher compared to RON95. For the compression ignition engine, the reactivity-controlled compression ignition (RCCI) was investigated using DnBE and 2-butanone as high- and low-reactivity fuels. Efficiencies above 45% and ultra-low emissions were achieved.

Project IRF-B3-6 “Formation and Aftertreatment of Regulated and Non-Regulated Pollutant Emissions with Tailor-Made Fuels”
Institute for Combustion Engines (Prof. Stefan Pischinger), Institute of Inorganic Chemistry (Prof. Ulrich Simon)

Aim The impact on the exhaust-gas emissions will be analyzed by means of gas chromatography-mass spectroscopy of exhaust-gas samples from the SI and CI single-cylinder engines (IRF-B3-5) and the impact on the performance of the exhaust aftertreatment system is investigated at the laboratory gas test bench. The aim is the identification of fuels with low harmful exhaust-gas emissions as well as good conversion rates in the exhaust-gas aftertreatment system.

Results While the combustion of TMFB fuels decreases the HC emissions in both spark and compression ignition engines, species similar to those resulting from combustion of similar fuels – except for unburned fuel – were found in the HC emission, but with changing shares. In both cases the quantification showed decreasing amounts of aromatics like the carcinogenic benzene. First investigations at the laboratory gas test bench showed a storage capability at low temperatures for some species like alcohols, which is helpful to decrease HC emissions during cold start.
The vision of the Core Interaction Field (CIF) and at the same time the overall goal of the Cluster of Excellence is the definition and the establishment of the Fuel Design Process as an interdisciplinary tool to derive optimized, tailor-made fuels. The major challenge here is that an optimized fuel is not only characterized by an efficient and clean combustion but also by an energy-efficient and sustainable synthesis from biomass. Therefore, chemistry, biology and biotechnology as well as mechanical engineering have teamed up to find the overall optimum fuel with regard to life-cycle emissions and greenhouse warming potential. As the disciplines involved in the Fuel Design are multifaceted and work on different scales, model-based tools have to be developed in order to enhance the communication and exchange of data and results and finally enable the development of the envisaged, interdisciplinary Fuel Design Process. Since TMFB also wants to address societal effects more detailed in the future, the methodological scope will be significantly expanded by the integration of a systems-wide perspective. A holistic system perspective on fuel design is taken covering process design, society, policy, eco-sphere and technosphere.
Main Results

The model development within the CIF has evolved enormously since the last status update in 2012/2014. The model-based identification of possible fuel components by data-driven methods like QSPR was enhanced, and also new characteristic fuel numbers like the Oxidation Potential Number (OPN) were derived. In parallel, the description and fast evaluation of the production pathways of these fuel components were improved by introducing a novel methodology, called "Process Network Flux Analysis", which analyzes the process performance of biorefinery pathways already at early-stage. Both will be described more detailed in the following.

Strongly related to the model improvement was the build-up of fast screening methods which allows the calibration of the data-driven fuel design tools. Here, all relevant fields, ranging from tribological characteristics via combustion and ignition properties up to eco- and humantoxicology, were actively promoted. By today, we have an increased number of both experimental and simulative tools available to continue the evolution of the Fuel Design Process.
Core Interaction Field 1: Performance Indicators for Biofuel Production

// Prof. Dr. rer. nat. Jürgen Klankermayer
// Mechanisms in Catalysis
// jklankermayer@itmc.rwth-aachen.de

// Vision
The overall goal of the research domain CIF-1 is the exploration of novel synthetic pathways and a comprehensive evaluation of novel TMFB production routes from biomass to biofuel. Within this approach, a focus is set on the assessment of catalyst and process alternatives, based on established sustainability criteria. This methodology will provide the basis for the ranking of the diverse pathways, using a distinct set of defined performance indicators as well as the identification of key parameters for reaction pathway optimization. The application feedback of the CIF-1 evaluation in IRF-A, on selected reactions and unit operations, will be comprehensively collected and steadily updated to form the base for an optimized analysis and benchmarking. For promising candidates, the level of analysis will be increased step by step and detailed process designs as well as life-cycle analysis will be provided in order to guide the fuel design process.

// Main Results Summary
The investigations within the Cluster of Excellence enabled to directly consider fuel characteristics and process performance in catalyst development and pathway strategy. This unique approach within CIF-1 correlated the respective research domains and paved the way to novel fuel structures via tailored catalysts systems, integrating process design and energy requirements. Based on this approach, unprecedented fuel structures and pathways, combining biomass related platform molecules, carbon dioxide and molecular hydrogen, could be established, yielding fuels with tailored combustion properties and synthetic pathways for subsequent fuel-prototyping, the basis for future reference processes.

