BOOK OF ABSTRACTS

2. International Conference of the Cluster of Excellence “Tailor-Made Fuels from Biomass”

June 16th - 18th, 2014
Eurogress, Aachen, Germany
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Speaker</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:30</td>
<td>Welcome and Introduction</td>
<td>S. Pischinger</td>
<td>Welcome and Introduction</td>
</tr>
<tr>
<td>08:45</td>
<td>Keynote Session</td>
<td>G. Centi University of Messina</td>
<td>Keynote Lecture: The role of biomass in changing scenarios for green &amp; sustainable energy and chemical production: from biorefineries to bio-factories</td>
</tr>
<tr>
<td>09:00</td>
<td>Keynote Session</td>
<td>M. Wubbolds Royal DSM</td>
<td>Keynote Lecture: Biobased solutions from DSM for renewable energy and materials</td>
</tr>
<tr>
<td>10:15</td>
<td>Coffee Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:45</td>
<td>Keynote Session</td>
<td>G. Huber University of Wisconsin-Madison</td>
<td>Keynote Lecture: Design of catalysts for hydrodeoxygenation of biomass</td>
</tr>
<tr>
<td>11:30</td>
<td>Keynote Session</td>
<td>J. Pérez-Ramírez ETH Zürich</td>
<td>Keynote Lecture: Zeolite catalysts for biomass conversion into fuels and chemicals: hopes and fears</td>
</tr>
<tr>
<td>12:15</td>
<td>Lunch Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13:15</td>
<td>Fuel Design</td>
<td>P. Emberger TFZ Straubing</td>
<td>Ignition and combustion characteristics of pure vegetable oils in a constant volume combustion chamber</td>
</tr>
<tr>
<td>13:45</td>
<td>Fuel Design</td>
<td>G. Walther RWTH Aachen University</td>
<td>Analysis of the legal boundary conditions to regulate the biofuels market</td>
</tr>
<tr>
<td>14:15</td>
<td>Fuel Design</td>
<td>J. Sutter Öko Institut</td>
<td>Environmental assessment as tool in a fuel design process</td>
</tr>
<tr>
<td>14:45</td>
<td>Fuel Design</td>
<td>F. Hoppe RWTH Aachen University</td>
<td>Biomass-based ketones as successful example for the Fuel Design Process</td>
</tr>
<tr>
<td>15:15</td>
<td>Coffee Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15:45</td>
<td>Combustion Chemistry 1</td>
<td>J. Mendes National Univ. of Ireland</td>
<td>Rate constant calculations of the H-atom abstraction…</td>
</tr>
<tr>
<td>16:15</td>
<td>Combustion Chemistry 1</td>
<td>B. Akih-Kumgeh Syracuse University</td>
<td>Reactivity trends in furan and alkylfuran combustion</td>
</tr>
<tr>
<td>16:45</td>
<td>Combustion Chemistry 1</td>
<td>S.M. Sarathy King Abdullah University</td>
<td>Alcohol combustion chemistry</td>
</tr>
<tr>
<td>17:15</td>
<td>Coffee Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17:30</td>
<td>Poster</td>
<td></td>
<td>Poster Session</td>
</tr>
<tr>
<td>18:00</td>
<td>Evening Reception at the Eurogress</td>
<td></td>
<td>Public Viewing World Cup Soccer Game Germany - Portugal</td>
</tr>
</tbody>
</table>
## Tuesday 17.06.2014

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Speaker</th>
<th>Presentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00</td>
<td>Keynote Session</td>
<td>T. Faravelli</td>
<td>Politecnico di Milano</td>
</tr>
<tr>
<td>09:45</td>
<td>Keynote Lecture</td>
<td>O. Honda</td>
<td>Osaka University</td>
</tr>
<tr>
<td>10:30</td>
<td>Coffee Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11:00</td>
<td>From Biomass to Biofuels</td>
<td>J. van Groenestijn</td>
<td>TNO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Biomass pretreatment by a continuous flow of superheated steam</td>
<td></td>
</tr>
<tr>
<td>11:30</td>
<td></td>
<td>O. Vozniuk</td>
<td>Università di Bologna</td>
</tr>
<tr>
<td></td>
<td></td>
<td>The chemical-loop approach in bio-alcohols reforming</td>
<td></td>
</tr>
<tr>
<td>12:00</td>
<td></td>
<td>K. Luska</td>
<td>RWTH Aachen University</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Selective deoxy-genation of Biomass-derived substrates...</td>
<td></td>
</tr>
<tr>
<td>12:30</td>
<td>Lunch Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13:30</td>
<td>Keynote Session</td>
<td>A. Faaij</td>
<td>Energy Academy Europe</td>
</tr>
<tr>
<td>14:15</td>
<td>Keynote Lecture</td>
<td>W. Cheng</td>
<td>Massachusetts Institute of Technology</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ethanol/Gasoline engines, status and prospect</td>
<td></td>
</tr>
<tr>
<td>15:00</td>
<td>Coffee Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15:30</td>
<td>Biomass Processing</td>
<td>J. Berg</td>
<td>the high throughput experimentation company</td>
</tr>
<tr>
<td></td>
<td></td>
<td>... Biomass processing enhanced using high throughput experiment.</td>
<td></td>
</tr>
<tr>
<td>16:00</td>
<td></td>
<td>S. Möhring</td>
<td>TU Kaiserslautern</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Assessment of regional lignocellulosic residue and waste availability</td>
<td></td>
</tr>
<tr>
<td>16:30</td>
<td></td>
<td>A. Spieß</td>
<td>RWTH Aachen University</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Integrated enzymatic hydrolysis of ionic-liquid-pretreated biomass</td>
<td></td>
</tr>
<tr>
<td>17:00</td>
<td>Coffee Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17:30</td>
<td>Biofuel Refinery and Reference Process</td>
<td>M. Schlüter</td>
<td>Deutsches Biomasse Forschungszentrum</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methanation studies with a high pressure fixed bed tube reactor ...</td>
<td></td>
</tr>
<tr>
<td>18:00</td>
<td></td>
<td>O. Ferrini</td>
<td>Max-Planck Institut für Kohlenforschung</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Catalytic biorefining of lignocelluloses to useful lignin feeds...</td>
<td></td>
</tr>
<tr>
<td>18:30</td>
<td></td>
<td>K. Ulonska</td>
<td>RWTH Aachen University</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Improvements in the process for the production of TMFB</td>
<td></td>
</tr>
<tr>
<td>19:30</td>
<td>Conference Dinner - forumM, Buchkremerstrasse 1-7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>Event</td>
<td>Speaker</td>
<td>Institution</td>
</tr>
<tr>
<td>-------</td>
<td>------------------------------------------</td>
<td>--------------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>09:00</td>
<td>Keynote Lecture</td>
<td>L. van der Wielen</td>
<td>Delft University of Technology</td>
</tr>
<tr>
<td>09:45</td>
<td>TMFB Report 1</td>
<td>W. Leitner</td>
<td>RWTH Aachen University</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:30</td>
<td>Coffee Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11:00</td>
<td>TMFB Report 2</td>
<td>H. Pitsch</td>
<td>RWTH Aachen University</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12:15</td>
<td>TMFB Report 2</td>
<td>S. Pischinger</td>
<td>RWTH Aachen University</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12:30</td>
<td></td>
<td>S. Pischinger</td>
<td></td>
</tr>
<tr>
<td>12:45</td>
<td>Lunch Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13:45</td>
<td>End of the Public Part of the Conference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17:00</td>
<td>IAB</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Keynote Lecture:
The role of biomass in changing scenarios for green & sustainable energy and chemical production: from biorefineries to bio-factories

G. Centi, University of Messina, centi@unime.it

Keynote Lecture:
Biobased solutions from DSM for renewable energy and materials

M. Wubbolts, Royal DSM, marcel.wubbolts@dsm.com

Keynote Lecture:
Design of catalysts for hydrodeoxygenation of biomass

George Huber, University of Wisconsin-Madison, huber@engr.wisc.edu

Keynote Lecture:
Zeolite catalysts for biomass conversion into fuels and chemicals: hopes and fears

J. Pérez-Ramírez, ETH Zürich, jpr@chem.ethz.ch
Session: Fuel Design
Target of the project was to research the ignition and combustion behaviour of pure vegetable oils in a constant volume combustion chamber apparatus. The oils were characterised by indices based on their fatty acid composition. The indices were their average number of double bonds $ADB$ and average number of carbon atoms $AC$. Main result is, that an increasing $ADB$ of the vegetable oils leads to a longer ignition delay $ID$. The longer the $ID$, the higher the amount of fuel burning in the first combustion phase. No differences were observed during subsequent combustion.

