Status Report
2012-2014
// Cluster of Excellence (EXC 236)
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The Cluster of Excellence „Tailor-Made Fuels from Biomass“ (TMFB) at RWTH Aachen University has now been working for more than 7 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 will last until 2017 which again provides an exceptional horizon for us to continue and intensify our research activities in the highly motivating and interdisciplinary world of biofuels.

Research wise, the start of the second funding period did not mark a big cut: the research aim and vision of TMFB, namely the description of an integrated Fuel Design Process to describe and derive optimized sustainable biofuels, remained unchanged. Some minor adjustments, like the reorganization of the TMFB research structure (see chapter 2) or redefinition of specific projects were undertaken, whereas these changes were all based on the experiences that our researchers had made in the first years 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 on to biofuels could be derived. At the same time, applied and fundamental combustion experiments revealed new potential of TMFB fuel components to lower emissions and decrease the combustion engine’s efficiency. All these results were also transferred into the Fuel Design Process in which the model-based description and projection of promising new fuels molecules was intensified.

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 2007, the vision that we are aiming to realize with 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 raw materials and new combustion processes.

// Scientific Activities and Organization
During the first years of our work we were able to demonstrate the feasibility of our approach in different instances: in a first step, a group of privileged molecules were identified and investigated with all available methods. In the next step, the first funding period was successfully crowned with the definition of the first two tailor-made fuel components, 2-MTHF and 2-MF.

Now, we are focusing all our efforts to realize the main goal of TMFB: the definition of the Fuel Design Process as a 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. Therefore, the structure of the overall project was reorganized so that today TMFB consists of the 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.

Figure 2.1: Scientific Structure: Integrated Research and Core Interaction Fields

Fuel Design Center
Aachen

IRF-A
From Biomass to Biofuels
Device:
// Biorefineries

IRF-B
From Biofuels to Propulsion
Device:
// Engines

CIF Fuel Design
Integrated Research Field A: From Biomass to Biofuels

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// 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 for 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).

// Main Results
Based on the previous work a reference process was designed to convert raw lignocellulose into tailor-made fuel candidates. The conceptual process design and analysis for the target molecules 2-MTHF and 3-MTHF showed a process capability of over 200 kg of fuel per ton of dry biomass. Furthermore, the process energy was lower than the energy content of the fuel and the global warming potential was reduced by ca. 40%. For the biomass fractionation into its main components (cellulose, hemicellulose and lignin), the previously developed OrganoCat Process was further improved concerning its efficiency and mechano-catalytical methods for the delignification of the biomass were developed. The valorization of lignin was investigated by selective cleavage of lignin linkages. The scope of the possible tailor-made fuel candidates was broadened to include the synthesis of target molecules with carbon content >C6 and facilitated by improved hydrogen management.
Integrated Research Field A1: Biomass Fractionation

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// Vision
The model-based mechanistic understanding of the biomass fractionation processes in electrolyte systems as well as of the subsequent enzymatic hydrolysis is the overall challenge of the IRF-A1. Assuming the complete characterization of the biomasses with respect to cellulose, hemicellulose and lignin content, the models should allow for drawing conclusions for different types of biomasses, fractionation processes as well as the enzymatic hydrolysis progress. These conclusions will help in the future to find the best combination of utilized biomass, and parameters of pretreatment and enzymatic hydrolysis. Thus, the new knowledge will lead to defined fractions that can be used for further downstream processing in order to gain tailor-made fuels.

// Main Results Summary
During the last two years, the focus of the IRF-A1 was placed on electrolyte systems leading to a great progress in the investigation of pretreatment and model systems. Using theoretical models, the mechanism of the dissolution process of cellulose in ionic liquids and the subsequent enzymatic saccharification could successfully be described. Nevertheless, investigations on the ionic liquid pretreatment in comparison to the Organosolv process show lower investment costs but do not eliminate the overall problem of the technically not feasible recycling of the ionic liquids. Thus, as an alternative pretreatment to ionic liquids, the mechanocatalysis could be established. Depending on subsequent reactions, high yields of sugars, sugar alcohols and sugar degradation products could be achieved. The model-based description of the enzymatic progress provides information about the accumulation of oligosaccharides during the reaction which can experimentally be followed by anion exchange chromatography.

// Results
Biomass fractionation is one of the major steps in order to gain cellulose, hemicellulose and lignin fractions suitable for conversion. To overcome the resistance of the cellulose against hydrolysis is one of the most important steps in the conversion of lignocellulosic material. To achieve this aim, there are two main approaches within the IRF-A1: first, the dissolution of cellulose with ionic-liquids (IL), and second, the dissolution using mechanocatalysis. Both dissolutions are followed by a highly effective conversion into sugars, sugar alcohols and sugar degradation products (5-hydroxymethyl-furfural (HMF) and furfural) because of the more efficient hydrolysis of water soluble fractions compared to water insoluble fractions. Furthermore, other electrolyte systems such as Organocat are investigated with the aim of finding an ideal pretreatment for different biomasses.

In order to describe the dissolution of cellulose in IL, 15 different IL were studied in order to elucidate the influence of the cation in the solvation of cellulose. In preliminary experiments it could be shown that the anion binds to the external hydroxyl groups (see Figure 3.2). However, the corresponding cations are able to intercalate between the anions while providing a nonpolar contribution to the hydrophobic regions of cellulose. This IL dissolution is described by a kinetic Monte Carlo model based upon explicit all-atom molecular dynamics. It could be shown that strand detachment from the interior is very important as it leads to dissolution within milliseconds.

After detailed dissolution studies with several ionic liquids in the past, the most promising process conditions for the pretreatment of wood with ionic liquids could be identified in terms of ionic liquid, wood species, and particle size. In particular, it was found that 1-ethyl-3-methylimidazolium acetate (EMIMAc) can be utilized to disintegrate chips of beech wood quickly at mild temperatures, which envisions a considerable reduction of the energy demand. The following enzymatic hydrolysis was faster by one order of magnitude in comparison to untreated wood and generated a sugar yield of up to 65 wt-% from wood.

For the mathematical description of this enzymatic process, we developed a population balance model. Special interest was set on the investigation of the final stage of the process when water soluble oligomers become predominant. In this reaction, environmental inhibitory effects that will hinder the conversion...
from cellulose to glucose were studied. Inhibition by short oligomers and site specific bond break age of the cellulose could be demonstrated to occur. For the description of this system a discrete population balance was used, while the description of the cellulose degradation requires a continuous model in order to reduce the calculation effort. For the entire reaction from cellulose via oligomers through to glucose a mixed continuous-discrete population balance model will be implemented.

To identify as well as quantify these oligosaccharides a High Performance Anion Exchange Chromatography system coupled to Pulsed Amperometric Detection was established. This system allows for the simultaneous determination of the oligosaccharides and monosaccharides which are derived from biomass. An additional benefit is the opportunity of the separation of sugar acids and alcohols. On the process level, the obtained data has been used to set up a process simulation in order to assess technical performance, viability, and possible bottlenecks.

The design implements recycling of washing solutions and solvents without the need for high pressure equipment due to the negligible vapor pressure of the ionic liquid. The comparison to an Organosolv process identifies lower investment cost and a moderate energy demand. However, the hydrophilic interaction of the liquid salt reveals to limit the efficiency of energy integration measures like vapor recompression. The energy demand of the recycling and the recycling efficiency has to be optimized for the economic prospect of a pretreatment with highly concentrated ionic liquors.

With the mechanocatalytic pretreatment, a promising IL free approach for the ligno-cellulosic dissolution was investigated. Here, no problems concerning the recycling potential occur. It could be shown that, depending on the conditions of subsequent hydrolysis steps, highly selectively sugar, sugar alcohols or sugar degradation products can be yielded. Especially the fractionation into C5/C6 sugars and sulfur-free lignin with an acidic saccharification (see Figure 3.3) and the microwave assisted degradation into HMF with a yield of 70 % and Furfural with a yield of 80 % are suitable for further downstream processing.

These results indicate that a clear separation of the biomass derived compounds cellulose, hemicellulose and lignin is possible. The essential dissolution of cellulose is also feasible with various pretreatment methods. The mathematical description of the pretreatment and the subsequent hydrolysis remains the next challenge to be addressed within IRF-A1.
Integrated Research Field A2: Valorization of Lignin

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// Vision
The main target of this research field is to achieve an efficient degradation of lignin by selective chemo- and biocatalysis in combination with advanced engineering providing fuels, additives thereof and platform chemicals.

// Main Results Summary
New catalytic approaches have been developed for the targeted degradation of lignin model compounds, Organosolv-lignin, and beech wood under both reductive and oxidative conditions. For reaching the goals, unprecedented metal catalysts have been identified, known metal-based catalytic systems have been optimized, and mechanochemical bond activations have been utilized. Biocatalytic lignin cleavage reactions have been achieved by using microbial β-etherases and laccases. The latter have also been applied in ionic liquids, and reengineered versions obtained by directed evolution have been studied. Furthermore, various genes coding for lignolytic enzymes and accessory proteins have been selected and they were heterologously expressed using K. lactis as host organism.

// Results
Within the biorefinery concept the utilization of lignin plays an important role. The cluster has various approaches, which link chemo- and biocatalysis with engineering providing fuels, additives thereof and platform chemicals. The goal is to degrade lignin in a selective manner leading to chemical entities applicable as fuels, additives thereof and platform chemicals. In order to gain a better understanding of the fundamental processes leading to bond cleavage reactions on a molecular level, most studies make use of well-defined lignin model compounds in the initial phase of the investigation. Later, the resulting knowledge can be applied in conversions of lignin itself or lignocellulose present in wood.

The chemochemical approach for the selective breakdown of lignin involved the identification of new ruthenium-based catalysts allowing a selective fragmentation of specific bonds in lignin model compounds such as 1 (Figure 3.4).

Compounds 1 comprise the predominate β-O-4-linkage of lignin, and the analytics of the resulting products are well established. Comprehensive mechanistic studies now allowed tailoring novel ruthenium catalysts leading to selective C-O and C-C bond cleavage reactions of 1. Subsequently it was demonstrated that those systems could be applied in conversions of Organosolv-lignin as well.

Reductive cleavage protocols have also been in the focus of a study employing metal alloy catalysts for lignin hydrogenolysis. Solvent effects were investigated in detail, and it was demonstrated that with Raney Ni and other Ni catalysts a transfer hydrodeoxygenation of the phenolic fraction of bio-oil to a mixture of cyclic alcohols and diols was feasible under unprecedented low-severity conditions (e.g. 160 °C and autogenous pressure). Finally, a mixture of aromatics and aliphatics was obtained that could very well serve as valuable fuel additives to synthetic fuels produced by the Fischer-Tropsch process lacking aromatic and branched hydrocarbons required for high-performance of fuels for aviation or Otto engines.

Lignin model compounds such as 1 have been the starting point for an investigation on lignin degradation in a ball mill. After establishing the optimal reaction conditions a solvent-free process was introduced which could also be applied in the cleavage of representative lignin bonds in Organosolv-lignin and beech wood. The resulting products were analyzed by advanced NMR spectroscopical techniques.

The electrochemical degradation of kraft and Organosolv-lignin in an aqueous system under very mild conditions (room temperature, ambient pressure) has also been investigated. Despite the heterogeneous substrates, the main parameters governing the cleavage reaction could be reliably identified and the reaction system was optimized in regards to the production of monomeric compounds in an electrochemical membrane reactor. In addition, the viability of shortcut methods (UV absorbance, acid solubility) to measure the reaction progress was shown.

The biocatalytic approaches towards lignin degradation involved an intense study of microbial β-etherases being able to cleave the relevant β-O-4 aryl ether linkages of lignin. So far, only four members are known and most reports are based on bacterial β-etherase systems (LigF, LigE and LigP) present in Sphingomonas paucimobilis SYK-6. Here, four novel enzymes with homology to known β-etherases were identified by database mining, recombinantly produced in E. coli, purified and subsequently characterized. One of them showed superior characteristics for ether

![Figure 3.4: Selective C-O and C-C bond cleavage in model compound 1.](image-url)
bond cleavage reactions as compared to known bacterial β-etherases. Aspects of substrate scope and applicability in stereoselective transformations are in the focus of currently on-going investigations.

The use of laccases in lignin modifications has been addressed from various sides. Laccases are of particular interest, because they only require atmospheric oxygen as a co-substrate and, with the help of mediator molecules, can also act under sterically-limited conditions within the lignocellulosic network (Figure 3.5). Here, a laccase from the white-rot fungus Trametes versicolor was studied concerning potential applications in bio refinery processes. The influence of relevant solvents such as the ionic liquid [EMIM][Ac] on enzyme activity and stability as well as on the reaction kinetics was investigated. It was found that in the presence of [EMIM][Ac] the enzyme activity was lower but that the ionic liquid helped stabilizing the laccase activity over time. This result in combination with the fact that ionic liquids have good lignin solubilizing properties led to the conclusion that [EMIM][Ac] should be regarded as a promising co-solvent for such biocatalytic lignin conversions.

Figure 3.5: Laccase-mediator system

In order to improve the laccase resistance towards ionic liquids and organic solvents, laccase lcc2 expressed in Saccharomyces cerevisiae was selected as the starting point for a directed evolution protocol aiming at an improved resistance of the laccase in ionic liquids. After two rounds of directed evolution, the lcc2 variant M3 (Phe265Ser/Ala318Val) showed about 4.5-fold higher activity than the lcc2 wild type (WT) in the presence of 15% (v/v) [EMIM][EtSO4] using ABTS assay. Furthermore, Lcc2 M3 revealed a 4-fold higher activity in oxidizing β-O-4 type lignin model compound in 10% [EMIM][EtSO4].

In an alternative approach towards lignin degradation, suitable genes, which coded for ligninolytic enzymes from P. chrysosporium (lignin peroxidase, manganese peroxidase), P. eryngii (versatile peroxidase), A. niger (Feruloyl esterases), and P. cinna babarus (laccase) were selected and heterologously expressed using K. lactis as host organism. Methods for the determination of the activity of the three enzymes lignin peroxidase, maganese peroxidase, and laccase have been established, and on-going studies shall prove the virtue of this very novel approach.