// Results
The strategic approach of CIF-1 is to establish novel fuel structures and evaluate fuel production routes by performance screening of value chains from a process point of view, with a focus on energy requirements and carbon dioxide (CO2) release. A large variety of oxygenates can be obtained from de-functionalization of biomass to platform molecules and refunctionalization of these intermediates to the various fuel candidates. From this large pool of chemical compounds, the most attractive candidates for future biofuels were largely established by a rational approach, using computational property prediction to efficiently decrease the number of molecular structures
for further production analysis. The following comprehensive CO2-footprint of the selected process pathways could be identified via lifecycle-oriented performance indicators, enabling a model-based ranking of the variants and generation of process pathway alternatives. Subsequently, the systematic process synthesis could be combined with fundamental research in the phase of reaction and catalysts development.

Within this computational approach, the importance of CO2 incorporation in the production pathway could be recognized. In various chemical and bio-chemical transformations, CO2 is liberated during the synthesis of the platform molecules and the subsequent transformations towards the envisaged fuel structures. Consequently, a reintegration of this CO2-fraction could pave the way to carbon-optimized production routes and to unprecedented fuels structures. The complementary fuel design process identified linear and cyclic dialkoxymethane ethers as highly interesting fuel compounds (Fig. 3.23). In the established industrial processes, these compounds are produced via a condensation reaction of alcohol components and formaldehyde. However, since the production of formaldehyde involves the oxidation of methanol, the chemical process is redox-inefficient and very energy intensive. Consequently, a novel tailored catalytic system could developed, opening a sustainable synthetic pathway to this liquid energy carrier via the combined utilization of bio-based feedstock and CO2 as carbon source together with “green hydrogen” from water electrolysis.

\[
\text{CO}_2 + 2\text{H}_2 + 2\text{ROH} \xrightarrow{\text{tailored molecular catalyst}} \text{R}-\text{O}-\text{C}-\text{O}-\text{R} - 2\text{H}_2\text{O}
\]

\[
\text{CO}_2 + 2\text{H}_2 + \text{OH} + \text{OH} \xrightarrow{\text{tailored molecular catalyst}} \text{O}-\text{C}-\text{O} - 2\text{H}_2\text{O}
\]

Figure 3.21: Novel catalytic pathway for the production of linear and cyclic fuel structures via the combination of biomass, carbon dioxide and molecular hydrogen.
Core Interaction Field 2: Performance Indicators for Biofuel Combustion

// Prof. Dr.-Ing. Heinz Pitsch
// Institute for Combustion Technology
// h.pitsch@itv.rwth-aachen.de

// Vision
The main target of this sub-project is to establish a link between engine application and design process of fuels. To accomplish this, two research targets are being pursued within CIF-2: (a) the establishment of the molecular structure dependent semi-empirical and quantitative models to predict fuels in-engine behavior and (b) the investigation of the fundamental combustion properties of such biofuels. Thereby, molecular structures of potential biofuels with optimal combustion characteristics and physical properties can be identified.

// Main Results Summary
A unique experimental database of derived cetane numbers (DCN) and ignition delay times of a large variety of oxygenated and non-oxygenated species was established using the ignition quality tester (IQT). This database was then used to derive a model for DCN predictions based on the fuel molecular structure. To assist the fuel design process, low-pressure flame species profiles and ignition delays of various TMFB fuels, e.g. dimethyl ether (DME) and 2-methyltetrahydrofuran (2-MTHF), were measured. The experimental findings were backed with analyses performed using chemical kinetic models developed within this project. Further, a modified version of the standardized lubricity test was applied to study the influence of specimen materials on fuel lubricity, which helped in improving the understanding of the tribological performance of biofuels. Finally, closing the gap between the fundamental models and engine applications, a group contribution model for the prediction of the threshold sooting index (TSI) based on a modified Joback-Reid’s approach was developed and validated. In order to validate the TSI model, a broad smoke point (SP) database of several TMFB fuels was obtained.
Results

Model-Assisted Experimental Screening of Novel Biofuels

In CIF-2-1, a comprehensive and rapid screening of fuels was carried out with a standard constant-volume combustion chamber, i.e., the ignition quality tester (IQT). This facilitated a good comparison across oxygenated as well as non-oxygenated fuels under well-controlled, reproducible conditions by establishment of a unique database containing ignition delay times and DCN values over a wide range (15–70). Subsequently, this database has been used to derive a new model for DCN prediction based on the group additivity principle. An estimate for the DCN of a novel compound can now be determined by evaluating several algebraic equations. The group contribution model has been thoroughly validated by means of cross-validation and external data sets. A comparison between the model and experimental DCN is shown in Figure 3.22.