**Introduction**

The usage of straight rapeseed oil as a fuel for vegetable oil compatible diesel engines was demonstrated with success during the last decade, especially in agricultural machinery\cite{1,2}. For other vegetable oils less information is available about their ability to be used as fuel. Particularly the ignition behaviour is of vital importance for fuels in diesel engines. Thus, purpose of the research was to investigate the ignition and combustion behaviour of different vegetable oils.

**Approach / Test set-up**

The study was done by using ten different vegetable oils and two mixtures of vegetable oil. Vegetable oils are triacylglycerides that can be characterised by using their fatty acid composition. Based on that, the indices average number of double bonds $ADB$ and average number of carbon atoms $AC$ of the fatty acid chains of the triacylglycerides were calculated. The calculation method and detailed fatty acid compositions can be found in Emberger et al.\cite{3}. Table 1 shows the resulting $AC$ and $ADB$ of the used vegetable oils.

**Table 1: Average number of carbon atoms $AC$ and average number of double bonds $ADB$ of the vegetable oils**

<table>
<thead>
<tr>
<th>Vegetable oil</th>
<th>$AC$</th>
<th>$ADB$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut</td>
<td>13.04</td>
<td>0.121</td>
</tr>
<tr>
<td>Palm</td>
<td>17.10</td>
<td>0.624</td>
</tr>
<tr>
<td>Mixture 1</td>
<td>15.91</td>
<td>0.629</td>
</tr>
<tr>
<td>Mixture 2</td>
<td>14.33</td>
<td>0.628</td>
</tr>
<tr>
<td>High-oleic sunflower</td>
<td>17.99</td>
<td>0.998</td>
</tr>
<tr>
<td>Jatropha</td>
<td>17.72</td>
<td>1.216</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>17.96</td>
<td>1.287</td>
</tr>
<tr>
<td>Corn</td>
<td>17.82</td>
<td>1.423</td>
</tr>
<tr>
<td>Soybean</td>
<td>17.89</td>
<td>1.433</td>
</tr>
<tr>
<td>Sunflower</td>
<td>17.93</td>
<td>1.477</td>
</tr>
<tr>
<td>Camelina</td>
<td>18.38</td>
<td>1.755</td>
</tr>
<tr>
<td>Linseed</td>
<td>17.93</td>
<td>2.040</td>
</tr>
</tbody>
</table>

The ignition and combustion behaviour was assessed using a Fuel-Ignition-Tester (FIT). The FIT is equipped with a fuel injection system with a single-jet injection nozzle. The chamber is pressurized and heated. Within this research the chamber was operated at different initial combustion chamber pressures (1.0, 2.2 and 3.4 MPa) and a constant combustion chamber temperature (798 K). After the fuel is injected and after the ignition delay, the fuel starts to burn. The heat release due to combustion leads to a pressure rise inside the chamber. This pressure rise is detected by a sensor. The ignition delay $ID$ is defined as the time between the start of injection (detected by a needle lift sensor) and the first pressure rise of 0.2 MPa related to the initial chamber pressure. The further development of the pressure in the chamber is used to identify differences in combustion. The $ID$ results were evaluated using multiple regression analysis using $AC$ and $ADB$ as independent variables.

**Results**

The analysis showed that especially the average number of double bonds $ADB$ has an influence on the $ID$. With an increasing amount of double bonds of the fatty acid chains of the vegetable oils the $ID$ is rising. The multiple regression analysis showed...
for every tested combustion chamber pressure a linear relationship between ADB and ID whereas AC had no significant effect within the model and therefore was neglected. Figure 2 gives an overview about the results.

Using the ID results we additionally performed some more intensive modelling using ID models known from the literature and adapting them to the vegetable oils. By that we recognized that also AC seems to have influence on the ID. With higher AC the ID is rising, but still the main influence was by ADB. Similar results were observed by Freedman et al. using technical triacylglycerides and a different type of constant volume combustion chamber apparatus. Because of the differing ignition delay the first combustion phase was affected. The longer the ID the more intensive was the first premixed combustion phase, recognized by the first peak in the speed of pressure rise curve (Figure 3). After falling from this peak, almost no variances could be observed between the curves. This indicates that there are no big differences between the vegetable oils during the further mixing and reaction controlled combustion phases.

### Figure 2: Ignition delay (arithmetic mean and maximum deviation) of vegetable oils in relation to the average number of double bonds ADB

![Figure 2: Ignition delay (arithmetic mean and maximum deviation) of vegetable oils in relation to the average number of double bonds ADB](image)

### Figure 3: Speed of pressure rise in the combustion chamber of the FIT (2.2 MPa chamber pressure) after injection of coconut oil, mixture 1, high-oleic sunflower oil, rapeseed oil and camelina oil

![Figure 3: Speed of pressure rise in the combustion chamber of the FIT (2.2 MPa chamber pressure) after injection of coconut oil, mixture 1, high-oleic sunflower oil, rapeseed oil and camelina oil](image)

### Summary

Vegetable oils with a short ignition delay are characterised by a low amount of unsaturated fatty acids. The developed models can be used to estimate the ignition behaviour in the FIT of unknown vegetable oils, using the information from the fatty acid composition. The longer the ignition delay, the higher the amount of fuel burning in the first combustion phase. No big differences were observed during subsequent combustion.

### Outlook

The ignition, combustion and emission behaviour of vegetable oils will be further researched in a new constant volume combustion chamber apparatus (Advanced Fuel Ignition Delay Analyzer). This system is equipped with a common rail like injection system and a high pressure and high temperature combustion chamber. With fuel injection pressures up to 120 MPa and combustion chamber conditions of up to 5.0 MPa and 723 K to 1000 K, more compression-ignition engine like conditions are achievable compared to the FIT. Target is to proof the results obtained by the FIT and to gain further information on the ignition and combustion behaviour of straight vegetable oils. Point of special interest is the influence of different combustion chamber conditions on the ignition quality. Moreover the relationship between the ignition quality, combustion characteristics and gaseous and particulate emissions will be analysed and linked to chemical composition of the used fuel. Besides vegetable oils other alternative biofuels for compression-ignition engines will be investigated.

### References


Analysis of legal measures for the regulation of the biofuel market

G. Walther¹, L. E. Hombach¹*
¹Chair of Operations Management
RWTH Aachen University, Aachen, Germany

Blending biofuels into fossil fuels allows for emission reductions in the transportation sector. However, biofuels are not yet competitive to fossil fuels. Thus, legal measures have to be issued, if biofuels are to contribute to European CO₂-reduction targets. Against this background, we develop an optimization model for simultaneously minimizing life cycle greenhouse gas emissions and maximizing discounted net present value in order to analyze the effectiveness and efficiency of legal measures for the regulation of the (bio)fuel market.

Introduction
The transportation sector consumes 26% of global delivered energy [1] and emits 22% of global CO₂ emissions, with 75% of these emissions resulting from road transportation [2]. In the future, the usage of fossil fuels must be reduced in order to ensure supply security and to reach projected emission savings within the transportation sector. One option for achieving these targets is the substitution of fossil fuels by biofuels [3]. However, high investments are necessary for installation of new biofuel production plants, and production costs for biofuels are still higher than for fossil fuels [4]. Thus, stipulation by political regulation is necessary, and long-term stable political regulations must be implemented in order to guarantee the planning reliability for investors. Currently, this planning reliability is not given as the development of the EU biofuel regulations between 1997 and 2012 shows (Fig. 1). As can be seen in Fig. 1, parameter values of the political regulations as well as the used political instruments changed constantly during the last years. These changes can mainly be attributed to unintended side effects, like the arising issues of fuel vs. food and land-use change.

To solve the model we used the augmented ε-constraint approach [5], which allows us to generate the solutions on the efficient frontier and to eliminate weak efficient solutions.

Case study of the German (bio)diesel market
The model is applied to the case study of (bio)diesel production in Germany. Fossil fuel as well as biofuels of the first (conventional biofuels) and second generation (advanced biofuels) can be used to fulfill the final fuel demand. The resulting efficient frontier as given in Fig. 3 shows the trade-off between the two objectives of emission minimization and profit maximization.

Fig. 1 Development of legal instruments for the (bio)fuel market within the EU

Concluding, there is a strong need for long-term stable political regulations, which avoid unintended side-effects and result in efficient as well as effective solutions for the fuel sector.