### Integrated Research Field A3: Carbohydrates to Intermediates

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**// Vision**

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

**// Main Results Summary**

In order to investigate the long-term stability of enzyme during high-throughput screening, a new model based technique called “enzyme test bench” was developed. It combines the high throughput screening approach with an extensive enzyme characterization procedure. DOT (dissolved oxygen tension) monitoring using fluorescence optodes was used to evaluate enzymatic activity. Tailor-made aluminum blocks in 96-well format were produced to ensure efficient heat transfer. Thermal resistance of enzymes at high-temperatures was found to correlate well with operational stability.

In order to identify novel and superior biocatalysts for selective and efficient conversion of carbohydrate to platform chemicals, Ustilago maydis MB215 was characterized towards its xylan-degrading and itaconate producing capabilities. An endo-1,4-beta xylanase UmXyn11A (um06350.1) was identified which is responsible for xylan degradation. The itaconate biosynthesis pathway of U. maydis including corresponding enzymes and their catalytic function was clarified and initial metabolic engineering led to a significant enhancement of Ustilago’s itaconate production.
In order to generate robust catalysts, novel types of biohybrid catalysts have successfully been prepared in which robust Rh-, Ru- and Cu-catalyst are embedded within a defined cavity of a β-barrel protein which enables to control selectivity through space. The novel types of biohybrid catalysts were developed based on a β-barrel protein FhuA and a Grubbs-Hoveyda type catalyst (Ru-based) using a ring-opening metathesis polymerization of a 7-oxanorbornene derivative as reference reaction in aqueous solution.

Results

Within industrial process development, efficient screening techniques are required to select the optimal biocatalyst/biohybrid catalyst regarding process characteristics, such as cost effectiveness, turnover number or space time yield. Conventional measurement of the initial enzyme activity, which is the established high throughput screening technique, disregards the long-term stability of an enzyme. A new model based technique called “enzyme test bench” was recently developed. It combines the high throughput screening approach with an extensive enzyme characterization, focusing especially on the long-term stability. The technique is based on modeling enzyme activation and deactivation as temperature dependent reactions in accordance with the Arrhenius law. Controlling these reactions by tailor-made temperature profiles using temperature control unit (Figure 3.6), the slow long-term deactivation effects are accelerated and characterizing models are parameterized. Thus, the process properties of an enzyme can be predicted and included into the screening procedure. Moreover, the optimum process temperature as function of the envisaged operation time can be found by these means. Predictions from this high throughput characterization were compared to long-term experiments in a RAMOS device (Respiration Activity Monitoring System), a technique for online monitoring of the oxygen transfer rate in shake flasks. Within the limits of the model validity, the enzyme test bench predictions are in good agreement with the long-term experiments.

Figure 3.6: Schematic representation of the modified temperature control unit. Top- and side-view on the microtiter plate (a) and the perspex frame for aeration (b). bottom- and side-view on the heat transfer block (c). Cut A-A-view (a. Fig. a) on the microtiter plate with attached heat transfer block and the optical measurement unit (d).

Figure 3.7: Itaconate biosynthesis pathway for Ustilago maydis. mtt: putative mitochondrial tricarboxylate transporter; act-isomerase: aconitate cis/trans isomerase; tad: trans-aconitate decarboxylase; mfs: putative Major Facilitator Superfamily extracellular transporter.
To identify novel and superior natural biocatalysts of possible platform chemicals, such as itaconate, malate, or succinate, 70 Ustilaginaceae of 13 species were screened for the production of organic acids. Ustilago cynodontis, Ustilago maydis, and Ustilago avenae were identified as promising production organisms for itaconate, malate, and succinate, respectively. The best itaconate producer U. maydis MB215 was further investigated towards the influence of carbon and nitrogen concentration on itaconate production in controlled batch fermentation.

The genes encoding the proteins responsible for the itaconate production of U. maydis MB215 were identified and a new biosynthesis pathway for itaconate was proposed and patented (Figure 3.7). This was confirmed by corresponding deletion and overexpression mutants as well as heterologous expression in recombinant E. coli and S. cerevisiae strains and resting cell assay experiments in U. maydis MB215 and S. cerevisiae. Initial metabolic engineering attempts (overexpression of involved regulator and transporter) led already to a doubled final itaconate titer, which shows the considerable promise towards an optimized U. maydis strain applicable for industrial itaconate production.

Furthermore, the biomass degradation ability of U. maydis was investigated in order to combine the utilization of raw biomass components such as cellulose and hemicellulose with the production of valuable platform chemicals. In this context the xylan degradation of U. maydis was investigated and an endo-1, 4-beta xylanase UmXyn11A (um06350.1), responsible for xylan degradation, was identified.

Biohybrid catalysts combine the structural diversity of biomolecular scaffold with the various types of metal catalyst/organocatalyst. Importantly, the biohybrid catalyst offers great opportunities for genetic optimization: genetic optimization by introduction of point mutations on the host protein allows both the activity and the selectivity of the hybrid catalysts to be fine-tuned.

Figure 3.8 shows the developed biohybrid catalyst based on an engineered FhuA variant and the Grubbs-Hoveyda type catalyst. The malimid linker chemistry proved to efficiently attach three different Ru-catalysts and linker length has been optimized yielding finally a water-stable Grubbs-Hoveyda type catalyst which is covalently bonded to an reengineered FhuA variant (FhuA ΔCVFtev). FhuA ΔCVFtev was reengineered in respect to adding TEV cleavage sites for MALDI-TOF analysis and introducing substitutions Asn548Val and Glu501Phe to make free –SH group accessible and to avoid additional complexation of other amino acid residue with the metal catalyst. Attachment of the Grubbs-Hoveyda type catalyst is confirmed through titration of non-conjugated Cys556 residues with MMBC (ThioGlo1®) and MALDI-TOF measurement.

The obtained biohybrid catalysts achieved a TON of 365 with a slight shift in selectivity (cis/trans ratio 56/44 compared to 48/52 of Grubbs-Hoveyda catalyst). Residues which govern selectivity are currently identified and additional Ru-, Rh-, and Cu-catalysts are characterized.

![Figure 3.8: Hybrid catalyst composed of FhuA ΔCVFtev protein and a Grubbs-Hoveyda type catalyst with a maleimide linking unit.](image-url)
Integrated Research Field A4: Intermediates to Fuels
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// Vision
IRF-A4 focuses on catalytic transformations of cellulose derived intermediates into potential fuel molecules. For production of targeted oxygenates, selective catalytic deoxygenation strategies have to be developed aiming for
- An efficient hydrogen management;
- Selective defunctionalization pathways and
- Novel fuel motifs applying CC-coupling reactions.
Main intermediates under study cover 5-HMF and furfural, formic, levulinic and itaconic acid as well as hydroxyalkanoate. Potential fuel compounds under investigation can be summarized under the following categories including alcohols and aldehydes, ethers and esters, lactones, furan and tetrahydrofuran derivatives.

// Main Results Summary
Major progress concerning a selective hydrogenation of 5-HMF into 2,5-dimethylfuran catalyzed by PtCo enclosed in hollow carbon nanospheres could be reached. Also novel catalysts for aldol condensation of furfural and 5-HMF followed by hydrogenation to novel C8 and C9 fuel compounds were demonstrated covering molecular as well as solid catalysts. While molecular ruthenium catalysts enabled the production of 1-octanol, supported copper-based catalysts offer access to 2-butenyl-5-methylfuran. A selective hydrogenation of levulinic acid under solvent free conditions and in the presence of water could be achieved. Also a direct hydrogenation of levulinic acid into 2-MTHF over heterogeneous catalysts could be demonstrated but requires removal of water released during the reaction. Without water removal levulinic acid is converted into a mixture of 2-propanol, 2-butanol and methane. Also progress concerning a microbial electrocatalytic reduction of intermediates into fuels has been achieved. Alternative pathways via sorbitol and hydroxyalkanoate as intermediate allow broadening the fuel scope to cover e.g. C2-C12 alcohols, hexatrien, vinylfuran as well as isosorbide derivates.

// Results
Based on further developments concerning synthesis of 5-HMF, a selective transformation into 2,5-dimethylfuran (2,5-DMF) as C6 fuel compound. Schüth et al. developed a novel catalyst composed of PtCo nanoparticles with a diameter of 3.6±0.7 nm encapsulated in hollow carbon spheres (HCS). Up to 98% yield of 2,5-DMF at full conversion could be achieved within 2h at 180°C (Figure 3.9).

A promising technology enhancing the carbon chain length of furfural and 5-HMF is aldol condensation with e.g. acetone catalyzed by bases. In line, C8 compounds based on furfural and C9 compounds based on 5-HMF are accessible. For aldol condensation, Pupovac and Palkovits could confirm high activity and selectivity of mesoporous spinels such as MgAl2O4, ZnAl2O4 and CoAl2O4 overcoming the need for molecular bases, e.g. NaOH. Additionally, these materials can serve as catalyst support for copper nanoparticles resulting in a bifunctional catalyst for aldol condensation and subsequent hydrogenation. The hydrogenation over such Cu catalysts results in a selective formation of alkyl-functionalized furan molecules avoiding ring saturation. Therein, 2-butenyl-5-methylfuran and 2-butenyl-5-methylfuran could be formed as novel fuel candidates. Additionally, in the group of Leitner a tailored catalyst system based on Ru nanoparticles and an acidic additive could be identified. The catalyst facilitates the formation of primary alcohol, e.g. based on aldol condensation of furfural and subsequent hydrogenation, a yield of 1-octanol and diocctylether of 93% could be reached.

Figure 3.9: Scheme for the synthesis of three different materials. a. The synthesis of uniform HFS. b. The synthesis of Pt@HCS. c. The synthesis of PtCo@HCS.
Current progress in the hydrogenation of levulinic acid over heterogeneous catalysts has been reached. Especially a selective hydrogenation of LA over Ru/C to yield 98% γ-valerolactone could be developed. Interestingly, both solvent free conditions as well as efficient conversions with water or alcohols as solvents are possible providing new opportunities for a combined reaction and process design. Also a further hydrogenation of γ-valerolactone into 2-MTHF over Ru/C is feasible yielding 43% 2-MTHF together with 2-butanol and 2-pentanol. To start from levulinic acid as substrate, water has to be removed from the system to suppress side reactions enhancing the formation of 2-butanol and 2-pentanol. Consequently, levulinic acid can be converted into 2-MTHF with 60% yield based on levulinic acid. In this regard, a potential utilization of alkyl levulinates as well as α-angelica lactone as substrates are under investigation, both enabling 2-MTHF formation avoiding water as by-products.

Further biomass derived intermediates under investigation comprehend sugar alcohols such as sorbitol and xylitol and hydroxyalkanoates, respectively. Concerning sugar alcohols, a novel versatile strategy facilitating oxygen removal comprehends deoxydehydration (DODH). Therein, sorbitol can be transformed into hexatrien and xylitol into penta-2,4-dienol. Investigations of reaction mechanism, substrate scope and catalyst development are currently under progress in the groups of Prof. Klankermayer and Palkovits. Other promising biomass-derived substrates are hydroxyalkanoates with tailored carbon chain-length available starting from Acetyl-CoA via the de novo fatty acid synthesis to the product specific enzyme RhlA (Blank group). RhlA esterifies two activated fatty acids and is present e.g. in the bacteria Pseudomonas aeruginosa. Based on first experiments, the group of Klankermayer could demonstrate a selective hydrogenation of these feedstocks into octanol. Further studies are under progress.
Integrated Research Field A5: Multiphase Reaction Integration

// Vision
The sub-IRF addresses new approaches and methodologies for the separation of products, the recycling of catalysts in complex fluid mixtures, and the control of molecular processes under multiphasic conditions. Major goals are (1) to promote selectivity and rates of conversion by controlling (bio-)catalyst performance and reaction equilibria, (2) to facilitate in-situ product removal, and (3) to allow integration of unit operations.

// Main Results Summary
Two multi-phase reaction systems emerge as viable candidates: (a) the simultaneous saccharification and fermentation (SSF) and (b) a cascade two-phase system for the acid-catalysed dehydration of glucose to 5-hydroxymethylfurfural (5-HMF) and subsequent transformation to 2,5-dimethylfuran (2,5-DMF).

// Results
For the SSF system, two microorganisms are envisioned to cooperate on the direct conversion of cellulose to itaconic acid. T. reesei produces cellulases which then are used subsequently for the depolymerization of cellulose: A. terreus converts the glucose finally into itaconic acid. The challenge of this system lies in the difference of optimum fermentation and reaction conditions of each of the microorganisms and enzymes. T. reesei operates best at pH 3-4 while A. terreus produces ItAc best at pH=2. Cellulases show highest activity at pH=4.8. Also optimum operation temperatures differ requiring probably new reactor designs with temperature looping. First fermentations are performed and glucose production could be identified, however, subsequent ItAc production remains difficult. Critical limiting reaction steps in this cascade system are currently identified.

In the cascade bi-phasic system to turn glucose to 2,5-DMF Nickel based catalysts have demonstrated to perform the transformation of 5-HMF to 2,5-DMF. Appropriate solvent combinations are in developmental state. Yields and reaction selectivity are currently characterized. For the analytics to quantify reaction kinetics in-situ spectroscopic methods are integrated into the biphasic system. ATR-UV/Vis and Raman Spectra indicate the consumption of 5-HMF and production 2,5-DMF. Using chemo-metric modeling tools are currently applied to extract kinetic data under various process conditions.
**Integrated Research Field A6: Reference Process**

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**Vision**

The integrated research field (IRF) A6 is heading for an entirely new approach with the design and realization of a complete reference process for a TMFB-based biorefinery ranging from biomass to a target fuel. In contrast to commercially oriented bio-refinery projects, the IRF-A6 aims at providing a generally-applicable scientific methodology on the basis of a realistic case study, rather than optimizing a proprietary single solution. The overall conceptual process design will be based on a holistic mathematical model incorporating sustainability criteria.

**Main Results Summary**

Within the IRF-A6 a considerable number of process units are combined. The scientific problems resulting from the integration of different process units are specifically investigated. To gain knowledge on the transfer of a model to a real process, each unit will provide its product stream to the subsequent unit. Therefore, impact of impurities and feasibility of recycling of components and solvents are currently under investigation to assess how often and under which conditions enzymes, solvents and other valuable process streams can be (re)used.