![Figure 3.22: comparison for calculated and measured DCNs.](image)

Rapid Screening of the Combustion Behavior of Novel Biofuels

In CIF-2-2, ignition delay times and flame species profiles of various TMFB fuels were measured. In order to revalidate the laminar flow reactor facility, the first stage ignition delay time measurements of several straight chain alkanes and ether were performed. These measurements were compared against recent models and experimental data from literature. The case for DME is shown in Fig. 3.23a, where a satisfactory agreement between the measured data and the models based on previously validated experiments can be observed. Furthermore, flame temperatures and species concentrations
of the lignocellulosic biofuel γ-valerolactone (GVL) were measured in a premixed flat flame at a pressure of 50 Torr in collaboration with international researchers. A high-temperature specific kinetic model was also developed and its predictions showed a good agreement with the species data in the preheat and reaction zones of the flame. Additionally, a comprehensive ignition delay time study of 2-MTHF was carried out in collaboration with IRF-B1, and a satisfactory agreement between the experimental data and numerical simulations was achieved (Fig. 3.23b). The importance of ring opening reactions and low-temperature peroxy chemistry in 2-MTHF ignition was revealed through reaction path and sensitivity analyses.

In CIF-2-3, a modified version of the standardized lubricity test, high frequency reciprocating ring (HFRR) was applied to study the influence of specimen materials on fuel lubricity. The analysis of measurements of non-ferrous metals, ceramics, and different steels revealed that the overall lubricity and lubricity ranking depend significantly on the specimen material. The results show that although the overall wear is affected by the test load and duration, the lubricity ranking among the studied biofuels does not change. Further, three-dimensional surface scans of selected HFFR specimens were performed, and upon analysis of these results gained from balls and discs, previously unknown wear patterns could be identified. It was identified suitable test procedures and pass/fail criteria for the TMFB.

// Identification of Characteristic Fuel Numbers
Within CIF-2-4, characteristic fuel numbers (CFN) were introduced to assess the sooting behavior of fuels in diesel engines. The TSI and oxidation potential number (OPN) were identified to describe the characteristic sooting tendency of fuels and the inherent soot reduction within a diesel spray plume, respectively. All the TMFB-relevant
hydrocarbon classes were analyzed by means of SP tests and TSIs were derived for several pure components as well as their blends. The results showed that the carbon saturation degree influences the sooting tendency negatively and the oxygen functional group plays a fundamental role on soot reduction. Among the TMFB-relevant oxygenates, aldehydes generally demonstrate the lowest sooting tendency, followed by ketones, alcohols, and ethers. The TSI database served to validate the group contribution method featuring a modified Joback-Reid’s approach.
Core Interaction Field 3: Model-Based Fuel Design

// Prof. Dr. rer. nat. Kai Leonhard
// Model-Based Fuel Design
// kai.leonhard@ltt.rwth-aachen.de

// Vision
The vision of CIF-3 is a fuel design procedure based on the formulation of a multi-objective optimization target that encompasses the most relevant aspects of fuel production and combustion. Efficient mathematical methods have to be adapted and employed to accomplish the search of the vast range of molecular structures and process and engine parameters for optimal conditions. Various required activities are bundled in CIF-3 since model development, problem formulation and mathematical optimization are tightly interwoven. The resulting set of target molecules will be investigated further by highly accurate theoretical and experimental methods including the evaluation from a life cycle perspective in the whole cluster.

// Main Results Summary
For the first time in our cluster, the model-based design of fuels has actually been performed successfully taking production and combustion aspects into account. This was possible through the combination of simplified models for the production of biofuels and their physical, chemical, and combustion properties with a rule-based structure generator. This design step performed in CIF-3 led to proposals of fuel molecules and mixtures that have subsequently been validated experimentally by other parts of the TMFB cluster. At the same time, more sophisticated models have been developed in CIF-3 that lead to optimally designed sub-processes in the cluster, e.g. for product separation and fuel-air mixing.

// Results
The integration of computer-aided molecular design (CAMD) and conceptual process design leads to the optimization of product and manufacturing characteristics. In traditional CAMD of chemical products, the molecular structure of a product is not necessarily structurally related to the platform chemicals available for synthesis of the product in such a way that this relationship could be thought of as a series of predefined chemo-catalytic refunctionalization reactions. In an attempt to exploit such structural similarity as an early indicator for the feasibility of production of a molecule in the context of CAMD, a heuristic enumeration-based generator of molecular structures has been developed in the CIF. This algorithm allows a targeted generation of fuel candidates by resembling carbon- and energy-efficient refunctionalization steps starting from a pre-defined set of platforms and transformation rules. In combination
with group contribution and quantitative structure-property relationship modeling, the structure generator allows to perform a virtual fuel screening, as can be seen from Figure 3.24. The computational approach has been successfully applied to the design of pure component fuels for the spark-ignition (SI) engine and for the compression-ignition (CI) engine. In the latter case, it is only the combination of the targeted approach and a new DCN (Derived Cetane Number) prediction model that has allowed the identification of the most promising molecular motifs for this engine type. Recently, the model-based fuel design methodology has been extended to the rational formulation of biofuel mixtures by means of integrated product and process design. This optimization-based procedure identifies a set of optimal conversion pathways for the production of a blend with tailored properties which is composed of few, well-defined biogenic components so that a process-related objective, e.g. mass yield, is maximized.