Bi-objective optimization model
Against this background, we developed a bi-objective, multi-period optimization model, considering cultivation of biomass, production of biofuels, import of biofuels and biomass, as well as blending of fuels with corresponding costs and emissions as objectives. The model contains capacity as well as mass balance constraints. Our aim is to identify Pareto-efficient solutions and to derive trade-off information for political decision makers regarding profit maximization and emission minimization. The structure of the resulting mixed integer linear optimization model is shown in Fig. 2.
2. TMFB International Conference  
Day 1: June 16th, 2014

Fig. 3 Efficient frontier of the German (bio)diesel market as well as the regulations of the EU

Furthermore, Fig. 3 presents the results of an evaluation of all EU regulations for biofuels implemented between 1997 and 2012. It can be stated that there is always a gap to the efficient frontier, i.e. regulations were not efficient. When comparing the overall impact of the various regulations with regard to net present value and emissions, only marginal differences result between these regulations. Thus, the constant changes of regulations over the last years mainly caused confusion and led to uncertainty of investors, but had very limited impact on total efficiency with regard to environmental and economic results of the overall system. One exception was COM (2000)769 with very ambitious biofuel targets, which were already withdrawn in 2001. The changes within the political regulations became necessary because of unintended side effects, like land-use change. By analyzing the optimal solutions of the different political regulations, it becomes apparent that these side effects still appear, and that even recent regulation of the biofuel sector is not able to avoid these known unintended side effects.

Fig. 4 Opened/used production facilities for the optimal solution of the EU regulation 2009/28/EC

Furthermore, when analyzing the results, another unintended side effect becomes apparent. As can be seen within Fig. 4, overcapacities for biofuel production might arise on the long-term. The reason lies within the required relative market share quotas of the EU regulation. Since total biofuel demand depends not only on required market share, but also on total diesel demand, biofuel demand might decrease as soon as total fuel demand decreases in the EU (e.g. due to alternative drive-trains, increasing fuel efficiency) despite stable biofuel quotas. Concluding the results’ section, it becomes clear that political regulations have to be carefully analyzed ex-ante regarding unintended side effects in order to provide long-term, stable regulations and thus, planning reliability for investors.

Summary

In this paper a bi-objective, multi-period, technology and capacity choice and blending optimization model for the (bio)fuel sector is developed and applied to the case study of the German (bio)diesel market. The results allow for an evaluation of efficiency and effectiveness of current and past legal requirements of the EU.

Outlook

The model can be extended in order to account for other important aspects. Advanced biofuels of the third generation are not yet accounted for in the case study, as are new biofuels based on waste materials. Also, the model should be extended in order to consider the trade-off between land-use change and emissions as well as net present value explicitly. Also, dynamic yield factors, incorporation of seasonality and land rotation effects could be integrated within the model. To implement these aspects, the interaction of the optimization model with a Geographical Information System (GIS) seems promising. Additionally, there are many uncertainties respectively ambiguities that should be regarded. To do so, the model could be extended as robust optimization model.

References

Environmental assessment as tool in a fuel design process

C. Merz¹, J. Sutter¹
¹Oeko-Institut, Darmstadt, Germany

The Excellence Cluster "Tailor-made fuels from biomass (TMFB)" aims to develop future advanced fuels derived from biomass and optimized for internal combustion engines. Oeko-Institut accompanies this research by analyses from an ecological point of view. A Life Cycle Assessment was made for an integrated concept in which the two variations of the reference process hydrogenation of itaconic or levulinic acid are assessed consistently from an ecological point of view. Potentials for further optimization are identified.

Introduction
The tailor-made fuel methyltetrahydrofuran (MTHF) can be produced by hydrogenation of itaconic or levulinic acid which can be synthesized from the sugars present in lignocellulosic biomass. Both concepts are preceded by biomass fractionation which separates the lignocellulosic biomass into its three main components: a cellulose-rich stream, a hemicelluloses- or xylose-rich stream and a lignin-rich stream.

Methods
In the itaconic acid route the cellulose- and the xylose-rich stream are subject to hydrolysis and the resulting C6- and C5-sugars are fermented to itaconic acid. After purification itaconic acid is hydrogenized to 3-MTHF. In the levulinic acid route cellulose is thermochemically converted to levulinic acid and hydrogenated to 2-MTHF and a small fraction of pentanol. Hemicelluloses remaining in the cellulose-rich stream can also be converted to levulinic acid and subsequently to 2-MTHF via furan.

As a third option an integrated concept was assessed in which the two reference processes are combined in one setting: the combination is achieved by processing the xylose-rich stream from biomass fractionation to itaconic acid fermentation and the cellulose-rich stream to levulinic acid synthesis as depicted in Figure 1.

Information on the proposed conversion steps and process data were provided by the researchers at RWTH. They rely on lab-scale experiments as well as simulation results. In cases where this information was still unavailable or incomplete, generic data from literature were used, e.g. for biotechnological processes¹. For the assessment of the levulinic acid synthesis we referred to data on the Biofine process². Life-cycle assessment methodology was applied in order to assess the global warming potential (GWP) and the non-renewable cumulative energy demand (CED n.r.). The system boundaries included all processes from the biomass input (beech wood chips) to the output of the target biofuel component (MTHF). For the complete assessment the upstream impact of the wood chips was included, however without considering effects due to land use change.

Results
For the itaconic acid route a base scenario with present performance data and an optimized scenario with an improved fermentation yield were modeled. In both cases demand for electricity and heat dominate the environmental impact of the process in the categories global warming potential (GWP) and non-renewable cumulative energy demand (CED n.r.). The energy gained by the combustion of the side streams (lignin-rich stream and surplus cell mass) cannot satisfy the energy demand of the process. Moreover, in the optimized scenario due to an increased yield the energy gained from the combustion of the surplus cell mass is considerably reduced while process energy demand remains high in some steps. Thus the net GWP and CED n.r. differ only slightly between the two scenarios. However, the biomass requirements are drastically reduced in the optimized scenario.

Due to the very high biomass requirements in the base scenario, the upstream processes (comminution and Organosolv) make a significant contribution to the result. Concerning electricity demand effects can also be made out for stirring and aeration during fermentation as well as electrodialysis. The main contributor for heat demand is the energy required to dry the itaconic acid. In the optimized scenario the highest contribution related to electricity demand comes...
from electrodialysis, also the Organosolv step is still prominent. For heat the drying step remains crucial. With respect to auxiliary materials, the main impact is due to hydrogen demand for MTHF-synthesis in both cases. For the base scenario, ethanol for the Organosolv fractionation also plays a role.

Figure 2 shows energy flows for the optimized scenario for MTHF production via itaconic acid route.

Summarizing, the currently most determining issues for the environmental performance of the itaconic acid route are the fermentation yield, and the link between electrodialysis, which provides purified itaconic acid in aqueous solution, and the MTHF-synthesis, for which itaconic acid is required either dry or in an organic solution. For the levulinic acid route, too, the energy requirements of the process dominate the GWP and the CED n.r. of the MTHF production. The combustion of the side streams from the Organosolv and Biofine steps only partly cover this demand. The main share of the overall impact is attributable to the heat requirement for LA-synthesis (Biofine) step. Heat integration still needs to be considered here. For electricity the highest contribution comes from the Organosolv step. Comminution as well as the LA-synthesis (Biofine) also contribute. Concerning the auxiliary material inputs, the impact of the hydrogen for the MTHF-synthesis dominates.

In general the GWP of the integrated concept lies in the range of the GWP of fossil gasoline. Beside process energy requirements a relevant fraction is related to the hydrogen demand for the MTHF-synthesis steps. As for the separate production routes the latter is determined stoichiometrically and cannot be brought down by optimization. The biomass requirement currently 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.

In the sensitivity analysis it was found that the Organocat process exhibits a considerably better fractionation 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 lower performance concerning GWP and CED n.r. These points to the fact that improvements are especially needed here. To make the itaconic acid route viable in parallel to the increase of the fermentation yield the operating parameters in the other process steps need to be improved.

Outlook
At RWTH research is progressing towards optimized concepts which take into account these findings. As an example, the more efficient Organocat fractionation is being developed which yields cellulose, hemicelluloses and lignin streams of higher purity. Concerning itaconic acid fermentation, beside research into an increased fermentation yield, conceptual process design is being applied to find an energy-efficient way for itaconic acid downstream processing. Especially the route with a complete drying before MTHF synthesis should be replaced by another extraction technique. Another task is to find another organism which does fermentation at a lower pH value so that itaconic acid exists in its acid form. In this case solubility of itaconic acid is much higher which leads to a reduced reaction volume. Also options to use the lignin stream as feed for the production of promising tailor-made fuel components are being investigated.