**Results**

The first steps of the reference process are the mechanical disintegration (Qingqi Yan) and the chemical fractionation also referred to as the OrganoCat process (Philipp Grande) of the plant biomass. To prove the feasibility of the OrganoCat with real substrate, reed was pretreated with mills and a screw press at the Chair of Mechanical Engineering and subjected to chemical fractionation at the Institute of Technical Chemistry. The fractionation of the pretreated reed could successfully be performed, additionally resulting in a higher sugar yield in the subsequent enzymatic hydrolysis step. The results are being prepared for publication. To further investigate the impact of the chemical biomass pretreatment, the Chairs of Technical Chemistry and Biochemical Engineering performed joint experiments. The fermentative production of itaconic acid was achieved on pretreated cellulose in seawater as well as on the hydrolysed hemicellulosic fraction of pretreated beech wood. The results were published in Microbial Cell Factories in 2012.

To increase the efficiency of cellulose hydrolysis (Megan Garvey) new designs for cellulosomes are under investigation. In 2013 the Institute of Molecular Biotechnology published a review article on this topic in Trends of Biotechnology.

The first funding period of the Cluster of Excellence has shown that itaconic acid production with Ustilago maydis is quite challenging. To ensure a high product concentration in the fermentation process, which is a fundamental element of the reference process, Aspergillus terreus is under investigation as an alternative production strain (Dirk Kreyenschulte, Sandra Wewetzer). To avoid product inhibition, the Chairs of Chemical and Biochemical Engineering developed a membrane reactor which enables the in-situ recovery of itaconic acid from a continuous culture. These results were published in 2013 (two publications in Bioresource Technology).

Depending on the different options for fermentation (organism, mode of operation), various ways for the downstream processing are possible. For this reason, the Chair of Process Systems Engineering (Kirsten Ulonska, Christian Redepenning) simulates and optimizes energy demand and efficiency for downstream scenarios including filtration, crystallization, extraction, reverse osmosis, electrodialysis and rectification. To confirm these simulations with empirical data the Chair of Chemical Process Engineering (Frederike Castensen, Jan Stodilick) performs experiments with model solutions and fermentation broth of Ustilago maydis and Aspergillus terreus. First results for the application of an electrodialysis were published in the Journal of Membrane Science. To investigate several options for an in-situ extraction of itaconic acid directly in the bioreactor, the Chairs and Institutes of Technical Chemistry (Lotte Wiermans), Chemical Process Engineering (Axel Böcking) and Biochemical Engineering (Dirk Kreyenschulte, Sandra Wewetzer) test various extracting agents to elucidate their efficiency and biocompatibility.

The heterogeneous conversion of itaconic acid to 3-MTHF is currently under investigation at the Institute of Technical Chemistry (Sven Wiezorkowski). The Institute of Applied Microbiology and the Chair of Biochemical Engineering provide fermentation broth from Ustilago maydis and Aspergillus terreus.

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![Figure 3.14: Possible downstream route based on crystallization.](image-url)
**List of Projects IRF-A**

**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 a quantification and a mechanistic understanding of pretreatment and conversion of biomass in media of high ionic strength with the aid of spectroscopy. This includes quantification of the pretreatment as well as modelling the ionic interaction, which should then be exploited in the design of a solvent mixture with most favorable properties including simple recycling.

**Results**  
The pretreatment of wood was investigated in ionic liquids in order to assess feasibility and viability on process level. Though the pretreatment shows superior effects in comparison to other established process concepts, the ionic liquid recycling poses an economic challenge. Further mechanistic analyses of diverse concentrated electrolytic media now aim at the design of efficient but cheap electrolytic media.

**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 celluloses.

**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).

**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 aim of this project is the mechanocatalytic depolymerization of lignocellulose and the downstream of the water-soluble products.

**Results**  
A new method for biomass fractionation was successfully developed. Also the investigation of the downstream processing of „water-soluble wood“ was successful.

**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**  
Kinetic modelling of an enzymatic hydrolysis process using population balance modelling. The model should describe various enzyme activities, micro- and macroscopic biomass substrate properties.

**Results**  
The interaction of the enzyme with cello-oligomers was modelled by a mechanistically correct modelling approach based on a discrete population balance. Inhibiting effects of the oligomers on the enzyme could be identified.
Aim
We developed a kinetic Monte Carlo model to simulate the break-up of large, realistic cellulose bundles in pretreatment solvents. This model was based upon the results of explicit, all-atom molecular dynamics simulations, extending the length and time scales accessible via simulation to the process scale.

Results
The results of the model showed that separation of strands from the middle of the bundles was extremely important in addition to strand unzipping from the bundle edges. Moreover dissolution times were predicted to be on the order of a few microseconds, with large variance from simulation to simulation.

Aim
Our work is focused on protein engineering of laccase for improved resistance in ionic liquids/organic solvents, which can be subsequently employed for efficient depolymerization of lignin in ionic liquids/organic solvents. The enzymatic conversion of lignin is addressed using fungal laccases in combination with certain mediator molecules. The identification of suitable reaction conditions is crucial to realize laccase catalysed lignin degradation.

Results
A biocatalytic pre-oxidation of lignin, facilitating further chemical cleaving reactions, has already been realized. Laccases have also been successfully applied for an enzymatic disintegration of biomass promoting the subsequent cellulose hydrolysis.

Aim
Aim of this project is to investigate the fractionation of ligno-cellulosic substances and solvent recovery via membrane technology. The applicability of membrane technology is broad as it allows for separation of charged and neutral substances on particulate and molecular level under mild conditions.

Results
Membrane technology by means of nanofiltration was applied to purify ionic liquids from residuals of the wood dissolution process. A downstream process including ultrafiltration, nanofiltration and electrodialysis was set up to recover glucose from an ionic liquid assisted cellulose dissolution process.

Aim
We are applying non-precious metal catalysts or metal-free conditions for the selective degradation of lignin and lignin model compounds and developing a molecular understanding for the observed reaction pathways.

Results
We established a solvent-free process in the ball mill for the cleavage of representative lignin bonds in model compounds, Organosolv-lignin and beech wood. Furthermore, heterogeneous hydrotalcite-like catalysts in the selective oxidative cleavage of lignin model compounds, Organosolv-lignin and kraft lignin were employed.
Project IRF-A2-3 “Knowledge-Based Identification of Lignin Degrading Enzymes from Non Conventional Sources”  
Fraunhofer Institute for Molecular Biology and Applied Ecology (Prof. Rainer Fischer)

Aim  
Our aim is the identification of suitable genes which code for ligninolytic enzymes as well as the creation of tailored enzyme cocktails containing different sets of ligninolytic enzymes which can be used in lignin degradation.

Results  
We selected promising ligninolytic enzymes from fungi. Heterologous expression of these enzymes within a yeast expression system that allows high and active protein yields.

Project IRF-A2-4 “Development of Metal Alloy Catalysts for the Hydrogenolysis of Lignin”  
Max-Planck-Institut für Kohlenforschung (Dr. Roberto Rinaldi)

Aim  
The objective of this project is the depolymerization and conversion of lignin into biofuels.

Results  
We were able to perform following results: Assessment of solvent effects on the catalytic activity of Raney Ni / Pioneering the use of H-transfer reactions in the upgrading of lignin and bio-oils / Tandem conversion of lignin into arenes / Catalytic biorefining through H-transfer reactions.

Project IRF-A2-5 “Electrochemical Membrane Reactors (ecMR) for Conversion of Bio-Renewables”  
Aachen Chemical Engineering – Chemical Process Engineering (Prof. Matthias Wessling)

Aim  
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-Functionalization of Lignin”  
Mechanisms in Catalysis (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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Our aim is the identification of suitable genes which code for ligninolytic enzymes as well as the creation of tailored enzyme cocktails containing different sets of ligninolytic enzymes which can be used in lignin degradation.

Results  
We selected promising ligninolytic enzymes from fungi. Heterologous expression of these enzymes within a yeast expression system that allows high and active protein yields.
Project IRF-A2-7 “Bio-Cracking: Enzymes for Tailor-Made Lignin Fractionation”
Biocatalysis (Prof. Anett Schallmey), Institute of Technical Chemistry and Macromolecular Chemistry (Dr. Pablo Domínguez)

Aim
Cloning, overexpression, and exploitation of bacterial b-etherases for the efficient and selective conversion of lignin into valuable aromatic compounds.

Results
Novel bacterial b-etherases have been identified, recombinantly produced and characterized in the conversion of different lignin model compounds. Furthermore, the enzymes have been shown to work on lignin polymers as well.

Institute of Technical Chemistry and Macromolecular Chemistry (Prof. Walter Leitner), Institute of Biotechnology (Prof. Ulrich Schwaneberg)

Aim
The aim is the synthesis of artificial metalloenzymes via the incorporation of transition metal complexes into FhuA channel protein.

Results
A tailored multidentate phosphine ligand for selective binding to the cysteine in the engineered FhuA channel protein could be developed. Peptide fragments containing free cysteine as binding site were also produced as reference.

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
Our project is focused on the development of biohybrid catalyst systems (composed of a protein backbone FhuA and a metal catalyst) for catalyzing TMFB relevant reactions from biomass-derived intermediates. The FhuA channel acting as a second ligands sphere will be reengineered to tune the selectivity of the biohybrid catalyst.

Results
A FhuA based hybrid catalyst was successfully prepared by covalently anchoring a Grubbs-Hoveyda type olefin metathesis catalyst at a single accessible cysteine in the interior of FhuA. Activity of this hybrid catalyst was demonstrated by ring-opening metathesis polymerization of a 7-oxygenborne derivative in aqueous solution (published).

Project IRF-A3-1 “Automated Screening System for Rational Selection and Characterization of Most Efficient Biocatalysts and Process Parameters”
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
A pre-screening of an E.coli clone bank for recombinant cellulase expression could be performed with the automated RoboLector screening platform and was followed by an improvement of cellulase production in yeast. Moreover a new tempering system for microtiter plates was investigated which allows a fast determination of temperature optima for microbial and enzymatic processes.
Project **IRF-A3-4 “Rational Strain Engineering: Constructing a Hyper Itaconic Acid Producer”**
Institute of Applied Microbiology (Prof. Lars Blank)

**Aim**
Within this project, we construct a hyper itaconate producer by rational strain engineering.

**Results**
*Ustilago maydis* MB215, showing the highest biocatalytical potential out of 70 tested Ustilaginaceae concerning itaconate production, was characterized towards its xylan-degrading and itaconate producing capabilities. Within this project the itaconate biosynthesis pathway of *U. maydis* including corresponding enzymes and their catalytic function was clarified and initial metabolic engineering already led to a significant enhancement of *Ustilago*’s itaconate production.

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

**Aim**
The aim of this project is to establish a biological route for the synthesis of precursors for fuel production from sugars. This will be achieved by using a recombinant whole-cell biocatalyst.

**Results**
A preliminary expression system led to microbial production of the molecule of interest using glucose as carbon source with a low titer (<0.5 g/L). First purification protocols were evaluated and up to 500 mg of the material were isolated.

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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 are the density functional theory (DFT) guided studies of the mechanisms of hydrogen transfer reaction relevant for TMFB. Those include: the hydrogenation of methyl benzoate, the conversion of CO2 to methanol, and the re-catalyzed deoxydehydration of sorbitan.

**Results**
Within our studies, a coherent understanding of the hydrogenation of methyl benzoate, as well as the deoxydehydration of sorbitan was achieved. A variety of possible mechanisms for the conversion of CO2 to methanol were found and examined in detail.

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Project **IRF-A4-1: “New Synthetic Pathways for Tailor-Made Fuels – Selective Catalytic Defunctionalization of Platform Chemicals”**
Institute of Technical and Macromolecular Chemistry
(Prof. Walter Leitner, Prof. Jürgen Klankermayer)

**Aim**
The objective of this project is the development of effective ruthenium catalysts based on the Ru(triphos) structure for the selective conversion of platform molecules.

**Results**
New derivatives of Ru(Triphos) catalyst were developed and showed excellent activity in the reduction of itaconic acid. Based on the highly stable catalyst a reaction system for the conversion of itaconic acid in water could be developed.

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**Summary**

Activities 2012-2014
### 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**
The project focuses on making use of the deoxydehydration reaction as novel deoxygenation method for the conversion of sugars and sugar alcohols to valuable fuel additives.

**Results**
The viability of the deoxydehydration in biomass conversion was improved by making use of an open reaction system. Activity and selectivity were enhanced and the system was 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**
Transformation of carbohydrate fractions to platform chemicals and subsequently to fuel components relies in many cases on catalysts based on rare and therefore expensive metals. Project A4-4 focuses on fundamental research on alternative catalytic systems based on (early) transition and main group metals.

**Results**
Molybdenum complexes for homogeneous catalysis were synthesized and tested in deoxydehydration reactions of di- and polyols. In the continuing search for substitutes for chromium in the production of HMF, Group 3 and Group 13 metals were identified as potential candidates and Lewis basic ligands offer the possibility to adjust activity and selectivity.

### Project IRF-A4-5: “Conversion of Glucose to Methyl-THF over Polymeric Catalysts”
Max-Planck-Institut für Kohlenforschung (Prof. Ferdi Schüth)

**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 96% 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-A4-6: “Microbially-Catalyzed Reduction of Biomass Intermediates to Tailor-Made Fuels”
Microbial Electrocatalysis (Prof. Miriam Agler-Rosenbaum)

**Aim**
This project aims to screen for new biocatalysts and explore the microbial reduction of precursor chemicals (itaconic and levulinic acid) to target compounds, whereby a cathode or renewable hydrogen provide the necessary reducing equivalents for the microbial reaction.

**Results**
The bacterial strains were tested for their ability to oxidize the cathode in a entirely new designed medium-throughput reactor and the positive ones were tested for the acids reduction. Four were able to metabolize itaconic acid while three were successful with levulinic acid. Further analyses are being performed in order to confirm whether the acids are being consumed or reduced into other compounds, and which compounds are being produced.
Project: IRF-A4-7 “Reactive Molecular Dynamics of Biomass Compounds in Novel Solvents”
Aachen Chemical Engineering - Molecular Simulations and Transformations (Prof. Ahmed Ismail)

Aim: Using molecular dynamics method to simulate and investigate the behavior of ionic liquids as solvents in the process of dissolution of lignocellulosic biomass and conversion to biofuels.