We supplement the mainly data driven structure-property relationships by more physical models to improve the accuracy and the range of applicability of these models. For this purpose, we focused on the predictive PC-SAFT (Perturbed-Chain Statistical Associating Fluid Model) equation of state. This model is based on molecular properties computed by means of quantum mechanics and statistical mechanics. It permits the calculation of many properties required for modeling fuel injection as well as for designing solvents in chemical engineering. In the last two years, predictive PC-SAFT was combined with the Conductor-like Screening Model for Realistic Solvation (COSMO-RS) to improve the accuracy of the models. The models developed and used in CIF-3 were employed to design and experimentally validate more efficient solvents and processes for biofuel production and separation, e.g. for γ-valerolactone and 2,3-butanediol in cooperation with IRF-A.
Whereas we can describe production and combustion properties of fuel candidates reasonably by models nowadays, this is more difficult for their environmental and toxicity assessment. Therefore, we investigate the most sensitive ecotoxicological endpoints, e.g. genotoxicity and acute toxicity, of promising biofuel candidates experimentally. Acute toxicity tests for different trophic levels of aquatic ecosystems (green algae Desmodesmus subspicatus, aquatic invertebrate Daphnia magna, zebrafish embryo Danio rerio) as well as an in vitro genotoxicity test (V-79 cells) were adapted for the screening of the biofuel candidates 2-MF, 1-octanol, DnBE, MIPK, 2-MTHF, 3-MTHF and MEK. A fossil diesel fuel was used as reference fuel. For the reliable testing of this complex mixture, a special exposure system had to be developed. Currently, this exposure system using silicone tubes has been successfully established for test systems using the aquatic invertebrate D. magna. Results showed that 2-MTHF, 3-MTHF and MEK are much less toxic for D. magna than fossil diesel fuel. 2-MF and 1-octanol, however, induce toxic effects in similar low concentrations as fossil diesel. In the next step, this test system will be established for more endpoints, such as genotoxicity.

The phase behavior of biofuel blends with water is a key performance indicator for the development of biofuels. Knowledge of the temperature-dependent maximum amount of water in biofuel blends is necessary because water can lead to several problems such as reduced energy density, component fouling or phase splitting at low temperatures. The maximum solubility of biofuel blends in water is also very important, e.g. with regard to aqueous toxicity. The prediction of water solubility is still difficult today since phase splits occur due to complex molecular interactions. Therefore, new and efficient experimental methods are needed to determine the water partitioning behavior of biofuel blends. Within the last years, an automated setup for the characterization of liquid-liquid equilibria has been developed using a combination of GC and HPLC. Now, the experimental setup has reached a mature status and is regularly employed to generate LLE data on TMFB-relevant mixtures. However, GC and HPLC are not very fast methods for sample analysis. Spectroscopic methods, such as Raman spectroscopy, are usually much more rapid. Therefore, a new measurement setup for the time and material efficient determination of liquid-liquid equilibria has been set up and validated using microfluidics and Raman microspectroscopy.
Fig 3.25: A microchannel for the determination of phase equilibria illuminated by LASER light.
List of Projects CIF

Project CIF-1-1 “Electrocatalytic Conversion of Biogenic Compounds to Value-Added Chemicals and Fuels”
Institute of Technical Chemistry and Macromolecular Chemistry (Prof. Regina Palkovits)

Aim The electrocatalytic oxidation or reduction of biogenic compounds to value-added chemicals under consideration of various electrochemical factors has been the subject of investigation in this project. Another focus was on the development of different electrocatalysts for reduction and oxidation reactions and the integration of crude substrate mixtures in electrochemical processes.

Results Crude itaconic acid fermentation broth has been successfully integrated as substrate solution for the electrocatalytic upgrading to methylsuccinic acid. Different Ru-based electrocatalysts have been developed for the electrocatalytic oxidation of 5-hydroxymethyl-2-furfural to 2,5-furandicarboxylic acid and 2,5-diformylfuran.

Project CIF-1-2 “Performance Screening of Next-Generation Biofuels”
Aachen Chemical Engineering - Process Systems Engineering (Prof. Alexander Mitsos)

Aim The project aims at a fast process evaluation screening tool for biorefinery production pathways, considering economic as well as life-cycle analysis criteria in a bicriterial optimization. In order to bridge the gap between first laboratory results and conceptual process design, a methodology has to be developed taking into account the laboratory results in terms of reaction yields and process decisions like the choice of solvents and the feasibility and effort of separations.

Results A novel methodology called "Process Network Flux Analysis" has been introduced, which analyzes the process performance of biorefinery pathways already at an early stage and has been applied to a case study of gasoline fuel candidates. The methodology has been (i) benchmarked against detailed conceptual design results, which revealed a sufficiently high accuracy, and (ii) coupled to a straightforward biomass supply chain model.
Project CIF-1-3 “Identification of Novel Tailor-Made Fuel Structures, Property Evaluation and Initial Feasibility Validation Based on Chemical Sustainability Criteria”
Institute of Technical Chemistry and Macromolecular Chemistry (Prof. Walter Leitner), Mechanisms in Catalysis (Prof. Jürgen Klankermayer)

Aim The objective of this project is the development of efficient catalytic procedures for novel TMFB fuel structures and subsequent preparation of lab quantities for comprehensive combustion tests.