References
Biomass-based Ketones as Successful Example for the Fuel Design Process


*Institute for Combustion Engines
**Institute for Fluid Power Drives and Controls
†Aachener Verfahrenstechnik - Process Systems Engineering
‡Institute for Organic Chemistry
RWTH Aachen University, Aachen, Germany

Computer-aided molecular design identified few distinct molecular motifs associated with promising properties in the development of novel oxygenated fuels for the spark-ignition engine. Based on predicted engine-relevant property data and despite limited experience on auto-ignition of ketonic fuels, ketonic carbonyles were chosen for further investigation. Exceptionally good knock resistance and mixture formation at challenging boundary conditions have been experimentally confirmed for 2-butanone, a prototype of a ketonic biofuel comprising tailored properties. To ensure the safe handling of the new fuel candidate its compatibility with seal materials and engine oils has been screened. Synthetic pathways from biomass derived platform chemicals to 2-butanone were examined.

Introduction

The TMFB fuel design aims at the identification of molecular structures comprising engine-relevant properties and their sustainable production pathways. The present contribution briefly summarizes recent progress in the fuel design process in the four areas: (i) computational identification of promising structural motifs, (ii) first experimental assessment of important fuel properties (e.g. ignition quality and material compatibility), (iii) engine-testing and -optimization, and (iv) synthetic accessibility and catalysis research.

Computer-Aided Molecular Design

In an attempt to identify fuels for the spark ignited engine an exhaustive computational search of the molecular space comprising all mathematically feasible CnH2On structures carrying one to eight carbon atoms has been performed\(^1\). Restricting molecule generation solely by the valence rules yielded an initial set of ~168.8 million structures, which was subsequently reduced by excluding infeasible substructures and molecular patterns difficult to obtain by selective chemo-catalytic transformations of biomass monomers\(^2\). The resulting ~12.4 million molecular structures were screened for oxygenates comprising a set of engine-relevant fuel properties (cf. Figure 1) by employing predictive property models based on Quantitative Structure-Property Relationships (QSPRs)\(^3\). The final number of 279 fuel candidates can be classified into acyclic ethers, ketones, aldehydes, alcohols, cyclic ethers and furans. Unsaturated and branched molecules constitute the majority of the identified structures\(^2\). Because of the favorable boiling characteristics ketones were chosen for further investigation despite the limited experience on ignition quality respectively knock resistance. Initial rapid screening in an Ignition Quality Tester\(^{TM}\) (IQT) revealed remarkably low auto-ignition capabilities for 2-butanone (DCN <5), methyl isobutyl ketone (DCN 12.6), diisopropyl ketone (DCN 16.6), and methyl isopropyl ketone (DCN <5). Subsequent experimental testing yielded exceptionally high research and motor octane numbers (RON and MON, respectively) in case of 2-butanone (cf. Table 1).

**Figure 1** – Computer-aided molecular design to identify fuel candidates for the SI engine\(^*\)

Fuel compatibility

To ensure a safe and reliable handling of the biofuel candidates in combustion engines and test rigs their compatibility with critical components needs to be analyzed. As part of this research the impact of several TMFB fuel candidates on common-rail fuel pumps, engine oils and seal materials is investigated in experimental and theoretical approaches. Immersion tests are a common and standardized procedure to screen the compatibility of a given combination of seal material and fluid\(^4\). Ideally these model tests are performed using utilizing the seal material from the technical application. However due to the multitude of different sealing applications and fluids within the cluster this is not a viable approach. Hence, the first analyses of new biofuel candidates are performed with the standard reference elastomer ISO 13226 SRE-NBR 28...
(cf. Figure 2). The strong swelling and loss of hardness of the SRE specimen when paired with 2-butanone indicates the insufficient resistance such seals would possess when exposed to ketones. Hence additional seal materials like EPDM and FKM were screened to identify suitable seal materials.

Figure 2 – Relative changes of NBR specimen after 28 days

Fuel properties

Table 1 lists the most relevant properties of the experimentally studied fuels.

<table>
<thead>
<tr>
<th></th>
<th>RON 95</th>
<th>Ethanol</th>
<th>2-Methylfuran</th>
<th>2-Butanone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling temperature / °C</td>
<td>41.5-173.5</td>
<td>78</td>
<td>64</td>
<td>80</td>
</tr>
<tr>
<td>Specific enthalpy of vaporization / kJ/kg, λ = 1</td>
<td>28.08</td>
<td>101.6</td>
<td>35.52</td>
<td>46.10</td>
</tr>
<tr>
<td>Lower heating value / MJ/kg</td>
<td>42.13</td>
<td>26.84</td>
<td>30.37</td>
<td>31.45</td>
</tr>
<tr>
<td>Lower heating value / MJ/l</td>
<td>31.05</td>
<td>21.09</td>
<td>25.32</td>
<td>27.63</td>
</tr>
<tr>
<td>Stochiometric air requirement / -</td>
<td>14.14</td>
<td>8.98</td>
<td>10.08</td>
<td>10.52</td>
</tr>
<tr>
<td>RON MON</td>
<td>96</td>
<td>109</td>
<td>101</td>
<td>117</td>
</tr>
</tbody>
</table>

Table 1 – Fuel properties

Ethanol is known as an excellent biofuel for gasoline engines especially at high engine loads due to its high knock resistance and high heat of vaporization. These characteristics enable efficiency improvements of up to ~13% compared to conventional RON 95 gasoline fuel\(^9\). Therefore ethanol is defined as the benchmark biofuel for spark ignited engines. However drawbacks arise from the low volumetric heating value and the weak cold start capability. The high heat of vaporization and low vapor pressure in combination with an increased fuel demand due to the lower stoichiometric air requirement lead to a deterioration of mixture formation\(^7\). Previously performed calculations revealed that for the formation of an ignitable stoichiometric mixture at ~30 °C ambient temperature a specific heat of vaporization smaller than 60 kJ/kg\(_m\) is needed\(^8\). The engine test bench investigations revealed 2-methylfuran as a potential candidate for a future gasoline fuel\(^9\). The high vapor pressure and only moderate enthalpy of vaporization lead to a superior mixture formation at cold start conditions compared to ethanol. Efficiency improvement of up to ~10% compared to conventional RON 95 gasoline fuel can be achieved at full load operation. 2-Butanone is a potential biofuel candidate combining a knock resistance significantly higher than 2-methylfuran, a moderate volumetric heating value and a good mixture formation especially at cold start conditions.

Experimental results

The engine test bench investigations were carried out on a homogeneously operated direct injection spark ignition single cylinder research engine known from previous publications\(^8,9,10\). In contrast to the previously used outward-opening piezo injector, a 6-hole solenoid injector was installed. The achievable thermal efficiency of a gasoline engine predominantly depends on the compression ratio which in turn is limited by the knock resistance of the fuel. Figure 3 depicts the knock resistance in terms of the 50% mass fraction burned point using a compression ratio of 13.5 at an engine speed of \(n = 2000\) min\(^{-1}\) and full load at 27 bar indicated mean effective pressure (IMEP). A 50% mass fraction burned point (MFB50) at or close to the optimum of 8° CA ATDC indicates a high knock resistance and hence the highest possible engine efficiency. The evaluation of the performance of 2-butanone was conducted by a comparison of measurements under equal boundary conditions for both ethanol and 2-butanone. The full load investigation confirmed the high knock resistance of 2-butanone under real engine conditions.
Figure 4 – Engine test results at catalyst heating point

The short burn delay and duration in case of 2-methylfuran result in a good combustion stability of 2-methylfuran indicated by the low standard deviation. For ethanol and 2-butanol a nearly equal cyclic variation is measured. Although the level of HC emissions is partially influenced by the differences in post-oxidation occurring in the exhaust system due to the different temperature level, it can be stated that the low HC emissions of 2-butanol similar to those of 2-methylfuran indicate a good mixture homogenization. Hence the expectation of 2-butanol being a fuel with excellent knock resistance and mixture formation at challenging boundary conditions is experimentally confirmed.

Synthesis

2-Butanone is synthetically accessible from a variety of biomass based platform chemicals. Figure 5 shows the synthesis of 2-butanone with 2-butanol and levulinic acid as starting materials.  

Figure 5 – Synthesis of 2-butanone from 2-butanol and levulinic acid

For both the oxidative decarboxylation of levulinic acid and the formal dehydrogenation of 2-butanol heterogeneous copper catalysts have been employed. While the former process affords 2-butanone in moderate to good yields, excellent selectivities and high yields have been reported for the latter making it attractive for large scale applications.