Results: Important physiochemical quantities of several ionic liquid-water mixtures have been analyzed, namely: liquid densities, structural properties (radial distribution functions, molecular volumes, water clustering and hydrogen bonding) and dynamical properties (shear viscosity and diffusion coefficients) have been analyzed.

Project: IRF-A4-8 “Genetic Manipulation of Clostridium ljungdahlii for the Reduction of Biomass Intermediates to Tailor-Made Fuels”
Microbial Electrocatalysis (Prof. Miriam Agler-Rosenbaum)

Aim: Within this project, we explore the genetic manipulation of a microbial biocatalyst for the microbial reduction of precursor chemicals (e.g., itaconic acid, levulinic acid) to target compounds (reduced alcohols and lactones (e.g., γ-butyrolactones and γ-valerolactones) with a cathode as the source for the necessary reducing equivalents for the microbial reaction.

Results: Proof of electro-reductive activity of Clostridium ljungdahlii on the cathode and development of an improved microbial synthesis cell operation mode. Success in the development/improvement of new molecular biological methods for Clostridia (e.g. transformation protocol, inducible promoters for controlled gene expression) and the construction of a whole cell rapid evolution tool.

Project: IRF-A5-1: “Biphasic Reaction Systems for Selective Transformation of Glucose into 5-Hydroxymethylfurfural Based Fuel Molecules”
Institute of Technical and Macromolecular Chemistry (Prof. Regina Palkovits, Prof. Marcel Liauw)

Aim: The research includes investigations on a biphasic reaction system for the dehydration of glucose to 5-hydroxymethylfurfural in an aqueous phase, the continuous extraction into an organic phase, and the hydrogenation into less polar dimethylfuran. These investigations are accompanied by the development of a reactor setup for in-situ spectroscopy of these multiphase conversions allowing the analysis of phase behavior, extraction and reaction kinetics.

Results: Among other results, catalyst screenings and measurement of separation coefficients resulted in a promising reaction system for the conversion of 5-hydroxymethylfurfural to dimethylfuran. The high-pressure reactor setup allowing simultaneous ATR-UV/Vis, ATR-mIR and Raman spectroscopic monitoring was successfully installed, first sugar dehydrations were performed and first insights into the reaction kinetics and humin formation were gained.

Institute of Technical and Macromolecular Chemistry (Prof. Jürgen Klankermayer)

Aim: The focus of the project is the development, understanding and optimization of new homogeneous catalysts for the selective reduction of biogenic compounds.

Results: 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.

Institute of Technical and Macromolecular Chemistry (Prof. Regina Palkovits, Prof. Marcel Liauw)

Aim: The research includes investigations on a biphasic reaction system for the dehydration of glucose to 5-hydroxymethylfurfural in an aqueous phase, the continuous extraction into an organic phase, and the hydrogenation into less polar dimethylfuran. These investigations are accompanied by the development of a reactor setup for in-situ spectroscopy of these multiphase conversions allowing the analysis of phase behavior, extraction and reaction kinetics.

Results: Among other results, catalyst screenings and measurement of separation coefficients resulted in a promising reaction system for the conversion of 5-hydroxymethylfurfural to dimethylfuran. The high-pressure reactor setup allowing simultaneous ATR-UV/Vis, ATR-mIR and Raman spectroscopic monitoring was successfully installed, first sugar dehydrations were performed and first insights into the reaction kinetics and humin formation were gained.
**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 a relevant TMFB chemical reaction using online measurement techniques and the Model-based Experimental Analysis methodology. The identified kinetics can be later used for the development of a new methodology that links reaction identification with conceptual design for a rapid reactor design.

**Results**  
Various biphasic reaction systems are being studied in order to find a suitable (and relevant to the TMFB cluster) reaction, in which it is possible to get on-line measurements in both phases. 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.

**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 Electro catalysis (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**  
We developed the fermentation medium for two possible mixed cultures, consisting of T. reesei and A. terreus or T. reesei and U. maydis. Afterwards, different parameters for the production of cellulolytic enzymes by T. reesei were evaluated.

**Project IRF-A5-4: “Holistic Design of Biofuel Separations”**  
Institute of Technical Thermodynamics (Prof. André Bardow)

**Aim**  
This project aims at the development of process flowsheet variants for the efficient production of biofuels. Furthermore, a methodology will be developed for the simultaneous design of processes and materials for biofuel production.

**Results**  
Flowsheet simulations were employed to investigate possible routes for the conversion of levulinic acid to γ-valerolactone. The evaluation of purification steps with respect to energetic costs shows promising separation strategies and challenges for further work.

**Project IRF-A6-1: “Conceptual Process Design for Biorenewable Fuel Production”**  
Aachen Chemical Engineering – Process Systems Engineering (Prof. Alexander Mitsos)

**Aim**  
In the reference process lignocellulose biomass is converted into the fuel candidate methyltetrahydrofuran, which will finally be produced in a demonstrator plant. This project targets at a conceptual development of promising process concepts. Systematic methodologies for the reliable evaluation and identification of optimal process configurations are developed, considering e.g. the complex electrolyte nature of bioprocesses in integrated hybrid separation steps.

**Results**  
Following a conceptual design methodology, bottlenecks of the reference process were systematically identified leading to alternative downstream concepts for an efficient path to methyltetrahydrofuran, which involved e.g. membrane separations, liquid-liquid extraction in combination with fermentation. Compared to early concepts the energy requirement was halved, yielding a cost-efficient and sustainable bio-process alternative.
Project: IRF-A6-2 “Integrated Mechanical Pretreatment of Biomass”
Aachen Chemical Engineering - Mechanical Process Engineering (Prof. Michael Modigell)

Aim:
The main research objective is the development of a novel pretreatment process for biomass which integrates mechanical and chemical decomposition of its structure and allows for efficient depolymerisation of the biomass.

Results:
The results indicate that screw press pretreatment leads to a higher disruption of the lignocellulosic structures and increases effectively the extraction process rate of lignin and hemicellulose from the biomass. The combination of mechanical and chemical (NaOH) pretreatment of lignocellulosic biomass in the screw press/reactor increases the glucose and xylose yields after enzymatic saccharification.

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 is the direct fermentative conversion of pretreated lignocellulosic biomass to the platform chemical itaconic acid. To improve process efficiency, an SSF process will be established as well as an integrated product recovery.

Results:
Sugar conversion from hydrolysate was performed with two different microorganisms (Ustilago maydis, Aspergillus terreus). In regards of integrated product recovery the biocompatibility of different solvents was investigated, additionally a fermentation with in-situ reverse flow diafiltration was conducted.

Fraunhofer Institute for Molecular Biology and Applied Ecology (Prof. Rainer Fischer)

Aim:
The objective is the production of cellulases for enzymatic degradation of cellulose pulp into glucose, as well as tailoring protein expression and structure to TMFB goals, such as through high yield recombinant expression systems and enzyme immobilization to produce recyclable enzyme complexes.

Results:
We were able to express multiple thermo-, pH- and salt-tolerant cellulase enzymes, originally from fungal and bacterial sources within a yeast expression system. Immobilization of an endoglucanase enzyme in an active form was performed.

Project: IRF-A6-5: “Organic Acid-Catalyzed Fractionation of Lignocellulose”
Institute of Technical Chemistry and Macromolecular Chemistry (Dr. Pablo Domínguez)

Aim:
Lignocellulose is pulped and fractionated with the completely biobased biphasic OrganoCat process. In the lower aqueous reaction phase hemicellulose is selectively hydrolyzed via oxalic acid while lignin is in-situ extracted into the upper 2-MTHF phase.

Results:
The processable biomass loading was enhanced to 400 g L-1 by „repetitive batches” and the process was successfully scaled up to 3 L scale. The process analysis shows reduced capital costs and energy demand in the solvent recovery at the same productivity which increases the annual earnings from 2.4 to 3.7 Mio $/a.
Project

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

Aim
In this project supported metal nanocatalysts were synthesized via different methodologies. Their performance was tested in the dehydration of sugars to levulinic acid, in the hydrogenation of levulinic acid to γ-valerolactone and in the synthesis of 1-octanol and dioctyl ether from furfural and acetone.

Results
Full conversions and γ-valerolactone selectivities of 99% were obtained in the hydrogenation of levulinic acid. Furfural-acetone could be converted into linear C-8 alcohol products in up to 93% yield.

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 lignocellulose platform chemical furfural can be employed in a reaction cascade towards the formation of an aliphatic alcohol, 1-octanol. The key step in this transformation is the development of a bifunctional catalyst required to catalyze the dehydration and hydrogenation/hydrogenolysis of tetrahydrofuran substrates.

Results
Integration of an acid and metal catalyst onto a silica support allowed for the creation of supported bifunctional catalysts required for the deoxygenation of lignocellulose platform chemicals. Bifunctional catalysts were employed under batch conditions in the selective formation of 2-butyltetrahydrofuran, 1-octanol and 1,1-diocytylether starting from furfural and were also used in the preparation of 1-nonanol starting from 5-hydroxymethylfurfural (HMF).

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
This project is about the downstreaming concept. Its main purpose is the connection between the fermentation and the chemical hydrolysis.

Results
The transport resistance of itaconic acid over ion exchange membranes has been characterized. In addition more process concepts for the downstreaming have been developed.
Integrated Research Field B: From Biofuels to Propulsion

// Prof. Dr.-Ing. Heinz Pitsch
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Vision

Custom-made bio-derived fuels provide new opportunities in tailoring fuels for specific engine needs as well as 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, the IRF-B is divided in 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 systems perspective in system scale facilities and test engines regarding their emission behavior, their tribology properties, and effects on exhaust gas aftertreatment.

Main Results

Within the first part of the second funding period, bio-derived fuel candidates for diesel and gasoline fuels have been investigated in the IRF-B. The chemical kinetics group (IRF-B1) provided new chemical mechanisms validated against ignition delay times and laminar burning velocities measured in the experimental projects for a broad variety of TMFB-fuels, e.g. 1-octanol, di-n-butyl ether (DnBE) for diesel engines and 2-MF and 2-MTHF for spark-ignition engines. Within the IRF-B2, the evaporation and atomization process, the spray formation, mixing and combustion as well as the effect of turbulence on the spray behavior were investigated in simulations and in experiments. With these results, new correlations of spray penetration length and spray cone angle for a wide range of fuel properties could be provided as an example. In the IRF-B3 group, mainly three TMFB fuels have been investigated in experiments and simulation. 1-octanol and DnBE as possible diesel engine candidates significantly reduce PM-emissions without efficiency losses. 2-butanone for SI-engine-type conditions allows for higher compression ratios and hence higher efficiencies due to its high knock-resistance. As a consequence, ketones and other carbonyl-containing fuels will be in the focus of fundamental future work on chemical kinetics and mixing.
// Vision
The combustion kinetics research domain IRF-B-1 is concerned with two major tasks. The first 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 systems design within the Fuel Injection and Combustion Systems research domain (IRF-B-3). The second task is to establish detailed descriptions of the chemical kinetic processes and to investigate the fuel structure’s impact on the combustion process. An emphasis 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. Further key aspects are the implementation of more detailed speciation measurements in all experiments and the characterization of emissions from biofuels.

// Main Results Summary
Accurate detailed chemical mechanisms for the oxidation of the new biofuels n-butyl formate, di-n-butyl ether (DBE) and n-octanol were developed, 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 shock tubes, a rapid compression machine, a flow reactor, and a spherical combustion vessel to quantitatively describe their combustion behavior. The determined ignition delay times and laminar burning velocities were used as primary validation targets for kinetic modeling. The proposed detailed mechanisms were reduced and successfully applied in CFD calculations in IRF-B3. In addition, a comparison of the novel biofuels, DBE and n-octanol, which have the same elementary composition (C_8H_{18}O), but different molecular structures, was conducted to analyze the impact of fuel structure and functional groups on combustion in real engines.

// 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 regard 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. In the previous research period, it was found that, because of the large number of possible oxygen-containing functional groups (e.g. alcohol, ester and ether groups) and molecular arrangements, and the variety of important combustion characteristics, it is imperative to study a large number of molecules in different relevant combustion regimes, including auto-ignition and both premixed and diffusion flames. In this sense, three novel biofuels, n-butyl formate, di-n-butyl ether, and n-octanol were studied as representative species for ester, ether, and alcohol fuels.

// n-Butyl formate
As example of an alkyl ester, n-butyl formate has been the focus of an experimental and numerical study. Ignition delay times have been measured for stoichiometric mixtures of fuel and air in a high-pressure shock tube and in a rapid compression machine. Laminar burning velocities have been determined for equivalence ratios ranging from 0.8 to 1.2 in a high-pressure chamber with an optical Schlieren cinematography setup at a pressure of 10 bar and a temperature of 373 K. A detailed kinetic model has been constructed including high- and low-temperature reaction pathways. The performed ab-initio calculations supported the mechanism development with reaction rate constants and thermochemistry of species and allowed for the analysis of species that are hardly accessible experimentally. For 23 species in the n-butyl formate mechanism, enthalpies of formation, entropies, and specific heats have been computed. In addition, rate constants of hydrogen abstraction by H and HO_2 radicals were determined. The experimental and numerical ignition delay times are compared in Figure 3.16 and good agreement is observed over the entire investigated temperature range. The importance of the low-temperature peroxochemistry in the n-butyl formate model has been revealed through sensitivity and reaction path analyses.

Figure 3.16: Ignition delay times of a stoichiometric n-butyl formate/air mixture at pressures of 20 and 90 bar.
// Di-n-butyl ether
A long-chain linear symmetric ether, di-n-butyl ether, has been identified recently as a candidate biofuel produced from lignocellulosic biomass and has been investigated in IRF-B1. Ignition delay times have been measured at low temperatures in a flow reactor. The laminar flame speeds of DBE/air mixtures have been determined in the framework of an international collaboration in a stagnation flame configuration for a wide range of equivalence ratios at atmospheric pressure and an unburned reactant temperature of 373 K. All experimental data have been modeled using the developed kinetic model. The agreement between measured and computed results is satisfactory, and the model has been further used to elucidate the oxidation pathways of DBE. The dissociation of keto-hydroperoxides, leading to radical chain branching is found to dominate the ignition of DBE in the low-temperature regime.