Results Based on effective catalyst development and tailored optimization of the respective reaction system, selected biobased furan and tetrahydrofuran fuels could be produced in large quantities.

Project CIF-2-1 “Model-Assisted Experimental Screening of Novel Biofuels”
Aachen Chemical Engineering - Process Systems Engineering (Prof. Alexander Mitsos)

Aim This project aims at establishing novel (semi-)empirical models for the prediction of key physico-chemical fuel properties, in particular fuel auto-ignition quality, by combining structural group contribution and quantitative structure-property relationship (QSPR) modeling with model-based optimal experimental design techniques identifying experimental conditions with maximum information gain. To this end, rapid screening devices are utilized to acquire property data for a large and diverse collection of oxygenated hydrocarbon species.

Results An experimental screening campaign targeting oxygenated hydrocarbon species from various functional families has yielded a database of auto-ignition data used for group contribution and QSPR modeling for unraveling relationships between the auto-ignition propensity and the molecular structure of a fuel. This led to a simple, yet predictive estimator for the derived cetane number of pure oxygenated (acyclic and cyclic, branched and straight, saturated and unsaturated) hydrocarbons as well as alcohols, ethers, esters, ketones, aldehydes, and aromatic and polyfunctional compounds.
Project  CIF-2-2 “Rapid Screening Method to Describe Ignition and Emission Characteristics of New Fuels under High Pressure and Temperature”
Institute for Combustion Technology (Prof. Heinz Pitsch)

Aim  The project aims at the experimental and numerical investigation of novel TMFB fuels in order to assist the fuel design process within TMFB.

Results  Extensive first-stage ignition delay measurements of several oxygenated and non-oxygenated fuels were conducted in a laminar flow reactor. Flame temperature and species concentrations of the novel lignocellulosic biofuel γ-valerolactone (GVL) were measured in a premixed flat flame at a pressure of 50 Torr. In order to evaluate the results chemically, a specific high-temperature GVL model was developed and validated. The numerical simulations were found to be in good agreement with the experimental findings. Furthermore, ignition characteristics of 2-methyltetrahydrofuran were studied. The importance of ring opening reactions and low-temperature peroxy chemistry in 2-MTHF ignition was revealed through reaction path and sensitivity analyses.

Project  CIF-2-3 “Molecular-Level Analysis and Prediction of Tribological Properties of Biofuels and Blends”
Institute for Fluid Power Drives and Controls (Prof. Hubertus Murrenhoff)

Aim  The research aims at gaining profound knowledge about the impact that the molecular structure of new biofuels and their blends have on the tribological performance in order to tailor them with improved tribological properties, enabling their usage with modern injection systems.

Results  It has been found that overall lubricity and lubricity ranking depend significantly on the specimen material but are hardly affected by load or test duration. Moreover, three-dimensional studies on HFRR specimens have revealed previously unknown wear patterns providing further insight into the highly complex process of boundary lubrication (lubricity).
### Project CIF-2-4 “Identification of New Characteristic Fuel Numbers (CFN) for Tailor-Made Fuels from Biomass”
Institute for Combustion Engines (Prof. Stefan Pischinger)

**Aim**
The project has worked on the determination of characteristic fuel numbers (CFN) to assess the sooting tendency of biofuels in CI engines.

**Results**
The oxidation potential number (OPN), the novel index proposed to assess the impact of mixture formation on soot emissions, correlated with engine-out soot emissions of several fuels. The sooting tendency of TMFB-relevant oxygenated classes was tested via smoke points, and threshold-sooting indices (TSIs) were derived for blends and neat compounds. The experimental data served to validate a new group contribution model to predict TSIs.

### Project CIF-3-2 “Model-Based Product and Process Design for Biofuels”
Aachen Chemical Engineering - Process Systems Engineering (Prof. Alexander Mitsos)

**Aim**
In addition to the model-based identification of fuel candidates to be used in pure or blended state, this project integrates computer-aided molecular design techniques with biofuel production pathway screening in an attempt to simultaneously design a product and solve a process development problem. Furthermore, early-stage screening of processing pathways is augmented by conceptual process design in case of selected fuel candidates.

**Results**
Computational identification of pure-component fuels with tailored properties for both SI and CI engines has been accomplished and has recently been extended to the rational formulation of biofuel mixtures by means of integrated product and process design. Conceptual process design for the production of 2-butanone has revealed that energy demand for the separation of 2,3-butanediol from the fermentation broth must be strongly reduced by innovative processing concepts before 2-butanone can be considered a serious competitor for lignocellulosic ethanol.
Summary

Activities 2015-2016

Project CIF-3-3 “Design Methods for QM-Based Property Models”
Aachen Chemical Engineering - Process Systems Engineering
(Prof. Alexander Mitsos)

Aim
The goal of this project is the design of molecular structures with desired macroscopic properties. The main focus thus lies on deriving physically-based property models and improving their accuracy.