Abbreviations

ATDC After top dead center
CA Crank angle
EPDM Ethylene propylene diene monomer rubber
FKM Fluorocarbon elastomer
HC Hydrocarbon
MFB50 50 % mass fraction burned point
MON Motor octane number
NBR Nitrile butadiene rubber
IMEP Indicated mean effective pressure
RON Research octane number
SRE Standard reference elastomer

References

Session: Combustion Chemistry 1
“Rate Constant Calculations of the H-Atom Abstraction Reactions of Oxygenated Fuels with OH and HO₂ Radicals”

Jorge Mendes*, Chong-Wen Zhou, Henry J. Curran
Combustion Chemistry Centre, National University of Ireland, Galway, Ireland

Oxygenated biofuels generated from biomass have received considerable attention in recent years. Alcohols, esters, ethers and ketones are the most promising biofuel candidates. Over the last thirty years or so the combustion community has built up significant knowledge on the fundamental reactions and associated rate constants for hydrocarbon fuels, but little is known of oxygenated compounds. High-level theoretical investigations on the H-atom abstraction by OH and HO₂ radicals are important to predict the reactivity of these fuels. This work serves as a guideline to assist the selection of appropriate rate constants for oxygenated biofuel molecules and other biofuel candidates to be used as possible petroleum fuel additives.

* Corresponding author: j.mendesferreira1@nuigalway.ie

Introduction

We have performed high-level ab initio quantum chemical calculations to study the influence of the functional group (esters¹,², ethers³,⁴, aldehydes, ketones⁵,⁶, alcohols⁷,⁸, and acids) on the rate constants for H-atom abstraction by OH or HO₂ radicals, under combustion relevant conditions. We found that, in general, the further the abstraction occurs from the functional group, the more similar were the rate constants when compared to those calculated previously for alkanes. On the other hand, abstraction from the carbon atoms adjacent to the functional group (α'/α) were slower for ketones and esters and faster for alcohols and ethers when compared to alkanes.

Rate constants for abstraction of a H-atom by an HO₂ radical from either side of the functional group on ketones and esters are very similar.

For ethers, the rate constants for abstraction at the α’ and α positions are calculated to be faster than for ketones and esters due to the fact that the electron lone pair on the oxygen atom is delocalized to the adjacent C–H anti-bonding orbital (α–σ*(CH)). This weakens the adjacent C–H bond and consequently lowers the energy required to abstract H-atoms.

Abstractions by OH and HO₂ radicals at the α'/α and β'/β positions are the most influenced by the hydrogen bond interactions that occur between the radical and the functional group, where the rate constants differ most when compared to alkanes. At the γ position, abstraction of a H-atom by OH radicals is not influenced by these interactions and the rate constants are most similar to alkanes. However, as the HO₂ radical is larger than the OH radical, abstraction by HO₂ radicals at the γ position is influenced (slightly) by these interactions. Only when abstraction by HO₂ radicals occurs at the δ position are the rate constants similar to alkanes.

When undergoing abstraction by an OH radical, esters are generally slower than ketones at the same site. The mechanism of H-atom abstraction by both OH and HO₂ radicals involves the formation of a hydrogen bond between an oxygen atom of the functional group and the hydrogen atom of the radical in the transition state. When determining the hindrance potentials the hydrogen atom of the radical interacts with an oxygen atom of the oxygenated species. When undergoing abstraction by OH radicals, these hydrogen bond interactions have a bigger impact on our rate constants when compared to abstraction by HO₂ radicals. This is due to the OH radicals being lighter and more sensitive to these interactions, as well as the calculated electronic energies, compared to HO₂ radicals.

Comparison with available experimental results

Here, we compare our calculated total rate constant results with available experimental results.

- Fig. 1, dimethyl ketone + OH radical. They are about 55% different.
- Fig. 2, ethyl methyl ketone + OH radical. They are almost identical.
- Fig. 3, esters + OH radical. Our calculated result is about a factor of 2 slower than the experimental data for methyl ethanoate. For methyl propanoate and methyl butanoate our rate constants are about 50% different. These differences are all within the estimated uncertainty in our calculations.
Fig. 1: Comparison of the calculated total rate constants for dimethyl ketone $^5 + \text{OH}$ (●) and experiments obtained by Lam et al. $^9$ ( ■ ) and Vasudevan et al. $^10$ ( ▲ ).

Fig. 2: Comparison of the calculated total rate constants for ethyl methyl ketone $^5 + \text{OH}$ (●) and experiments obtained by Lam et al. $^9$ ( ■ ).

Fig. 3: Comparison of the calculated total rate constants for esters + $\text{OH}^1$: methyl ethanoate (●), methyl propanoate (●) and methyl butanoate (●) and experiments obtained by Lam et al. $^{11}$ ( ■ , ● and ▲ , respectively).

References


Reactivity Trends in Furan and Alkylfurans Combustion

Mazen A. Eldeeb¹, Ben Akih-Kumgeh¹*
¹Department of Mechanical and Aerospace Engineering
Syracuse University, Syracuse, NY 13244, USA

In this work, results of a systematic study of the ignition behavior of furan, 2-methyl furan (2-MF), and 2,5-dimethyl furan (DMF) are presented. The experiments are carried out in a newly constructed shock tube facility. Quantifying reactivity trends among the various furans could aid in the development of fuel formulations with improved combustion dynamics and lower emissions. The structure-reactivity trends provide some insight on the complexity of furan combustion and also provide experimental data for further studies and validation of models for this promising class of oxygenated hydrocarbons.

Introduction
Bio-derived furans have attracted attention as alternative transportation fuels. Their physical properties are comparable with gasoline and their energy densities are greater than those of short-chain alcohols. There is active research, with initial positive results, investigating the feasibility of furan production from second generation biomass [1, 2] and system-level tests of furan combustion in research engines [3, 4]. At the fundamental level, the ignition behavior and laminar flame propagation of these furan fuels are being investigated, in combination with chemical kinetic model development [5, 6]. However, these studies have focused on the investigation of individual furans. Quantifying reactivity trends among the various furans could facilitate the development of fuel formulations with improved combustion dynamics and lower emissions.

Experimental Approach
Experiments are carried out behind reflected shock waves in a newly constructed shock tube facility. The stainless steel shock tube consists of 4.0 m driven section and a 2.7 m driver section. The inner diameter of the mechanically polished tube is 10 cm. Shock velocities are measured using four fast-response PCB transducers mounted 40 cm apart. Post reflected shock temperatures are determined from the one-dimensional shock equations. The greatest source of uncertainties in shock tube experiments remains the temperature, to which chemical reaction rates are very sensitive. The uncertainties arise from possible uncertainties in mixture compositions and shock velocity measurements. The average temperature uncertainty of the current facility is estimated at 20-30 K.

Ignition delay time measurements are performed by means of mounted optical fibers, connected to photodiodes. The photodiodes are equipped with 430±10 nm narrow band filters to obtain CH chemiluminescence signals for ignition delay time determination.

The ignition delay time is defined as the time from the arrival of the reflected shock wave at the optical fiber port to the intersection of line of maximum gradient with the initial baseline signal. The three furans, DMF, 2-MF, and furan are studied at equivalence ratios, Φ, of 0.5, 1.0 and 2.0.

Results and Discussion
The ignition behavior of the three furans was investigated at nominal pressures of 2, 5 and 12 atm with argon/oxygen ratio maintained at 3.76. This dilution level is reflective of air as a technical oxidizer.

Figure 1 features a comparison between the ignition delays of stoichiometric mixtures of the three furans at a nominal pressure of 2 atm.

![Fig. 1: Relative ignition behavior of furan, 2-MF, and DMF at stoichiometry and nominal pressure of 2.0 atm.](image)

The figure shows that DMF is the least reactive, while 2-MF ignites most readily. Furan reactivity lies between these extremes. This is a key finding which is eluded by focusing on each of the furans as in previous studies. This also implies that DMF could be well suited for combustion systems where ignition is least desired and that while 2-MF has hitherto only
been considered for gasoline applications, its high reactivity could also be used in compression-ignition engines. From a chemical perspective, it means that double alkylation of furan confers greater chemical stability while the singly alkylated 2-MF introduces higher reactivity. The same trend is observed at higher pressures. Figure 2 shows a comparison between the three fuels at stoichiometric conditions and a nominal pressure of 5 atm.

![Figure 2: Relative ignition behavior of furan, 2-MF, and DMF at stoichiometry and nominal pressure of 5.0 atm.](image)

The pressure effect is obvious in terms of decreasing the ignition delay time for the three furans with the pressure increase. The reactivity trend is consistent with the observations at the lower pressure. This reactivity trend is also observed for rich mixtures, as shown in figure 3, which displays relative ignition behavior of the three furans at equivalence ratio of 2, and pressure of 12 atm.