// n-Octanol
The first investigation on the combustion chemistry of n-octanol, a long chain alcohol, has been conducted in IRF-B1 to complete the study on the influence of ester, ether and alcohol functional groups on combustion. Ignition delay times have been determined experimentally in a high-pressure shock tube for a range of initial conditions. A detailed kinetic model has been developed to describe the oxidation of n-octanol at both low and high temperatures, and the model shows good agreement with the presented experimental dataset. The ignition delay times of n-octanol are compared in Figure 3.18 to those of n-octane and DBE to illustrate the effects of the functional group on ignition propensity. In comparison to n-octane, the hydroxyl moiety in n-octanol results in an inhibited fuel reactivity, while the ether group in the molecular structure enhances the ignition propensity of DBE.

// Furans
Furans have been widely regarded as potential gasoline alternative fuels. In the framework of IRF-B1, a chemical kinetic model to simulate the oxidation of 2-methylfuran/n-heptane blends under low to intermediate temperature conditions has been developed and validated against low temperature rapid compression machine data. In order to achieve a more detailed understanding of the reactions consuming the fuel, a reaction pathway analysis has been carried out at various conditions, which revealed that the main consumption pathways of 2-methylfuran are OH addition to the fuel followed by O₂ addition and H-abstraction reactions of the fuel by OH radicals. Ab-initio calculations have been carried out also for other furans such as tetrahydrofuran.

// Soot measurements
The soot formation of bio-derived fuels is known to be fairly different compared to crude oil based fuels. In spite of the rising importance of biofuels in the transportation sector, a detailed understanding of the effect of biofuels on structure and chemical properties of soot is still lacking. Within the scope of IRF-B1, this knowledge gap will be addressed. Experimental data on the soot formation of biofuels in flames will be obtained in a laminar counterflow burner and used to develop multi-variant soot models. Within the first year of the second funding period, a new counterflow burner has been designed and set-up. First, particle image velocimetry measurements have been performed to evaluate the flow profile at the nozzle exit. Afterwards, extinction strain rates of different gaseous fuels were measured and compared against literature data for the verification of the burner setup. Simultaneously, both a laser induced incandescence and a laser-extinction system have been set up, which will be used for the investigation of soot formation in the counterflow burner.
Integrated Research Field B2: Fuel Spray, Flow and Mixing

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// Vision
The Fuel, Spray, Flow and Mixing research domain thoroughly investigates the impact of the composition of novel biofuels on spray penetration, evaporation, mixing, and the resulting effect on ignition delay and pollutant formation under engine conditions, and a quantitative description of fuel structure and fuel performance in regard to these processes will be developed. To fully understand the flow physics of the novel biofuels, it is necessary to perform highly resolved experimental and numerical analyses, and thereby to determine the complete highly intricate three-dimensional flow structure.

// Main Results Summary
Considering the breakup of liquids into sprays the newly developed numerical and experimental data base, based on direct numerical simulations and double-imaging microscope measurements, possesses the potential to improve the atomization model. The high-speed visualizations of the mixture formation of the TMFB-fuels shows a strong influence of the viscosity and the density of the fuels on the axial and radial liquid spray penetration. The impact of cyclic variations on the mixing process is evidenced by comparing the temporal development of the instantaneous and cycle-averaged turbulent kinetic energy. As to the numerical simulation an extremely efficient formulation for gaps smaller than the mesh size is introduced. The hybrid method consisting of a state equation and experimental data yields an excellent result for binary vapor liquid equilibrium data. The varying mixing and ignition properties of TMFB fuels are evidenced by simultaneously applying shadowgraphy and OH-chemiluminescence.

// Results
The experimental Analysis in IRF-B2-1 shows the formation of a tumble vortex at early crank angles which dominates the flow field in the symmetry plane throughout induction and compression. At approx. 320 CAD atdc, the tumble breaks up into smaller and smaller vortices, and the resulting high levels of turbulence contribute beneficially to the combustion process. The comparison of the temporal development of the instantaneous and cycle-averaged turbulent kinetic energies shows significant levels of cyclic variations. Furthermore, variable valve timing (VVT) has a strong influence on the mean vorticity and the local and temporal distribution of the mean and turbulent kinetic energy. The tumble stability is improved by the late opening of the intake valves, which also determines the amount of turbulent kinetic energy in the intake phase.

In IRF-B2-2 a level-set based mesh refinement for moving boundaries has been introduced to a highly parallelized framework, i.e., O(1000) processors are used. Cut cells with sub-cell resolution can be treated consistently. This allows to maintain a sharp interface between piston and cylinder liner. Furthermore, the flow through the valve gap at very low valve lifts can be simulated without a reduction of the computational time step even if the gap is much smaller than the local mesh size. Thus, the accuracy of the predicted in-cylinder air mass at the end of the intake stroke is considerably increased. The method has been successfully validated for a high-resolution LES of a three-dimensional axisymmetric piston-cylinder assembly with central valve during the intake stroke.

In IRF-B2-3 the fundamental physics of the initial breakup of liquids into sprays is analyzed by direct numerical simulations to develop a detailed atomization model for large-eddy simulations of spray-guided combustion. It has been found that the liquid viscosity and the surface tension are the most important physical properties. In addition, there is a sub-Kolmogorov breakup regime where the turbulent stress balances the surface tension and the viscous stress is of lower rank. The Euler-Eulerian atomization and the Euler-Lagrangian spray simulations are validated by experimental data of partner projects (Figure 3.19). This data base possesses the potential to improve the atomization model.

The highly transient and microscopic primary breakup process is fundamentally investigated in IRF-B2-4. A unique double-imaging microscope was developed. Information on shape, size, and velocity of primary liquid structures with extreme image quality is obtained (Figure 3.20). For velocity validation, a proprietary laser correlation velocimetry method was used. Additionally, ballistic imaging is used to investigate primary breakup. Despite promising new insights into primary breakup, it was found that ballistic imaging suffers from image distortions, which prevents high resolution imaging of micro-scale structures.

Within IRF-B2-5 mixture formation of the TMFB-fuels was investigated using high-speed visualizations. Measurements were carried out for diesel- and gasoline-engine conditions. A strong influence of the viscosity and density on axial and radial liquid spray penetration was found. New empirical correlations for liquid penetration and cone-angle were deduced for both conditions and a wide range of fuel properties. Moreover, a new planar temperature measurement technique was established using 2-color-laser induced fluorescence (LIF). A calibration chamber was designed to investigate the suitability of various temperature sensitive tracers on the TMFB-fuels and two suitable tracers Rhodamine B and Pyromethene 597-8C9 were identified.
To support spray and combustion modelling, extensive vapor liquid equilibrium (VLE) measurements of binary mixtures of promising biofuel candidates were conducted in IRF-B2-6 at next to engine-like temperatures and pressures. Then, the experimental effort to describe high-pressure VLE over a wide range of compositions, temperatures, and pressures was reduced. An excellent description and even extrapolation of binary VLE data is provided by the hybrid approach combining a quantum chemically based equation of state approach with experimental data. That is, experimental data for a single pure substance vapor pressure per component suffice to significantly reduce the experimental effort.

IRF-B2-7 focuses on the optical characterization of fuel dependent properties like e.g. liquid spray penetration, evaporation, mixture formation, physio-chemical ignition delay, combustion behavior, and initial pollutant formation at part- and full-load related boundary conditions. Two measurement techniques have been used for the tests at the high pressure chamber. The simultaneous visualization shadowgraphy and OH-chemiluminescence was applied to show the differences of the TMFB fuels concerning mixture formation and ignition behavior. The secondary measurement technique was a stereoscopic 3-color high-speed ratio-pyrometry, which allows a double redundant quantification of temperature, topology and emissivity of optically opaque flames with a temporal and spatial resolution of 10 kHz and 16 Pixels/mm².

Figure 3.19: Comparison of numerical and experimental results of droplet size distributions of four reference fuels at 20 mm downstream of the injector. (Experimental data from IRF-B2-5 (WSA))

Figure 3.20: Exemplary image showing the potential of the new double imaging microscope.
Integrated Research Field B3: Fuel Injection and Combustion Systems

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// 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 the 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 on the advancement of the conventional combustion system like adjusting the injection strategy and piston bowl design. Since the engine hardware for the optimal combustion process is highly depending on the fuel's characteristics, this is an iterative optimization process, which requires high interaction with the CIF in order to feed back the fuel characteristics desired for the optimal combustion system. Overall, the combustion system shall 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.

// Results
The IRF-B3 focuses on the application of the newly derived fuels in the engine. For this purpose, the processes during combustion in the cylinder are investigated in detail as well as the fuel injection system and the exhaust gas composition and its aftertreatment. Within all subprojects of IRF-B3, the main focus has been on the two new fuel candidates 1-octanol and di-n-butyl ether for diesel type combustion, and 2-butane and 2-methylfuran for spark-ignited engines.

Prior to the engine tests, lubricity and material compatibility have been investigated. For both characteristics, QSFR-models (Quantitative Structure Property Relationship) have been developed based on the experimental results. In addition to laboratory scale tests for screening purposes, the lubricity of the most promising candidates has been investigated via elasto-hydrodynamic simulation as well as by means of complex tribological model tests. All test results are indicating a superior tribological characteristic of 1-octanol compared to conventional diesel. In contrast, the lubricity of di-n-butyl ether seems to be not sufficient and consequently lubricating additives have to be used. In terms of material compatibility results are very diverse. There are candidates which provide a sufficient compatibility to the standard materials in injection systems as well as candidates which show degradation and great swelling. The latter require non-standard materials with a high chemical resistance.

Thermodynamic experiments have been carried out at two single cylinder research engines. Since the last status report, in particular the new fuels di-n-butyl ether and 1-octanol have been investigated at the diesel engine, but also blends of 2-methyltetrahydrofuran and di-n-butyl ether. Current investigations with conventional fossil fuels aim for a low temperature combustion that enables low soot- and NOx-emissions simultaneously. The drawback of these highly homogenous combustion strategies is in the elevated level of HC- and CO-emissions as well as the high combustion noise. However, with the highly volatile and oxygenated fuel di-n-butyl ether a rather mixing controlled combustion with very low soot-emissions can be maintained. Due to the very smooth combustion and the short ignition delay with di-n-butyl ether, even the level of HC- and CO-emissions as well as combustion noise behave better than conventional diesel fuel. At low engine loads it has been proven that an increased compression ratio is an appropriate counter measure for elevated HC- and CO-emissions using 1-octanol without sacrificing soot-emissions at higher loads, see Figure 3.21.

In order to fully characterize the HC-emissions with these novel tailor-made fuels, the emissions have been sampled and investigated by means of gas-chromatography and mass-spectroscopy. These investigations have shown that the HC-emissions mainly consist of the same components as those of conventional diesel fuel.
except very small amounts of furans that were found with di-n-butyl ether. The particulate matter has been investigated as well with regard to the size/number distribution. Here, it could be shown that both the oxygenated fuels contribute to a reduction in total particle number of up to factor 4 and a significant shift of the mean diameter to reduced particle sizes.

At the optical single cylinder engine, di-n-butyl ether and 1-octanol, have been investigated at n = 1500 min⁻¹, IMEP = 6.8 bar with varied external exhaust supply for simulated EGR using a high-speed visualization of OH* chemiluminescence and soot radiation. The very fast igniting di-n-butyl ether shows a soot radiation signal during combustion, while the more premixed pronounced combustion of 1-octanol shows almost no soot radiation. However, since both fuels had hardly any tailpipe soot emissions at the thermodynamic engine, this suggests that the soot formed during combustion of di-n-butyl ether is being oxidized, see Figure 3.22.

Regarding the thermodynamic gasoline engine 2-butanone showed a very good combustion behavior in terms of knock-resistance. Even though the full potential was not determined until now, the compression ratio could be raised to 13.5:1, giving a very high fuel efficiency. Similar results were found with 2-methylfuran. The onset of autoignition using 2-methylfuran occurs at lower engine loads than for ethanol and 2-butanone, but at higher loads than for RON 95. Moreover, the required combustion retardation has a significantly shallower gradient with engine load than when using RON 95. Thus, the CR can be raised by more than 3.5 units, which enables efficiency improvements ranging from 2.5 to 9.9 % compared to RON 95. For both 2-butanone and 2-methylfuran it can be stated that the mixture formation under challenging boundary conditions is superior to ethanol.

The origin of pre-ignition was investigated for 2-methylfuran and 2-methyltetrahydrofuran and also for gasoline and ethanol, by endoscopic high-speed imaging at high load and low speed. The observed overall pre-ignition tendencies of the furans and gasoline correspond to the octane rating, RON. By contrast, ethanol has a relatively high pre-ignition tendency, which cannot be explained by its octane qualities. Pre-ignition is most likely promoted by droplets in the charge, in particular for ethanol. Fuel-oil droplets are likely formed via spray/liner impingement. For ethanol, it is apparently not induced by any hot hardware component in this engine. Pre-ignition occurs in a seemingly random fashion for all the fuels in the current engine. Thus, it is apparently not influenced by prior-cycle effects.

The engine experiments are accompanied by detailed CFD-simulation, the main goal of which is to enable computationally efficient and highly accurate Large Eddy Simulations (LES) of internal combustion engine flow and combustion using the ITV-in-house code CIAO. In the past project phase, the focus of the conducted developments was to reduce the computational cost for engine flow simulations and to extend the existing framework for accurate reactive engine LES. For the first part, a local mesh refinement capability using the overset grid approach was implemented into the code. This allows for increased resolution only in those parts of the domain where it is physically needed. The new method has been successfully implemented and is currently available for compressible cold flow simulations. Some additional efforts are necessary to be able to use local mesh refinement in unsteady engine simulations. Simulations for verification of the spray models revealed the need for model extensions. Modifications to the evaporation model have been successfully finished and improved results could be obtained. These results have already been verified with the experimental data. The pressure trace of the simulation matches the recorded traces with both the fuels di-n-butyl ether and 1-octanol very well. Even the emission trend is captured already quite well. Adaptations to the numerical boundary methods for compressible flows in engine geometries were necessary. Robustness was significantly improved by the developments.
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 The aim is the chemical kinetic modeling and computational chemical kinetic study of biofuel combustion using ab-initio methods.

Results Detailed kinetic modeling work was focused on low temperature 2mfn-heptane ignition. Rate of production analysis and sensitivity analysis at various conditions helped understanding of this furan based biofuel. The resulting model shows same trends as low temperature experimental data obtained in the RCM (IRF B1-2). Furthermore, accurate rate coefficients have been determined for the hydrogen abstraction reactions from isopentanol by H and HO2 radicals using ab-inito methods improving the kinetic model of this biofuel.