Results
The accuracy of the property prediction based on quantum mechanics and the PCP-SAFT equation of state could be improved by incorporating information from the independent property prediction method COSMO-RS. A QSPR model to predict the lubricity of biofuels based on molecular descriptors has been developed.

Project CIF-3-4 “Water Partitioning and Stability of Biofuel Blends”
Institute for Technical Thermodynamics (Prof. André Bardow)

Aim
The phase behavior of second generation biofuel blends with water is an important key performance indicator for the development of new biofuels. The goal of this project is the development of new and efficient methods for the experimental determination of water partitioning behavior and stability of biofuel blends.

Results
The phase behavior of many biofuel blends with water has been studied using an automated GC/HPLC platform. Moreover, a new measurement setup for the efficient determination of liquid-liquid equilibria using microfluidics and Raman microspectroscopy has been developed to further increase measurement efficiency.
Summary
Activities 2015-2016

Project  CIF-3-5 “Ecotoxicological Investigations of Biofuels as a Basis for Computational Model-Based Prediction of Ecotoxicological Potencies”
Institute for Biology V, Environmental Research (Prof. Henner Hollert)

Aim  Ecotoxicological bioassays are used in a "green toxicology" approach as screening tools to identify potentially harmful biofuel candidates during the fuel design process. In addition to the biotesting, computer-based tools for the prediction of toxic effects, e.g. on populations of aquatic invertebrates, are applied.
4 Thematic Working Groups
Supplementary Cluster Activities

// apl.-Prof. Dr. phil. Ingrid Isenhardt
// Center for Learning and Knowledge Management,
Department of Information Management in Mechanical Engineering
// isenhardt.office@ima-zlw-ifu.rwth-aachen.de

The Supplementary Cluster Activities (SCA) aim to enhance efficient networking between the cluster's scientific processes and to foster interdisciplinary collaborations [c.f. Cooperation Portal, Benchmarking Approach, Performance Measurement and Colloquia for Research Assistants]. Moreover, the SCA support the cluster management to make decisions that involve collaboration enhancing measures [c.f. Performance Measurement, Colloquia for Research Assistants, Further Trainings]. The SCA furthermore strive to create a successful strategic cluster development through performance measurements and supporting activities. Finally, the aim is to determine and develop specific key performance indicators to measure and steer the cluster performance [c.f. Benchmarking Approach, Performance Measurement]. Due to the collaboration of research teams from different scientific fields, the strategic management of interdisciplinary processes enhances scientific cooperation on the one hand and supports the transparency of communication, knowledge and scientific developments on the other hand. The main tasks of the SCA are personal development as well as knowledge management and dissemination within the Cluster of Excellence (CoE).

<table>
<thead>
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<th>I. Collaboration-Enhancing Research</th>
<th>II. Collaboration-Enhancing Services</th>
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<td>e.g.: Determination and measurement of cluster-specific key performance indicators; knowledge transfer by the aid of applying data science techniques etc.</td>
<td>e.g.: Colloquia for scientific staff; further trainings; implementation of knowledge tools etc.</td>
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Two descriptive columns guide the SCA activities: One contains the collaboration-enhancing research, the other one is dealing with collaboration-enhancing services.

Thus, the SCA constitute an integrative part within the organizational structure of the Cluster of Excellence “Tailor-Made Fuels from Biomass” (TMFB) at the RWTH Aachen University and contribute directly to the cluster’s management. The collaboration-enhancing services and research will be depicted in the following:
Thematic Working Group

// Cooperation Portal – “TMFB Insight”
“TMFB Insight” is a virtual cooperation portal that was initiated in 2014 to enhance transparency and scientific performances within the CoE. The idea behind it is to create a common working ground, to visualize competences of researchers and working groups, to make knowledge-like publications accessible to all co-workers and to find a remedy for creating synergies. As transparency is a key need in knowledge intensive organizations like the CoE, all basic features of the Knowledge Map originate from the demand to disseminate information across all members of the cooperation and to avoid hampering the flow of information across hierarchies.

Therefore, a modular system is developed with several functionalities such as an employee directory, including information on contacts and competences, a publication portal and a data sharing area in order to easily access common documents and literature as well as to simplify the internal flow of information. Particularly due to the internal project reviews taking place on an annual basis, employees were invited to update the publication data-base for review purposes. This guarantees that publication information and data are continuously updated and an up-to-date state of the portal is ensured.

Based upon the idea of generating synergies by using the cooperation portal, it is elementary that a linking of expertise and people is taking place. Therefore, the idea of adopting machine-aided techniques from the field of data science matured to support this process. For instance, by developing a process which automatically analyses publications and assigns the highest weighted keywords to the authors is one opportunity.