![Figure 3: Relative ignition behavior of furan, 2-MF, and DMF at an equivalence ratio of 2 and nominal pressure of 12.0 atm.](image)

Figure 4 reveals the effect of equivalence ratio on 2-MF ignition. It shows a comparison among three 2-MF/O₂/Ar mixtures at equivalence ratios of 1.0, 2.0 and 0.5, respectively. In most hydrocarbon ignition at high temperatures, the ignition delay times decrease with increasing equivalence ratio. Under the current conditions, the rich mixture is shown to be the most reactive, while the lean mixture has the longest ignition delay time, which confirms the expected reactivity trend.

![Figure 4: Equivalence ratio effect of 2-MF ignition delay times for 2-MF/O₂/Ar mixtures at nominal pressure of 12.0 atm.](image)

**Conclusion**

This study systematically investigates the ignition of a class of oxygenated cyclic hydrocarbons, furans, which are of interest to combustion technology as biofuels. Important trends are uncovered. The ignition results show a consistent trend among all investigated conditions, whereby DMF is the least reactive while 2-MF is the most readily ignitable. Generally, ignition delay times decrease with increasing equivalence ratios, as shown in the 2-MF case. The dataset contributes toward further understanding and modeling of furan combustion.

**References**

Alcohol combustion chemistry

S. Mani Sarathy¹, Patrick Oßwald², Nils Hansen³ and Katharina Kohse-Höinghaus⁴

¹ Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia
² Institute of Combustion Technology, German Aerospace Center (DLR), Pfaffenwaldring 38-40, D 70569 Stuttgart, Germany
³ Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA
⁴ Chemistry Department, Bielefeld University, Universitätsstraße 25, D-33615 Germany

¹corresponding author, Email: Mani.Sarathy@kaust.edu.sa, Tel.: +966 2 808 4626 (work) +966 (0) 544 700 142 (mobile) Fax: none

Abstract
Alcohol fuels have been used since the early years of automobile production, particularly in Brazil, where ethanol has a long history of use as an automobile fuel. While biofuel production and its use (especially ethanol and biodiesel) in internal combustion engines have been the focus of several recent reviews, a dedicated overview and summary of research on alcohol combustion chemistry is still lacking. Besides ethanol, many linear and branched members of the alcohol family, from methanol to hexanols, have been studied, with a particular emphasis on butanols. These fuels and their combustion properties, including their ignition, flame propagation and extinction characteristics, their pyrolysis and oxidation reactions and their potential to produce pollutant emissions have been intensively investigated in dedicated experiments on the laboratory and the engine scale, also emphasizing advanced engine concepts. Research results addressing combustion reaction mechanisms have been reported based on results from pyrolysis and oxidation reactors, shock tubes, rapid compression machines and research engines. This work is complemented by the development of detailed combustion models with the support of chemical kinetics and quantum chemistry. This presentation seeks to provide an introduction to and overview of recent results on alcohol combustion by highlighting pertinent aspects of this rich and rapidly increasing body of information.

Keywords: biofuel, combustion chemistry, alcohols, kinetic modeling, pollutant emissions, ignition, flame speed
Session: Spray and Mixture
Jet Breakup and Mixture Formation of Novel Biofuels

Introduction
Primary breakup of jets marks the initial condition for the subsequent mixing process inside the cylinder of direct-injection engines. Thus, understanding primary breakup is crucial to judge the overall mixing performance of tailor-made biofuels. In addition, the process of air-fuel mixing is significantly influenced by the following droplet evaporation and in-cylinder flow field. However, earlier results indicated the influence of the fuels properties on the mixing process. While the primary breakup is strongly influenced by the fuels viscosity and density, evaporation is determined rather by the heat of vaporization and the boiling point.

Approach
The mixture formation of fuel and air can be divided into several sub-processes, incorporating experimental and numerical approaches. Recent results give insight into i) the primary breakup of the liquid fuel jet exiting the nozzle. The primary breakup is analyzed by microscopic shadowgraphy in the near-field of the nozzle. Moreover, ii) overall spray behavior under engine-relevant conditions is investigated. This includes new information about the temperature distribution in diesel flames using stereoscopic 3-color high-speed ratio-pyrometry. All aforementioned investigations lack the presence of the in-cylinder flow field, which significantly influences mixing and the evolution of the flame front during combustion. The iii) in-cylinder flow field of the TMFB Otto engine is analyzed experimentally via stereoscopic particle-image velocimetry (PIV). In order to complement these experiments by numerical investigations, a new level-set based Cartesian cut-cell flow solver for complex moving boundaries was developed to enable highly resolved large eddy simulations of the flow field. To support spray and combustion modeling, iv) the evaporation properties of the biofuels are investigated. On the one hand, extensive vapor-liquid equilibrium (VLE) measurements of binary mixtures of promising biofuel candidates were conducted at engine-like conditions. On the other hand, a planar 2-color-Laser-Induced-Fluorescence (2cPLIF) technique has been set up to measure droplet surface temperature and size simultaneously.

Results
The primary breakup region close to the nozzle is characterized by small scales and a fast moving jet. Therefore, full-cone diesel sprays have been analyzed with a proprietary optical set-up with unmatched magnification and resolution. A pulsed, incoherent laser light source is used for this method to prevent nonuniform background illumination and motion blur [1]. Latest results have already been collected under engine-like ambient pressures.

Fig. 1: Microscopic images of the primary breakup of a full-cone spray on various scales [1].

Fig. 1 shows images of the primary breakup on various scales: the intact liquid jet of the spray surrounded by ligaments, films/bags and droplets, as well as droplet interaction and secondary breakup. Furthermore, the primary breakup has been investigated for hollow-cone injectors [2]. Fig. 2 exhibits 2-Methylfuran as the fuel with the smallest liquid structures already close to the nozzle. For this reason 2-Methylfuran outperforms even standard reference fuels like...
iso-Octane. Highly-viscous fuels such as THFA only show a limited breakup.

**Fig. 2:** Comparison of primary breakup of a hollow-cone spray at an injection pressure of 200 bar.

The overall spray behavior is studied in special chambers that provide in-cylinder temperature and pressure conditions. The chambers are equipped with windows so that optical measurement techniques can be applied. Fig. 3 shows the latest overall 3-dimensional surface temperature plot of a diesel flame, deduced from pyrometry measurements. Different regions of hot and cold zones of the combustion are shown.

**Fig. 3:** 3-dimensional surface temperature plot of the diesel flame (spray propagation from left to right).

In order to gain a complete picture of the entire mixing process of fuel and air, the in-cylinder flow field is studied in a transparent spark-ignition engine. Typically, a tumble vortex forms at early crank angles and dominates the flow field throughout induction and compression. At approx. 320 CAD atdc, the tumble breaks up into smaller vortices, and the resulting high levels of turbulence contribute beneficially to the combustion [3]. The comparison of the temporal development of cycle-averaged vortices shows that valve timing has a strong impact on the tumble vortex (see Fig. 4).

**Fig. 4:** Development of the cycle-averaged vorticity in the valve plane for three different intake valve timings.

The new Cartesian cut-cell based flow solver for Large Eddy Simulations (LES) of compressible flows complements the experiments in the transparent engine. The flow solver features fully automatic mesh generation and solution adaptive mesh refinement [4]. The boundary motion and topological changes in geometry due to the opening and closing events of the valves are captured accurately by using multiple signed distance functions to represent the different components of the engine. A continuous discretization of the flow equations in time near the moving interfaces is applied to prevent nonphysical oscillations in the simulated flow field. The overall method has been efficiently parallelized such that flow simulations on O(1000) processors can be performed.

In order to support the spray and combustion investigations, evaporation properties of the TMFB fuels have been analyzed by measurements of bubble point pressures using the Cailletet technique for blends of di-n-butyl ether (DNBE)/ 2-Methyltetrahydrofuran (2-MTHF) and iso-Octane/ 2-Methylfuran [5]. In addition, the experimental effort required for the description of high-pressure VLE over a wide range of compositions, temperatures and pressures was reduced. For this purpose, a hybrid approach was used combining a quantum chemically based equation of state (EOS) approach with experimental data. Now, experimental data for a single pure substance vapor pressure per component is sufficient to extrapolate the full binary VLE behavior, leading to a significant reduction of experimental effort (see Fig. 5).

**Fig. 5:** Bubble point pressures of the binary biofuel mixture DNBE/2-MTHF. Semi-predictive EOS (solid line) compared to our experimental data (circles). Experimental data points used for the semi-predictive EOS are highlighted by red circles.