Project IRF-B1-3 “Experimental Investigation of Ignition Delay Times in a High Pressure Shock Tube”
Shock Wave Laboratory (Prof. Herbert Olivier)

Aim Ignition delay time measurements and visualization of ignition processes in shock tubes.

Results The deviation between experiment and kinetic models can be attributed amongst others to the presence of pre-ignitions. With the aid of experimental data and Schlieren imaging it could be found that 1) the first pressure rise in the signals most likely is caused by compression waves produced by accelerated flame kernels and 2) the intensity and the amount of flame kernels have a direct impact on the ignition delay.

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 modelling is used for chemical mechanism improvement.

Results Improved oxygenated fuels, e.g. 2,5-DMF, have been investigated. Extensive validation campaign in close collaboration with international renowned research facilities has been performed on the basis of methane and ethanol. Detailed models for the combustion of bio-derived fuels, such as DnBE and n-octanol, as well as surrogate fuels were developed.

Project IRF-B1-2 “Experimental Determination of Ignition Delay Times in a Rapid Compression Machine”
Physico-Chemical Fundamentals of Combustion (Prof. Alexander Heufer)

Aim In order to assist the Fuel Design Process within TMFB, a rapid compression machine is used to experimentally determine the ignition delay times of possible TMFB fuel candidates. This can be done in a rapid-screening manner, using only smallest quantities of self-produced fuel samples.

Results The investigation of numerous possible fuel candidates derived within the Fuel Design Process showed the direct dependency of the ignition behavior on the molecular structure. Here, the group structural effects of the oxygen atom position, the side-chain position and length as well as the position and number of double bonds on the ignition behavior were described.
**Project** IRF-B1-5 “Detailed Characterization of Non-Premixed Combustion and Soot Formation 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 be fairly different compared to crude oil based fuels, so far mechanisms how bio fuels affect structure and chemical properties of soot are unknown. Therefore, experimental data of a laminar counterflow-burner are used to develop new multi variant soot models.

**Results** 
A new counterflow burner optimized for soot and species measurements was designed and setup up. Flow field measurements indicate a top-hat exit velocity profile and validation measurements of extinction strain rates are in good agreement with literature values.

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**Project** IRF-B1-6 “Ab-Initio Elementary Reaction Kinetics”  
Model-Based Fuel Design (Prof. Kai Leonhardt)

**Aim** 
In this project, rate constants of reactions in the ignition and combustion process are calculated with ab-initio methods. In conjunction with the calculation of heat capacities and heats of formation, this information supports the development of detailed mechanisms for biofuels.

**Results** 
Thermochemistry and reaction rate constants for butyl formate have been calculated and improved a mechanism developed within TMFB. In order to improve the description of (tetrahydro)furan-based fuels, we calculated rate constants for the thf+HO2 reaction and presented the results at the 34th International Symposium on Combustion 2012.

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**Project** IRF-B2-1 “Experimental Analysis of Turbulent Mixing of Tailor-Made Fuels in Internal Combustion Engines”  
Institute of Aerodynamics (Prof. Wolfgang Schröder)

**Aim** 
The objective of this project is to experimentally determine the suitability of new tailormade fuels for low-temperature combustion processes. Fully three-dimensional velocity and density measurement techniques are used to analyze the mixing process and the characteristic structures of the flow field during the intake and compression stroke of a four-valve single-cylinder internal combustion engine at different engine speeds.

**Results** 
Variable valve timing has a strong influence on the mean vorticity and the local and temporal distribution of the mean and turbulent kinetic energy, as well as on the amount of turbulent kinetic energy in the intake phase, which is important for the fuel injection and mixing. Furthermore, significant cyclic variations were identified in the temporal development of the mean and turbulent kinetic energy, as well as in the path of the tumble vortex core.

**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 aims 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, a new adaptive Cartesian cut-cell based flow solver for large eddy simulation of compressible flows in internal combustion engines is developed.

**Results** 
The developed flow solver has been efficiently parallelized so that highly parallelized computations (O(1000) processors) can be conducted. The overall model has been successfully validated for highly resolved large eddy simulations of in-cylinder flow.
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 initial breakup of liquids into sprays, in order to develop detailed atomization model for the large eddy simulation of spray-guided combustion.

Results: It has been found that the liquid viscosity and the surface tension are the most important physical properties. In addition, different from single phase turbulent flows where the Kolmogorov scales define the smallest length, time and velocity scales, there is a sub-Kolmogorov breakup regime where the turbulent stress balances the surface tension, and the viscous stress is of lower rank.

Institute of Heat and Mass Transfer (Prof. Reinhold Kneer)

Aim: We investigate fuel influence on primary breakup, which is responsible for spray formation and thus, overall mixture formation. Further, we aim at the development of outstanding measurement techniques to the region of interest close to the nozzle, such as double-pulsed transmitted light microscopy, LCV and Ballistic Imaging.

Results: The development, adaptation and application of unique measurement technique - the transmitted light microscopy - for primary breakup visualization under diesel conditions with outstanding spatial resolution was successful. Fundamental insights into the physics of ballistic imaging, suggesting new measures for improving the images could be gained.

Institute of Heat and Mass Transfer (Prof. Reinhold Kneer)

Aim: The aim of this project is the investigation of fuel influence on far-field mixture formation and evaporation with innovative methods, such as high-speed visualization, 2-color LIF, PDA, complemented by a fundamental spray modelling.

Results: New empirical correlations describing spray cone angle as a function of tailor-made fuel properties were developed and thus, the prediction accuracy for spray penetration was significantly optimized. A new planar temperature measurement technique was established, allowing a fundamental investigation of multicomponent evaporation of droplets.

Institute of Technical Thermodynamics (Prof. André Bardow)

Aim: The objective of this project is to support spray and combustion modelling by providing deeper and quantitative knowledge on the evaporation of novel multi-component biofuel blends.

Results: Extensive vapor liquid equilibrium (VLE) measurements of binary mixtures of promising biofuel candidates were conducted at next to engine-like temperatures and pressures. Next, we reduced the required experimental effort significantly by using a hybrid predictive method for the description of VLE of binary biofuel mixtures.
Institute for Combustion Engines (Prof. Stefan Pischinger)

Aim
The major aim of this project is the optical characterization of fuel dependent properties like e.g. liquid spray penetration, evaporation, mixture formation, physio-chemical ignition delay, combustion behaviour and initial pollutant formation at part- and full-load related boundary conditions.

Results
Firstly the simultaneous visualization of shadowgraphie and OH-chemiluminescence was realized, where due to the ignition instabilities of 1-octanol and the high 2-MTHF blends in part-load, DnBE is selected as the favourite molecule in the context of this investigation at the high pressure chamber. The second measurement technique is a stereoscopic 3-color high-speed ratio-pyrometry, which allows a double redundant quantification of temperature, topology and emissivity of optically opaque flames with a temporal and spatial resolution of 10 kHz and 16 Pixels/mm².

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 research aims towards a detailed understanding of the effects which the TMFB fuel candidates have on typical tribological contacts in standard injection equipment. Based on the gained knowledge, possibilities to modify these contacts for operating with low lubricity and low viscosity fuels are studied.

Results
Advanced tribological measurements on the disc-on-disc tribometer were conducted for pure fuel candidates and blends. The highly stressed tribological contacts in an injection pump were studied by measurements and corresponding elasto-hydrodynamic simulations.

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 objective of this project is the development of an accurate and efficient Large-Eddy simulation framework for the analysis of biofuel candidates in internal combustion engines.

Results
The existing LES code has been extended by numerical methods needed for engine cold-flow simulations. Physics models for spray modeling, spark ignition, and non-premixed combustion have been implemented and are currently being tested before they will be applied in reactive engine LES.

Project IRF-B3-3 “Cycle Resolved Multi-Parameter Laser Diagnostics under Real-Engine Conditions for TMFs”
Institute for Laser Diagnostics in Thermo-Fluid Dynamics (Prof. Gerd Grünfeld)

Aim
In this project, ignition, combustion and pollutant formation are studied in real diesel, SI, and GCAI engines for TMFs. This is conducted by using various optical imaging diagnostics, such as chemiluminescence, LIF, and Raman scattering.

Results
Optical investigation of the soot reduction mechanism for BLT in an HSDI diesel engine with and without port deactivation was performed, as well as optical studies on the origin of pre-ignition in a highly charged SI engine for TMFs.
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)

Aim
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. Therefore, this project is vital for the understanding and optimization of fuel dependent in-cylinder processes like e.g. mixture formation, ignition and combustion at transient boundary conditions and application relevant operation points.

Results
The combustion of two new fuel candidates, di-n-butyl ether and 1-octanol, has been investigated at \( n = 1500 \text{ min}^{-1}, \text{IMEP} = 6.8 \) bar with varied external exhaust supply for simulated EGR using a high-speed visualization of \( \text{OH}^* \) chemiluminescence and soot luminosity. With the very fast igniting di-n-butyl ether soot luminosity occurs during combustion, while the more premixed pronounced combustion of 1-octanol shows almost no soot luminosity. However, since both fuels had hardly any exhaust gas soot emissions (IRF-B3-5), this suggests that the soot formed during the combustion of di-n-butyl ether is being oxidized.

Project IRF-B3-5 “Advanced Combustion Systems for Tailor-Made Biofuels”
Institute for Combustion Engines (Prof. Stefan Pischinger)

Aim
The research target of this project is to completely optimize the combustion for the new biofuels. Simultaneously fuel blends will be explored to increase the fuel property parameter space, and to allow for an improved tailoring of the desired fuel properties.

Results
The investigation of 2-butanone revealed efficiency improvements equal to ethanol with a high knock-resistance and simultaneously improved mixture formation at cold start conditions. It could be proven that soot emissions can be reduced to a great extend compared to diesel fuel with new oxygenated compounds without increasing the homogenity of the mixture and thus without the drawbacks of high HC- and CO-emissions and high heat release rates.

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)

Aim
Within this project the impact on the exhaust-gas emissions will be investigated by means of gas chromatographic and mass spectroscopic analysis of exhaust-gas samples. Research target is to identify fuels with low harmful exhaust gas emissions as well as good conversion rates in the exhaust-gas aftertreatment system.

Results
Harmful aromatic hydrocarbon emissions as measured with conventional EN228 fuel are completely avoided with the investigated bio fuels. However furan-based fuels emit more possible carcinogenic Furan molecule than conventional fuel.
Core Interaction Field: Fuel Design

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// Vision
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 on the way to 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 a sustainable and energy-efficient synthesis from biomass. Therefore, chemistry, biology and biotechnology as well as mechanical engineering have to join forces to find the overall optimum fuel with regard to life-cycle emissions. 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 lead to the envisaged, interdisciplinary fuel design process.

// Main Results
The model development within the CIF has evolved enormously since the last status update in 2011. The model-based identification of possible fuel components by data-driven methods like QSPR was enhanced, so that new candidate fuel molecules could be derived: These molecules include 1-octanol for the Diesel engine and 2-butanone for the gasoline engine which will be presented in the following sub-chapters. In parallel, the description and fast evaluation of the production pathways of these fuel components was improved.

Strongly related to the model improvement was the build-up of fast screening methods which allow the calibration of the data-driven fuel design tools. Here, all fields from tribology via combustion and ignition properties up to ecotoxicology 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.

Figure 3.23: Tools and methods within the CIF to enhance the Fuel Design Process
CIF-1: Performance Indicators for Biofuel Production

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

// Main Results Summary
The initial investigations within the CoE clearly demonstrated the need to directly consider fuel characteristics and process performance in catalyst development. The innovative and comprehensive approach within CIF-1 correlated the respective research domains and first examples enabled to integrate data on process design and energy requirements in the evaluation of catalyst systems. Based on the corresponding performance indicators novel production routes to tailor-made-fuels could be successfully developed and this approach paved the way to effective fuel-prototyping, the basis for future reference processes.

// Results
The initial investigations within the CoE clearly demonstrated the need to directly consider fuel characteristics and process performance in catalyst development. The innovative and comprehensive approach within CIF-1 correlated the respective research domains and first examples enabled to integrate data on process design and energy requirements in the evaluation of catalyst systems. Based on the corresponding performance indicators novel production routes to tailor-made-fuels could be successfully developed and this approach paved the way to effective fuel-prototyping, the basis for future reference processes.

Figure 3.24: Alternative hydrogen-free pathway for the production of 2-MF.

Figure 3.25: RNFA analysis of the various pathways to novel tailor-made-fuels.
Core Interaction Field 2: Performance Indicators for Biofuel Combustion

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Vision
It is the goal of this research domain to establish novel, semi-empirical, quantitative models to predict the fuel’s in-engine behavior with regard to tribological properties, injection characteristics, mixing, ignition, and pollutant formation properties of bio-derived fuel blends, depending on the molecular structure. These quantitative models will then be used in the fuel design process in CIF-3. An essential intermediate step and goal will be to identify appropriate new characteristic numbers describing the link of fuel structure and properties to engine performance indicators.

Main Results Summary
In the search for models that link molecular structure to engine performance, several important intermediate results were reached: An accurate hybrid model for the prediction of a combustion property of biofuels was established which expresses laminar burning velocities in dependence of molecular descriptors. Further, the interconnection of a second combustion property, the auto-ignition delay, on molecular structure was investigated experimentally and theoretically for furanics and other oxygenated species. In addition to an understanding of the structural influences, such as side chain length and double bonds in furanic structures, a large ignition database was created, which is currently used to develop a semi-empirical model for the prediction of ignition properties. Furthermore, an extensive set of tribological properties was measured experimentally and applied to improve the previously developed quantitative structure-property relationship (QSPR) model for lubricity. Finally, closing the gap between fundamental models and engine applications, an analysis of the mixture formation process and from this the level of soot emissions in a diesel engine was performed, and a new virtual approach for the investigation of fuel properties in engines was established.

Results
Model-Assisted Experimental Screening of Novel Biofuels
A workflow for deriving predictive models assessing engine-relevant fuel properties based solely on the information of molecular structure is proposed in project CIF-2-1, enabling an efficient computational search for potential biofuel compounds.