// Benchmarking Approach
Increasing Self-Reflexiveness, Identifying of Synergies and Pointing Out Possible Future Developments
The above described idea of machine-aided analysis of publications mainly takes part in developing a benchmarking approach for the CoE. The demand for developing an instrument of benchmarking scientific output is not only related to the cluster management, but it is also part of the strategy of the German Research Foundation and German Council of Science and Humanities.

Due to the rapid growth of text documents that tends to double every 24 years, an automated way of analyzing scientific publications became necessary. The vision of this benchmarking approach is to support self-reflexivity and to identify trends and synergies within and outside the cluster. That is why it is evident to adapt text mining processes to the framework conditions of the CoE. In order to do so, cluster internal requirement engineering took place, and based on it, the process design of the benchmarking approach was defined. In the sense of benchmarking, which means learning from the best in class, it is essential to gather two data corpora. One, containing the CoE publica-
tions, another one containing community related publications. By applying text-mining algorithms to both corpora, relationships and differences become visible as examples.

Potential outcomes provide insights regarding chemicals and methods used over time, their corresponding authors and organizations as well as content based clustering and classification of publications in order to identify intersections within and outside the cluster.

// Performance Measurement & Determination of Cluster-Specific Key Performance Indicators

The Balanced Score Card (BSC) evaluation is a major cornerstone that supports the cluster management yearly. This approach is characterized by the measurement and comparison of performance indicators on various hierarchical levels such as the management level or the level of employees. It is based on a survey among all CoE-employees evaluating the interdisciplinary cluster performance and collaboration. The 7th evaluation took place from November to December 2016. With the aid of the BSC, the cross-hierarchical communications and cooperation efforts are evaluated. As a consequence, the transparency of measures and decisions is increased. For instance, based upon the results, general meetings were conducted to discuss and develop the strategic developments of the cluster. Also, further trainings were initiated to increase interdisciplinary skillsets of the cluster employees.

// Further Trainings

Due to the natural fluctuations of the CoE, new young PhD candidates join the TMFB on regular basis. The everyday work within a Cluster of Excellence requires more skills than just the scientific expertise and knowledge, namely presentation techniques and management skills. In coordination with the Cluster Office and in order to provide these PhD students with the possibility to learn, train and improve, diverse professional seminars are offered. The topics provided are designing of interdisciplinary research processes, scientific and target group adaptive presenting, creativity and innovation in university, project management in research and teaching as well as insights in the basic principles of management cybernetics.
// Thematic Working Group

// Colloquium for Research Assistants
The analysis of the annual BSC evaluation often shows discrepancies regarding the level of information about TMFB results as well as a cooperation divergence within its organizational levels. While the level of information within the sub-IRFs is judged good, there is a decrease towards the overall cluster. To increase the information flow between the different recursion layers, certain measures were derived. For instance, a colloquium for research assistants and PhD candidates of the CoE is conducted. This colloquium mainly focuses on creating a common understanding of the relevance of single projects and their importance in the scientific process of the entire CoE. Furthermore, it tends to identify the value of each project for the continuation of TMFB after the end of the DFG funding in 2017.

// CEO-Supporting Activities
Consulting sessions (primarily based on the results of the scientific accompanying research in terms of e.g. performance measurement and evaluation) between the COO and Supplementary Manager and its team are held on a regular basis. In this context, strategic planning, further measures and demands for action are carried out. The consulting sessions help to identify areas for development (e.g. necessity for colloquia for research assistants and general meeting, childcare support for TMFB employees and International Conference Speakers, further training opportunities etc.).
Analytics in Biomass Fractionation

// Dipl.-Chem. Nico Anders
// Aachen Chemical Engineering - Enzyme Process Technology
// nico.anders@avt.rwth-aachen.de

Biomass turned out to be heterogeneous in terms of composition, not only depending on the plants themselves, but also on the period of growth. Thus, in 2013 a junior research group dealing with the analysis of this heterogeneous material and the development of new analytical methods in the bio-refinery context was established.

To achieve the overall goal of a complete characterization of each solid or liquid occurring during a biorefinery process and, thus, of closing the overall mass balance of the biorefinery process, several analytical techniques (DSC, GC-FID, GPC-RI/UV, GPC-MALLS/RI, HPAEC-PAD, HPLC-UV, LC-MS, UV/Vis) are used.

Figure 4.1: Simultaneous determination of biomass derived degradation products of cell wall polymers cellulose, hemicellulose, lignin and pectin (Anders et al. 2015).
In this context, a method allowing a simultaneous determination of degradation products of all biomass derived natural polymers (cellulose, hemicellulose, lignin and pectin), using HPAEC-PAD, was established (see figure 4.1). Based on this method, several biomass fractionation steps, such as alkaline, acidic and organosolv, could be evaluated based on the removal of one specific natural polymer. Additionally, making these degradation products identifiable and quantifiable, the closing of the overall mass balance and identification of inhibitors for subsequent downstream processing will be supported.