**References**


Injection rate characteristics of a Piezo-Common-Rail-Injector fueled with straight rapeseed oil and its mixtures with orange peel oil

Koder A.¹, Altmann R.¹, Rabl H.-P.¹, Mayer W.²
¹CEEC Regensburg
²OTH Regensburg, Germany

It is well known, that rural produced straight vegetable oils can be an alternative fuel to fossil diesel and contribute to an effective reduction of greenhouse gas emissions. In this context, a test system is developed, including both injection rate analyzer and spray chamber. In case of the strong viscosity variations of pure plant oils, their injection rates are pointed to a meaningful reference temperature. Based on this measurement technique straight rapeseed oil and its mixtures with orange peel oil are examined and compared to fossil diesel, using a modern common rail diesel injection system.

Introduction

The use of straight vegetable oils in internal combustion engines offer new alternatives to fossil diesel but should be handled with care due to the strong variations of their physical properties in the occurring temperature range. For this reason Esteban et al. [1], Noureddini et al. [2] or Elsbett et al. [3] investigated the changing of viscosity in case of increasing fuel temperature. Some research due to the spray and atomization process of pure rapeseed oil has been done by Sapit et al. [4], Lüft et al. [5] and Wloka et al. [6]. To light up the changes in injected mass and injector dynamic regime with varying fuel temperature, this work compares the injection rates of pure rapeseed oil and promising oil mixtures to fossil diesel.

Test set-up

To analyze the injection rate of the different fuels, Moehwalds injection rate analyzer HDA is used. Furthermore a preheating system is adapted at the test bench, to adjust different temperatures to the fluid downstream the high pressure pump. The high pressure parts of the system are also temperature controlled, using an electrical heating unit.

Finally the injector contains three temperature measuring points that allow a determination of the injection rate in dependence to a defined reference temperature. Extensive test series have shown that the leakage temperature of the Injector correlated most with the measured injection rates. A first injection rate measurement of Diesel and pure rapeseed oil at different leakage temperatures can be seen in Figure 1. The shown injection rates are measured at a fully ballistic regime of the injector which leads to strong variations in the hydraulic start and end of injection. The favorable physical properties of rapeseed oil with increasing fluid temperature lead to an enormous increase of the injected mass. Therefore, oil mixtures with lower viscosity levels are built up by mixing rapeseed oil with orange peel oil. The kinematic viscosity depending to the temperature is shown in Figure 2 in which mixture 1 is a 2,5% orange peel oil solution in rapeseed oil (w/w) and mixture 2 is a 5% orange peel oil solution in rapeseed oil (w/w).

Results

The following results show the relationships of a warm up cycle which starts at a room temperature of 20 °C. This warm up cycle is divided in 4 sections of 4000 shots. In the first section the
entire system, including the injector is heated up without any external energy source. At the following three sections the electrical heating unit of the high pressure part helps to reach higher fuel temperatures. In the sequence an example with a rail pressure of 50 MPa and an injector energizing time of 1,0 ms was chosen to see the strongest impact of viscosity variations on the injection rate and therefore the injected mass. Figure 3 shows four injection rates of diesel fuel, pure rapeseed oil and the above mentioned oil mixtures at the same leakage temperature of 45 °C.

It can be noticed that a lower viscosity of the fluid due to preheating or mixing leads to a faster actuation of the needle because of a better fluid flow through the inlet and outlet throttle of the injector. Also the start of injection and therefore the opening delay time varies greatly with the viscosity variation. Thus, it is also possible that the dynamic regime of the injector changes from ballistic to non-ballistic by increasing the fuel temperature. In summary, Figure 4 shows the variation of the injected mass over a wide temperature range.

With the use of rapeseed oil it can be seen, that an injection is only possible at leakage temperatures over 40 °C instead of a lowest injector opening temperature of 28 °C for mixture 1. Mixture 2 and diesel fuel are always injectable over the observed temperature range. Figure 4 also shows, that diesel fuel is nearly independent of varying temperatures instead of the other fuels that show strong variations in the injected mass. At higher rail pressures than the ones shown in Figure 3 and 4 the point of the first injector opening is shifted to colder conditions.

**Summary**

The presented results show strong viscosity variations of pure rapeseed oil and the investigated oil mixtures in the occurring temperature range by using them in a common rail diesel injection system. These changes in flowability are certainly one reason for the strong variations of the injected mass during a warm up cycle. With the described test setup it is also possible to determine the temperatures of the first injector opening at different rail pressures. The largest differences in the injected mass occur at ballistic regimes of the injector where little changes of the oil temperature could strongly affect the mass flow rate.

**References**

Analysis of the Atomization Characteristics of 2nd Generation Bio-diesel (2GEN) in Comparison to Diesel-Fuel

P. Dragomirov1*, J. Sauerhering1, J. Schmidt1, H. Rottengruber2 and J. Hadler3
1Institute of Fluid Dynamics and Thermodynamics
2Institute of Mobile Systems
3Institute of Automotive Expertise
Otto von Guericke University Magdeburg, Magdeburg, Germany

Driven by the attempts to decrease exhaust emissions and to find a suitable alternative diesel fuel first and second generation bio-fuels often fall into the scope of scientific investigations. In order to give a more detailed insight of the atomization and spray characteristics of a new 2nd generation bio-diesel, a series of experiments such as Phase Doppler Anemometry (PDA) and high speed visualization were performed. A pressure chamber was employed to investigate the influence of the fuel properties as well as of the surrounding air pressure and temperature under conditions comparable to those of a DI diesel engine.

*Corresponding author: plamen.dragomirov@st.ovgu.de

Introduction

The demand for middle distillate fuels will continue to grow over the next X years [1]. European legislation requires 10% Biofuel by 2020, which might not be achievable using vegetable oil derived biofuels, therefore there is a need for 2nd generation biofuels. Diesel fuel replacements can be divided into two major groups, alternative fuels of the first and second generation. Despite the more complex production process, second generation bio diesels could be the solution for ensuring a considerable portion of mankind’s fuel demand. Furthermore great expectations have been laid upon 2nd generation bio diesel such as; bio mass to liquid (BTL) and Hydrogenation of microbial oil due to the ability to produce a low cost, sustainable and scaleable bio-fuel.

Although 2nd generation bio-diesel in principle should behave in a similar manner to 1st generation bio-diesel and crude diesel, small differences in the atomisation and air-fuel mixing properties may have a pronounced influence on the combustion process and exhaust emission. On this account investigations are necessary to provide sufficient information about this 2nd generation bio-diesel (2GEN) fuel and it’s suitability as diesel fuel replacement. Therefore a series of experiments using high speed visualisation and Phase Doppler Anemometry (PDA) are conducted.

Experimental setup

In order to analyse the influence of the fuel properties on the spray characteristics, a vertically-flown (top to bottom) pressure chamber was utilised. In its current state this pressure vessel is laid out for air pressures up to 60 bar and can be heated to 300° C. The 8-hole BOSCH injector with a seat hole nozzle was mounted in the pressure chamber by adapting the injector holder previously introduced by [2]. To avoid interference of the remaining 7 spray jets while investigating one of them, a separation device was developed, see Fig. 5. Similar approaches to separate the desired spray jet from the rest were used by [3] [4].

The pressure chamber has 2 by 2 opposite-facing windows with a diameter of 80 mm, whereas one of them is shifted 20° with respect to his opposite providing good measurement conditions with Dantec’s 2D PDPA-System, see Fig. 6.

The spray propagation was captured with a 12bit high-speed camera (LaVision HighSpeedStar 6) at a frequency 20 kfps/ 16 LED’s in pulse mode with a combined power of 1,3 kW was used for the illumination of the sprays, which allowed the reduction of the exposure time to 10 µs. The camera and light source alignment can be seen in Fig. 6.

Results

The investigation of the spray by means of PDA showed that the fuels of interest possess quite similar atomisation characteristics. However in the case of the 2GEN slightly larger droplets were
detected, see Fig. 7. The same tendency could be observed for the Sauter mean diameter.

![Fig. 7 Droplet diameters at 16.8 bar and 50°C air pressure and temperature](image_url)

The geometrical analysis of the spray jets also showed some small differences between them concerning the spray penetration, see Fig. 8. The 2GEN has a slightly higher penetration rate at early stages after the start of energising (SOE), which could be contributed to its lower density and viscosity resulting in higher nozzle in- and outflow velocities. Afterwards the spray tip of the 2GEN decelerates faster probably also as a result of the lower density and hence smaller droplet impulse.