Within this context, as shown in Figure 3.26, a semi-empirical model for the laminar burning velocity has been derived from a reformulation of a physically motivated asymptotic approximation of laminar flames. Its fuel dependent parameters are estimated from flame simulations and subsequently expressed as functions of molecular structure by means of QSPR modeling.

The hybrid model accurately reflects burning velocities of eight alkane compounds used in the training and has been demonstrated to predict burning velocities of multiple other alkanes within experimental accuracy. In order to rapidly build up an experimental database on novel fuels, a strategy based on model-based optimal experimental design is proposed, which is capable of characterizing a new fuel compound by few targeted experiments only. A similar screening campaign on a highly diverse set of oxygenated hydrocarbons is currently being performed with the aim of establishing a structural group contribution method relating a fuel’s auto-ignition delay in a standardized constant-volume combustion chamber to its molecular structure. Theoretical investigations on the value of quantum mechanics in QSPR modeling focus on the implications of different computational methods for molecular geometry optimization on three-dimensional molecular descriptor calculations. Results indicate a moderate benefit of using 3D descriptors in QSPR for fuel property modeling. However, descriptors derived from quantum mechanics are shown to substantially improve the prediction of melting points.

Figure 3.26: Hybrid model relating the laminar burning velocity as a function of temperature and stoichiometry to the fuel’s molecular structure
// Identification of Characteristic Fuel Numbers

The C2F-2 project aims to establish a link between the fuel design process and engine applications. The final goal is the identification of characteristic numbers that describe optimal features of the fuel molecule for ICE application. Within this project, a new methodology named Virtual Fuel Approach (VFA) was introduced to study the impact of a fuel’s thermo-physical properties on the mixture formation process at part load engine operating conditions. A sensitivity analysis on liquid density (cf. Figure 3.28), dynamic viscosity, surface tension, and vapor pressure was carried out through a direct virtual decoupling of the fuel thermo-physical properties, while accounting for complex engine-like thermodynamic boundaries conditions.

Air utilization was established as monitoring parameter of the study, as it is a measure for the quality of the mixture formation process linking local equivalence ratios to soot formation and oxidation. The sensitivity analysis showed that the mixture formation process yields the best results for ether fuels, followed by alcohols and alkanes at a given engine operating load. Furthermore, it was found that fuels with a carbon chain length of 8 − 10 atoms belonging to the ether family allow for an overall improvement of the mixture formation process.

// Rapid Screening of the Ignition of Saturated and Unsaturated Furanic Species

Within the project CIF-2-2, the ignition characteristics in form of derived cetane numbers (DCN) of the class of saturated and unsaturated furans were investigated experimentally in an ignition quality tester. Further, quantum chemistry calculations at the CBS-QB3 level of theory were applied to determine bond dissociation energies (BDEs) and thereby the most probable initial reactions of the ignition process for all fuels. Using the calculated BDEs, it was found that the ignition characteristics are similar within the groups of furans and tetrahydrofurans, but strongly differ from one group to another. It was shown that the ignition behavior of unsaturated furans is determined by the ring structure, which correlates with a negligible side chain influence, as also shown in Figure 3.27.

Hence, the length of the side chain can solely be determined with respect to available production pathways and ease of applicability in engines. For tetrahydrofurans (THFs), on the contrary, the side chain length was found to define the area of application: Tetrahydrofurans with short side chains were shown to be potential candidates for SI application, whereas 2-butyltetrahydrofuran could be an option for application in diesel engines.

// Tribological Properties of Biofuels and Fuel Blends

The research within the CIF-2-3 project investigates the impact of the molecular structure of new biofuels and blends with respect to their tribological properties to ensure their applicability with modern injection systems. By screening more than 40 new TMFB fuel candidates and additional fluids with the HFRR method (DIN EN ISO 12156-1), the influence of the molecule size, form, and functional groups on the lubricity has been analysed. The results of this tribological fuel screening were used to further improve the QSIFR model for fuel lubricity established in the first funding period. Furthermore, an SLBOCLE facility (ASTM D 6078) has been added to the array of tribological test rigs. Comparative measurements with the two lubricity testers were performed to identify suitable test procedures and pass/fail criteria for the TMFB.
Core Interaction Field 3: Model-Based Fuel Design

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 space 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

A novel rule-based generator of molecular structures has been implemented taking synthesis requirements into account. The generated molecules have been evaluated by tailored structure-property relationships for the estimation of key fuel properties and the synthetic pathways of the most promising candidates have been analyzed in more detail. A physically-based predictive equation of state has been extended to hydrogen-bonding compounds and to provide surface tensions for the calculation and assessment of thermochemical fuel properties relevant to injection. It is presently integrated into the molecular structure generator. Experimental investigations are performed for the evaluation of the designed molecules with respect to properties that cannot yet be predicted in silico accurately enough. An automated platform has been set up and validated to determine liquid-liquid equilibria (LLE) of biofuel blends with water. Biotests were designed and performed for fuel candidates to investigate their biocompatibility. The results of these experimental investigations are used furthermore to develop and improve predictive models for LLE and ecotoxicological effects that will be implemented in the model-based design process.

Results

The rule-based structure generator is designed to conserve distinct molecular patterns found in bio-derived platform chemicals. It allows for several modifications of functional groups and for introducing carbon-carbon or carbon-oxygen-carbon couplings in order to increase the molecular weight of potential fuel compounds. The type and number of reactions is limited to those reasonably applicable to bulk chemicals like fuels. By employing tailored structure-property relationships for the estimation of key fuel properties, the most promising molecules can be identified. Short-chain ketones have been identified as novel promising fuel candidates for spark ignition engines. These molecules are presently further investigated experimentally with respect to the efficiency of their synthesis, their ignition properties, and their application in engines. In a second step, phase stability and ecotoxicology will be investigated.

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 quantum mechanics and statistical mechanics. It permits the calculation of many properties required for modelling fuel injection as well as for designing solvents in chemical engineering. In the last two years, PC-SAFT was extended to predict properties of hydrogen-bonding compounds and surface tensions. Furthermore, optimal experimental design strategies have been used to augment the predictive PC-SAFT model with experimental data using only a minimal amount of substance to further increase its accuracy.

Some fuel candidates are produced in aqueous solution and need to be separated from the water to be used as a fuel. When in contact with moisture after purification, most biofuels can absorb water again. Depending on the solubility of water and its temperature dependency, this can lead to the formation of an incombustible second liquid phase or degradation of the biofuel. These effects could render otherwise interesting fuel candidates unusable in practice, but cannot yet be computed accurately by models. Therefore, an automated platform consisting of a robotic dosing and sampling system plus a gas chromatograph has been set up, validated and applied to investigate the phase behavior of biofuel blends with water. Moreover, the potential to reduce the experimental effort for the characterization of liquid-liquid equilibria further has been studied by model-based experimental design.
Not only toxicity to humans but also ecotoxicologic compatibility of new chemical products is relevant. Because of the multitude of mechanisms of toxic effects, this problem can hardly be tackled by a physical model. Therefore, promising fuel candidates are experimentally investigated with respect to their ecotoxicology at an early state. Acute and chronic biotests with Daphnia magna were performed for 2-MTHF to provide data for the modelling tool and a method for the chemical analysis of 2-MTHF and 2-MF was established to verify the test substance concentration in the test medium. Results for the first potential biofuel (2-MTHF) are available and the test systems now have to be modified and optimized for the investigation of 2-MF as well as reference fuels (e.g. fossil diesel fuel).

Figure 3.29: The most interesting in-sicilo-generated-and-evaluated molecules are evaluated experimentally. Ideally, these experiments are automated, optimally designed and require only small substance quantities. The experimental results are fed-back into the models to improve their accuracy.
List of Projects CIF

**Project CIF-1-1 “Validation and Optimization of Catalytic Tailor-Made Fuel Processes”**
Institute of Technical Chemistry and Macromolecular Chemistry (Prof. Regina Palkovits)

**Aim**
In this project, we work at the design and construction of a reaction plant for the continuous hydrogenation of biogenic carboxylic acids like itaconic and levulinic acid. Based on the generated data a statement on the energetic demand of the plant and the catalyst activity/stability under continuous flow conditions is possible.

**Results**
The parts for the reaction set-up, for a range from 1-150 bar and from 25-300°C, were designed and purchased and a program for the automation of the reactor was written. Batch experiments on the feasibility of itaconic acid hydrogenation in aqueous systems with heterogeneous catalysts were performed.

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

**Aim**
The project aims at a fast process evaluation screening tool for possible TMFB production routes, considering economic as well as life-cycle analysis criteria in a multi-criterial optimization. Cutting down the high number of envisaged processing pathways, a methodology, called „Reaction Network Flux Analysis“ (RNFA) is developed and extended stepwise bridging the gap between RNFA and conceptual process design.

**Results**
The RNFA methodology was developed and successfully applied to a large number of processing pathways, including a sensitivity analysis covering uncertainties in the analysis. In addition a purification strategy for the pathway starting at itaconic acid and converting it to 3-methyltetrahydrofuran, was developed and can now be transferred to similar processing pathways, raising the level of detail within the RNFA to a new level.

**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**
The project aims at establishing novel semi-empirical property models for the prediction of kinetic and thermodynamic properties of biofuels, as they are of utmost importance for the fuel design process. To overcome property data scarcity in case of oxygenated fuels, experiments are performed with support of model-based optimal experimental design techniques identifying experimental conditions with maximum information gain.

**Results**
A predictive hybrid model for the laminar burning velocity has been derived from a reformulation of a physically motivated asymptotic approximation of laminar flames linking the fuel dependent parameters to molecular structure by means of quantitative structure-property relationship (QSPR) modeling. Computational methods, commonly employed to the determination of the spatial molecular alignment have been investigated with respect to the calculation of three-dimensional molecular descriptors and their ability to improve the predictive quality of QSPRs for engine-relevant fuel properties.
**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 developing and applying rapid combustion experiments as basis for the evaluation of relations between molecular structure and combustion characteristics of novel biofuels.

**Results**
The dependence of the auto-ignition behavior of saturated and unsaturated furanic species on their molecular structure was investigated experimentally and theoretically. The double bond influence was found to dominate the ignition behavior, whereas the side chain length was shown to determine the ignition behavior within the group of saturated furans. Further, 2-butyletherhydrofuran was identified as promising diesel fuel candidate.

**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 towards a profound knowledge about the impact of the molecular structure of new biofuels and blends on their tribological properties in order to tailor them with improved tribological properties, enabling their usage with modern injection systems.

**Results**
By screening more than 40 new TMFB candidates and additional fluids with the HFRR, the influence of the molecule size, form and functional groups on the lubricity have been analyzed. These results were used to further improve the existing QSPR model for fuel lubricity.

**Project CIF-2-4 “Identification of New Characteristic Fuels Numbers for Tailor-Made Fuels from Biomass”**
Institute for Combustion Engines (Prof. Stefan Pischinger)

**Aim**
The CIF-2-4 aims to establish a link between fuel design process and engine application. Final goal is to identify the molecule’s features which are optimal for IC engines application.

**Results**
A new methodology named Virtual Fuel Approach was introduced to study the impact of fuel thermo-physical properties on the mixture formation process, in order to trace a link between local in-cylinder lambda distribution and the molecular structure of the fuel. It was found that an ester with a chain length of 8-10 carbon atoms and the oxygen in central position improves the mixture formation process and is beneficial with regards to soot formation and oxidation.

**Project CIF-3-1 “Systems Fuel Design”**
Institute for Organic Chemistry (Prof. Carsten Bolm)

**Aim**
The project aims at identifying potential fuel candidates containing not more than 10 carbon atoms after applying chemical and physico-chemical restraints as well as analyzing existing and developing new synthetic path-ways to attain the identified fuels candidates from biomass.

**Results**
Chemical restraints on algorithmically generated molecules (QSPRs) from AVT.PT were applied. Existing synthetic pathways for biofuels candidate 2-butanone from biomass based platform chemicals were analyzed.

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**Summary**
Activities 2012-2014
Project **CIF-3-2 “Model-based Product- and Process Design for Biofuels”**
Aachen Chemical Engineering - Process Systems Engineering (Prof. Alexander Mitsos)

**Aim**
The project aims at establishing an holistic framework for model-based assessment of relations between a fuels’ molecular structure, engine-relevant fuel properties and process performance indicators. The computational approach solves the inverse problem of fuel design, i.e., generating new molecules considering optimal product and process performance indicators as constraints.

**Results**
A novel rule-based generator of molecular structures as part of a computer-aided molecular design process has been proposed conserving distinct molecular patterns in the bio-derived platform chemicals, adjusting functional groups and introducing carbon-carbon or carbon-oxygen-carbon couplings in order to increase the molecular weight of potential fuel compounds. By employing tailored structure-property relationships for the estimation of key fuel properties, the most promising molecules are determined for subsequent experimental investigation in compression-ignition and spark-ignition engines.

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Project **CIF-3-3 “Design Methods for QM-Based Property Models”**
Model-Based Fuel Design (Prof. Kai Leonhard)

**Aim**
The goal of this project is the design of molecular structures with desired macroscopic properties. One focus is on the derivation of physically-based property models. Another is on the development of effective structure search-and-test algorithms to identify the optimal molecular structures.

**Results**
The PC-SAFT equation of state has been extended to allow for the calculation of surface tensions without using any experimental data. Optimal experimental design strategies have been developed to augment the predictive PC-SAFT model with experimental data to further increase its accuracy.

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

**Aim**
The phase behaviour of second generation biofuel blend with water has not yet been studied properly. The goal of this project is to set up a platform which allows the automated and model-based characterization of such liquid-liquid equilibria.

**Results**
An automated platform has been set up, validated using liquid-liquid equilibrium data from literature and been applied to biofuel blends with water. Moreover, the potential to reduce the experimental effort for the characterization of liquid-liquid equilibria further has been established by model-based experimental design.

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Project **CIF-3-5 “Ecotoxicological Investigations of Biofuels as a Basis for Computational Model Based Prediction of Ecotoxicological Potencies”**
Department of Ecosystem Analysis (Prof. Henner Hollert)

**Aim**
The fundamental target of the project is the development of a test strategy for a comprehensive risk assessment of biofuels, aiming at the investigation of the ecotoxicological impact of biofuels and the use of computer-based tools to predict the ecotoxicological potential of cluster-relevant substances (e.g. furane/furanose).