In the future the junior research group will tackle the challenge of quantifying hydrolysis products occurring during the process via an at-line automated sampling in order to identify both degradation pathways and process inhibition.
Life Cycle Assessment and Benchmarking

Dipl.-Biol. Jürgen Sutter
Öko-Institut e.V. - Institute for Applied Ecology
j.sutter@oeko.de

The Öko-Institut is a leading European research institution providing scientific support for academia, governments, private enterprises and civil societies, to substantiate and support a sustainable future. In the years 2015 and 2016 of the Cluster of Excellence “Tailor-Made Fuels from Biomass”, the Öko-Institut undertook studies on the environmental performance of two new reference processes envisioned by the cluster and on local biomass potentials.

Assessment of two new TMFB reference processes (MF concept and MEK concept)
In order to find optimum “tailor-made” fuel components, new fuel candidates are continuously being proposed and investigated at the TMFB Cluster. Two promising fuels are 2-methylfuran (MF) and butanone (methyl ethyl ketone, MEK), both gasoline substitutes. The production routes for these two have been investigated at the TMFB by experimental studies as well as conceptual process design, so that basic data for a first environmental assessment are available.

Starting from wood chips as biomass input, the assessment of the new routes is modelled consistently with the previous studies on 2- and 3-MTHF. Thus, in both scenarios, a previous organocat fractionation step is assumed. The cellulose-rich stream (CRS) is processed via the newly analysed MF- and MEK-production routes. The other streams represent co-products: The lignin-rich stream is assumed to be combusted for the generation of on-site process energy. The C5-sugars of the xylose-rich stream are also assumed to be utilized in fuel production. Here the production of MF via furfural is chosen.

MF synthesis from cellulose proceeds via two consecutive catalysed reactions: in the first reaction cellulose is converted to hydroxymethylfurfural (HMF) which reacts with carbon monoxide to form 2-methylfurfural (MFF), CO2 and water. Secondly, MFF is converted to MF by abstraction of CO.

MEK synthesis starts from glucose, which is produced by a hydrolysis step of the CRS. Glucose is fermented to 2,3-butanediol (2,3-BD). In a chemo-catalytical reaction, 2,3-BD is converted to MEK.

The MF concept shows the lowest net GWP and CED n.r. compared to MEK concept and the MTHF concept studied in the years 2012 to 2015. This is due to the fact that
this concept is approximately energetically self-sustaining. This means that using the biogenic side streams for on-site process energy generation covers the process energy requirements. However, the process is in a very early stage of development with experimental evidence from small-scale reaction experiments in ideal environments. The GWP of the MEK concept is around five times higher. Also, it is technologically more advanced concerning both the fermentation and dehydration steps. The MTHF concept, where the fermentation step is already realized on commercial scale, has considerably higher values comparable to the impact of the fossil references. This is mainly due to high process energy requirement but also due to hydrogen input.

// Analysis of Biomass Potentials
The contribution of biomass supply to the environmental impact of biofuel is rather small if forest residues are used as input. If dedicated energy crops are used, the impact can make a significant contribution to the environmental burden. Especially due to land use change (LUC) effects, the global warming potential can be significantly increased.
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<td>Grünefeld, Gerd Prof. Dr.rer.nat.</td>
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<td><a href="http://www.bio5.rwth-aachen.de">www.bio5.rwth-aachen.de</a></td>
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<td>Isenhardt, Ingrid apl. Prof. Dr. phil.</td>
<td>Institute of Computer Science in Mechanical Engineering / Center for Learning and Knowledge Management / Assoc. Institute for Management Cybernetics e.V. (IMA/ZLW &amp; IfU)</td>
<td><a href="http://www.sima-zlw-ifu.rwth-aachen.de">www.sima-zlw-ifu.rwth-aachen.de</a></td>
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<td>Aachen Chemical Engineering – Molecular Simulations and Transformations (AVT.MST)</td>
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<td>Aachen Chemical Engineering – Fluid Separation Processes (ACT.FVT)</td>
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<td>Institute of Technical Chemistry and Macromolecular Chemistry (ITMC), Chair of Technical Chemistry and Petrochemistry</td>
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<td>Institute of Technical Chemistry and Macromolecular Chemistry (ITMC), Chair of Industrial Chemistry</td>
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<td>Shock Wave Laboratory (SWL)</td>
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<td>Institute of Technical Chemistry and Macromolecular Chemistry (ITMC), Chair of Nanostructured Catalysts</td>
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<td>Institute for Combustion Engines (VKA)</td>
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<td>Institute for Combustion Technology (ITV)</td>
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Publications (selection) of CIF: Fuel Design


Publications

Published Publications


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Publications (selection) of CIF: Fuel Design


7 Acknowledgements
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