**Results**
Acute and chronic biotests with Daphnia magna were performed for 2-MTHF to provide data for the modelling tool and a method for the chemical analysis of 2-MTHF and 2-MF was established to verify the test substance concentration in the test medium. Results for the first potential biofuel (2-MTHF) are available and the test systems now have to be modified and optimized for the investigation of 2-MF as well as reference fuels (e.g. fossil diesel fuel).
Thematic Working Groups

Supplementary Cluster Activities

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The Supplementary Cluster Activities (SCA) aim firstly to enhance efficient net-
working between the cluster’s scientific processes and foster interdisciplinary
collaboration [c.f. Knowledge Map, Performance Measurement and Colloquia for
Research Assistants]. Secondly, the SCA are supposed to support the cluster man-
gagement to make decisions onto collaboration enhancing measures [c.f. Perfor-
mance Measurement, Colloquia for Research Assistants, Supporting Activities].
Thirdly, SCA aim to create a successful strategic cluster development [c.f. Perfor-
mance Measurement and Supporting Activities] and fourthly specific key perfor-
ance indicators to measure and steer the cluster performance are determined and
developed [c.f. Performance Measurement]. Due to the collaboration of research
teams from different scientific fields, the strategic management of interdisciplinary
processes is essential to enhance scientific cooperation on the one hand and sup-
port 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).

In the second funding period, two columns guide the SCA activities: one contains
the collaboration-enhancing research, the other deals with collaboration-enhanc-
ing services.

Thus, the SCA constitute an important part within the organizational structure of
the Cluster of Excellence “Tailor-Made Fuels from Biomass” (TMFB) at the RWTH
Aachen University and are directly related to the cluster management. The collab-
oration-enhancing services and research will be depicted in the following:
The Knowledge Map, a virtual collaboration platform to enhance scientific performance within the CoE, is a web-based tool that gives the user an illustrative overview of the internal cluster knowledge and was introduced by representatives of the SCA in spring 2009. With the aid of this virtual collaboration platform, transparency and overarching communication were enhanced.

With the aid of the BSC, objectives of the CoE are improved and the cross-hierarchical communication and cooperation is promoted. Thus, the BSC is adapted to the needs of the CoE as a measurement system of performance. This approach is characterized by the measurement and comparison of performance indicators on various levels (e.g. level of management and level of employees) and is based on a survey among all CoE-employees that is used for the evaluation of the cluster performance. The 4th evaluation took place from September 2nd to November 11th, 2013. 70.2 percent of the cluster employees altogether participated and answered the questionnaire.

In addition to content-related analysis, statistical analysis on the method was done. In this context, for instance indicators to identify key performance indicators by two statistical methods were analyzed: firstly, all variables were calculated by using Spearman’s rank correlation coefficient. Secondly, the amounts of correlation pairs per indicator were compared to verify the results. Indicators whose size effects were >0.3 (literature on scientific analysis refers 0.3 to a medium statistical correlation) were identified and a significance test (p<0.01) was set. This procedure provides the universal validity of key performance indicators for research alliances like the CoE—“TMFB”. Successfully identified KPIs are, for example, frequency, quality and benefits of meetings, scientific cooperation and publications. Based upon these results, the BSC was lightly adjusted in the beginning of the 2nd funding period and less informative indicators were substituted.

Taking this as groundwork, a workshop to determine further requirements of the Knowledge Map was conducted together with the cluster management. Furthermore current research results in developing a virtual collaboration platform to enhance scientific performance are considered. In 2013, the software advancement was already initiated. Thereby, functionalities such as networking activities and simplifying the internal flow of information will be enhanced. Also the implementation contains: layout and surface of the Knowledge Map (usability becomes further intuitive and information can be simply prompted across all TMFB employees), connection possibilities between TMFB members by a full member list (containing information about involved institutes and researches as well as their contact details), TMFB calendar which shows all CoE-related appointments. Accessibility and access privileges are granted to the employees individually.

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 flow of information across hierarchy.

// Performance Measurement & Determination of Cluster-Specific Key Performance Indicators
In the first funding period, steering and regulating “TMFB” as a system with knowledge-intensive, interdisciplinary research structures became possible. In order to support the cluster management, a specific form of a Balanced Score Card (BSC) was implemented. As one of different feasible performance measurement approaches the BSC (based on Kaplan and Norton) was chosen because of its flexibility and adaptability. Thereby, the BSC meets the requirements of CoEs by considering their complexity and dynamic, focusing on strategies, fostering objective- and results-transparency and overarching communication.

After using the Knowledge Map within the first funding period, potentials for a future development were exposed. The BSC evaluation results and comments were also helpful for developing the software tool and managing a reasonable accommodation. Moreover, the Knowledge Map and the BSCW Server (database to share content) should be combined, so that data (e.g. presentations, publications, protocols) can be shared with a single tool.

// Knowledge Map – “TMFB Inside”
The Knowledge Map, a virtual collaboration platform to enhance scientific performance within the CoE, is a web-based tool that gives the user an illustrative overview of the internal cluster knowledge and was introduced by representatives of the SCA in spring 2009. With the aid of this virtual collaboration platform, transparency within the cluster increases. Moreover points of intersections between entities can be depicted. To improve the usability of the Knowledge Map, optimizations (e.g. usability, visualization, functionality) were carried out over the last years of usage and will be implemented and released within 2014 with a graphical redesign of the entire website.

The SCA research activities deal with topics on cooperation and cooperation management. Especially to promote the scientific discourse and to interchange with the community several publications were submitted and presented. Topics are for instance: Management of inter- and transdisciplinary research alliances (like CoE), Performance Measurement and Management (e.g. Key Performance Indicators) and Virtual Collaboration Platforms to enhance the scientific performance within the CoE. Visited conferences in this context are themed in terms of technology, education and development (INTED), as E-Learning in the Workplace (ICELW) and Industrial Engineering and Engineering Management (IEEM).
**Analytics in Biomass Fractionation**

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Lignocellulosic biomass is a heterogeneous material which consists mainly of cellulose, hemicellulose and lignin but, depending on the type of feedstock, also of several minerals, lipids, protein, pectin and remaining water. This heterogeneity requires a complex analysis technique. Due to this complexity, several chromatographic (IC, GC and LC coupled to MS, PAD, RI or UV detection), spectroscopic (IR) and calorimetric (DSC) methods have to be used for a complete characterization. This characterization is essential in order to find a feedstock which is suitable for a biorefinery process (see Figure 4.1).

The usually applied pretreatment steps which alter the structure of all biopolymers lead to three different fractions which have to be analyzed. In this content, the crystallinity of the cellulose fraction is of particular interest because the crystallinity can be correlated to a simpler and more rapid enzymatic hydrolysis.

An analysis protocol which enables the characterization of all types of feedstock as well as all pretreated feedstock fractions is essential for a rapid feedstock screening. Therefore, the overall vision of this Junior Research Group is not only the characterization of the feedstocks but also the correlation of the discovered analytical data with commonly used saccharification steps (e.g. pretreatment and enzymatic hydrolyzation step or acid saccharification).
Life Cycle Assessment and Benchmarking

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The Öko-Institut is a leading European research institution providing scientific support for academia, governments, private enterprises and civil society to substantiate and support a sustainable future. In the years 2012 and 2013 of the Cluster of Excellence on Tailor-Made Fuels from Biomass the Öko-Institut undertook studies on the environmental performance of an integrated and optimized concept of the TMFB reference processes, envisioned by the cluster and on alternative biofuel production routes and biomass potentials.

// Assessment of the Combined TMFB Reference Processes (“Integrated TMFB Concept”)

Two TMFB reference processes are proposed: the itaconic acid (IA-) route where biomass is hydrolyzed and fermented to itaconic acid followed by hydrogenation to 3-MTHF and the levulinic acid (LA-) route where biomass is thermochemically converted to levulinic acid and hydrogenated to 2-MTHF. Their combination is achieved by processing one of the sugar-rich streams from biomass fractionation (xylose-rich stream) to itaconic acid fermentation and the other one (cellulose-rich stream) to levulinic acid synthesis.

The lignin-rich stream constitutes a co-product. As frequently reported material application for lignin the substitution of phenol in formaldehyde phenolic resins is modeled within the assessment. It proves beneficial with respect to global warming potential (GWP) and non-renewable cumulated energy demand (CED n.r.). However, even if material applications for lignins other than those for the presently commercialized lignosulphonates exist, the markets and technologies are still in the phase of development. The potentially high lignin volumes from Kraft pulping results the Organocat process exhibits a considerably better performance than the Organosolv process. More lignin is separated into a virtually pure lignin stream and more hemicelluloses sugars are sent to itaconic acid fermentation. The second aspect leads to a higher contribution of the itaconic acid route in the whole concept which results in a less good performance concerning GWP and CED n.r. This points to the fact that improvements are especially needed here. To make the IA-route viable in parallel to the increase of the fermentation yield the operating parameters in the other process steps need to be improved. Moreover, a value-added material use of itaconic acid should be analyzed.

In general the GWP of the integrated concept lies in the range of the GWP of fossil gasoline (reference value). Beside process energy requirements a relevant fraction is related to the hydrogen demand for the MTHF-synthesis steps. The latter is determined stoichiometrically and cannot be brought down by optimization. The biomass requirement lies around 2 – 3 MJ/MJ-fuel depending on the itaconic acid yield. The results for GWP and CED n.r. were found to be rather insensitive with respect to selected methodological choices within the assessment.

// Assessment of Optimized Concepts of the TMFB Reference Processes

The required amounts of energy for the IA-route are the main focus of the optimization concept, especially the high requirement for the electrodialysis and the drying step. In addition to the continuous fermentation process using Ustilago maydis as microorganism, also batch fermentation with Aspergillus terreus was studied. The alternative process concepts comprise ultrafiltration to remove residual biomass, electrodialysis and either evaporative crystallization, cooling crystallization to gain solid itaconic acid, or extraction of itaconic acid into an organic phase. Other scenarios refer to different flow rates and final itaconic acid concentrations of the continuous fermentation using Ustilago maydis. The concepts with A. terreus show higher yield of 3-MTHF. As fermentation with A. terreus is carried out at a pH of 2 the higher solubility of itaconic acid at this pH leads to a lower volume of water, which has to be removed before MTHF synthesis. Moreover, the sterilization step before fermentation can be skipped because of the low pH. The consumption of energy for itaconic acid route can also be reduced significantly if other drying steps like evaporative crystallization, cooling crystallization or extraction with reverse osmosis are used.

// Analysis of Alternative Biofuel Production Routes

The analysis of the alternative biofuel production routes (from literature) showed that the assumption that a conservation of the complex chemical structures in natural biomass keeps the energy in the product streams while fragmentation into smaller pieces does not, does not hold true. This is especially important for biofuels where the main criterion is their energy content.
In the biomass-to-liquid (BtL) process the gasification is linked to high losses. However, in high-temperature reactions a part of the liberated energy can either be integrated chemically into the syngas or used in steam turbines for combined heat and power generation.

The comparison of ethanol production vs. the itaconic acid route shows that the ethanol production route has some major advantages. Firstly, the anaerobic fermentation to ethanol exhibits lower energetic losses than the aerobic itaconic acid fermentation. Secondly, the itaconic acid has to be converted to 3-MTHF by addition of high-caloric hydrogen. Additionally, the purification steps for ethanol (rectification, molecular sieve) are less demanding than those for itaconic acid (membrane filtration, electro-dialysis, and drying/extraction).

// Analysis of Biomass Potentials and Direct and Indirect Emissions from Biomass Supply
The contribution of biomass supply to the environmental impact of the 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.
## Personnel

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<tr>
<th>Surname, First name, Acad. title</th>
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<tr>
<td><strong>Investigators</strong></td>
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<td>Ismail, Ahmed E.</td>
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New Junior Professor

Junior Professorship “Physico Chemical Fundamentals of Combustion”
Prof. Dr.-Ing. Alexander Heufer

The Junior Research group “Physico Chemical Fundamentals of Combustion” is engaged in research and teaching activities on fundamental combustion chemistry and advanced diagnostics of combustion processes. Since April 2014, Prof. Dr.-Ing. Karl Alexander Heufer has been appointed director of PCFC.

The goal is to deeply understand the underlying reaction mechanisms of the combustion processes of conventional and novel transportation fuels towards clean and efficient combustion. Since advanced combustion engine concepts such as Homogenous Charge Compression Ignition (HCCI) are in the research focus with a promise to reduce emissions and boost efficiency, high pressure chemical kinetics of the fuel oxidation plays a central role in controlling auto-ignition. Pollutant formation and abatement in combustion systems is also closely linked to the fuel chemistry.

Our main research goal is therefore to investigate this chemistry using diverse experimental facilities (e.g. shock tubes and Rapid Compression Machine (RCM)). Both optical and mass-spectrometry based diagnostic techniques facilitate the interrogation of this chemistry. A further aim of the group is to develop detailed chemical kinetic models based on the strong interactions of theory, computational kinetics, thermo chemical and group additivity based rate estimation methods. The mechanisms are then validated with experimental data to develop predictive models which will facilitate the fuel design process.
Publications

Reviewed Publications

Publications (excerpts) of IRF A: From Biomass to Biofuels


Publications

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Publications (excerpts) of IRF A: From Biomass to Biofuels


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**Publications (excerpts) of IRF A: From Biomass to Biofuels**

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Publications (excerpts) of IRF A: From Biomass to Biofuels


Publications (excerpts) of IRF B: From Biofuels to Propulsion


Publications

Publications (excerpts) of IRF B: From Biofuels to Propulsion


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Reviewed Publications

Publications (excerpts) of IRF B: From Biofuels to Propulsion


Publications (excerpts) of IRF B: From Biofuels to Propulsion


Publications (excerpts) of CIF: Fuel Design


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<td>[13]</td>
<td>Villeda, Juan Jose Victoria; Dahmen, Manuel; Hechinger, Manuel; Voll, Anna; Marquardt, Wolfgang</td>
<td>Towards model-based design of biofuel value chains.</td>
<td>Current Opinion in Chemical Engineering</td>
<td>10.1016/j.coche.2012.08.001</td>
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</table>
The activities and results presented in the “TMFB Status Report 2012-2014” are part of the Cluster of Excellence “Tailor-Made Fuels from Biomass”, which is funded by the Excellence Initiative of the German federal and state governments to promote science and research at German universities.