![Fig. 8 Spray penetration at 16.8 bar and 50°C air pressure and temperature](image_url)

The spray angle appeared to be relatively insensitive to the differences in the properties of the two investigated fuels, see Fig. 9.

![Fig. 9 Spray angle at 16.8 bar and 50°C air pressure and temperature](image_url)

Summary

High-speed visualization as well as PDA was applied on a pressure chamber to investigate the atomisation and spray characteristics of a 2GEN and diesel fuel.

This preliminary study showed some small differences between the investigated fuels. In matter of droplet size slightly larger sauter mean diameter could be observed in the case of 2GEN. The investigated alternative fuel exhibited slightly larger penetration after the start of injection followed by a higher deceleration rate presumably due to its lower density. No strong dependence of the spray angle on the fuel properties could be observed.

Outlook

In order to validate the trends observed in this preliminary study further measurements are necessary. The upcoming efforts will be to expand the operating parameters as well as to include other alternative diesel fuels. Afterwards a correlation between the acquired results and the analysis of the air-fuel mixing and combustion characteristics of the investigated fuels carried out on an optically accessible diesel engine will be pursued.

References


Keynote Lecture
T. Faravelli, Politecnico di Milano, tiziano.faravelli@polimi.it

Keynote Lecture:
Construction of an in vitro synthetic pathway with thermophilic enzymes
O. Honda, Osaka University, honda@bio.eng.osaka-u.ac.jp
Session: From Biomass to Biofuels
Biomass pretreatment by a continuous flow of superheated steam

J.W. van Groenestijn*, H.C van Deventer
TNO, PO Box 360, 3700 AJ Zeist, the Netherlands

It is known that the lignocellulose complex can be disintegrated under acidic conditions at high temperatures. In case heating is carried out by steam injection, most of the time such steam is stagnant and saturated. The use of superheated steam (SHS) that flows through the biomass is an alternative with several advantages. By passing steam through heaps of e.g. straw an efficient and uniform heat transfer is established. Tests were carried out with wheat straw and reaction conditions were varied. The straw could be successfully pretreated within a few minutes at dry matter concentrations between 30% and 65%, steam pressures of 6 bara and temperatures of 160-180°C. During superheated steam treatment hemicellulose was 90% hydrolyzed into its monomers. SHS makes the cellulose well accessible to enzymes. E.g. after cooling and neutralization the cellulose could be 90-95% converted into glucose by the use of enzymes. Ethanol fermentations were demonstrated using 38% biomass dry matter content. Further diluted, but concentrated during pretreatment, and as a consequence the catalyst (the acid) in the peripheral zones of the biomass particles is not diluted. That is important when efficiencies near 100% must be reached. A continuous flow of superheated steam through the material (the heap) is important as well: to keep the steam superheated and to distribute the hot steam evenly over the heap of biomass. That will avoid overcooking and undercooking in the same reactor. The biomass should be dry enough to allow spaces between the biomass pieces. Pieces of straw and grass naturally act as spacers: these allow steam ventilation near to every piece of biomass.

Pilot plant tests
In our tests we used wheat straw, sugar cane bagasse, corn stover and hard wood chips. The material was first soaked in a solution of dilute acid and subsequently drained by gravity: this yields 20-30 % biomass dry matter content. Higher concentrations could be attained by pressing: even to 60% dry matter. This material was transferred to the 250 litre SHS pilot plant to test the performance at different reaction conditions. Steam was obtained from an in-house 6 bara steam pipeline and superheated in an indirect electrical heater. One of the test was the accessibility of the cellulose and hemicellulose to hydrolytic enzymes.

Results
Hundreds of tests have been carried out with wheat straw at different reaction conditions. The set of experiments shown in Table 1 is most informative. By evaporation of water the final dry matter content can be increased to values between 30% and 60% w/w. The amount of water evaporation can be adjusted by the pressure. A flexibility in sulfuric acid concentration has been observed as well. The

* corresponding author: johan.vangroenestijn@tno.nl

Introduction
Biomass residue streams are attractive as a source of raw material for the biobased economy. Such materials can be wood, straw and grass and mainly contain lignocellulose, a complex of cellulose, hemicellulose and lignin. However, most fermentation production strains require mono- or disaccharides as substrates, therefore cellulose and hemicellulose first should be hydrolysed. To improve the accessibility of these polysaccharides for hydrolysis catalysts, such as enzymes or acids, the lignocellulose is pretreated. In a pretreatment process the bonds between the three polymers are broken. Worldwide more than 10 different pretreatment methods are in development based on physical, physico-chemical, chemical or biological action, each with its own advantages and disadvantages. Pretreatment by heating at low pH seems to be most popular. Under these conditions the hemicellulose can be hydrolysed, which saves on catalyst (e.g. hemicellulases) addition in the subsequent hydrolysis operation. In case heating is carried out by steam injection, in most applications such steam is stagnant and saturated.

The use of superheated steam
Higher dry matter concentrations in pretreatment reduces the heating costs (less mass to be heated) and may be beneficial in the fermentation and downstream processing. TNO is exploring the possibilities of pretreatment at higher dry matter concentrations, while minimising reaction time and temperature. For that purpose TNO uses dilute acid treatment in combination with continuously passing superheated steam (SHS) through heaps of biomass. Superheated steam is steam at a temperature higher than water’s boiling point. When heating biomass using SHS, heat transfer occurs by convection instead of condensation. Therefore, the biomass is not subjected to boiling point. When heating biomass using SHS, heat transfer occurs by convection instead of condensation. Therefore, the biomass is not subjected to boiling point. When heating biomass using SHS, heat transfer occurs by convection instead of condensation. Therefore, the biomass is not subjected to the use of enzymes. Ethanol fermentations were demonstrated using 38% biomass dry matter content.
user can choose between less acid and longer reaction times or more acid and shorter times. The process can be carried out within a few minutes and a temperature of 160°C: sufficient to make cellulose accessible for enzymes. Even a biomass concentration as high as 65% dry matter still yielded acceptable results. Hemicellulose already was hydrolysed during the pretreatment: xylose was found as a monomer at a yield of more than 90% of the theoretic value (the xylose amount contained in wheat straw).

After SHS treatment 0.1 mg HMF, 0.6 mg furfural and 8.3 mg acetic acid per gram of wheat straw dry matter was found, levels of inhibitors which will not cause problems in most fermentation processes. A few samples have been successfully subjected to ethanol fermentations using *Saccharomyces cerevisiae* which were carried out at a wheat straw dry matter concentration of 38% [1].

Pretreatment using SHS can be carried out in conventional steam dryers, with some modifications. In such systems the continuous feed in and out of relatively dry pieces of biomass through the superheated steam process, against a pressure drop of 6 bara, is feasible.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Reaction time (min)</th>
<th>Sulfuric acid concentration (%)</th>
<th>Final dry matter content (%)</th>
<th>Glucose produced after enzymatic hydrolysis (yield % of theoretical maximum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>165</td>
<td>15</td>
<td>0.4</td>
<td>24</td>
<td>82</td>
</tr>
<tr>
<td>160</td>
<td>1.5</td>
<td>1.5</td>
<td>28</td>
<td>84</td>
</tr>
<tr>
<td>160</td>
<td>3.5</td>
<td>2.0</td>
<td>29</td>
<td>95</td>
</tr>
<tr>
<td>175</td>
<td>3.5</td>
<td>2.0</td>
<td>44</td>
<td>92</td>
</tr>
<tr>
<td>190</td>
<td>1.5</td>
<td>2.0</td>
<td>49</td>
<td>81</td>
</tr>
<tr>
<td>180</td>
<td>3.5</td>
<td>2.0</td>
<td>65</td>
<td>81</td>
</tr>
</tbody>
</table>

**Conclusions**

Pretreatment of lignocellulosic biomass using a continuous steam of superheated steam is fast and efficient and can be implemented in the near future.

**References**

The chemical-loop approach in bio-alcohols reforming

O. Vozniuk*a, C. Trevisan*ª, J. Velasquez Ochoaª, M. Mariª, S. Albonettiª, F. Cavaniª, J.-M. M. Milletb

ªDipartimento di Chimica Industriale “Toso Montanari”, Università di Bologna, Bologna, Italy

ªInstitut de Recherches sur la Catalyse et l’Environnement de Lyon, IRCELYON, CNRS—Université Claude-Bernard Lyon Villeurbanne Cedex, France

The “Steam Iron” process was developed in the late 19th century to produce hydrogen from gasified coal. Nowadays, it becomes a subject of renewed interest because of its simplicity, feedstock flexibility (including renewable energy sources) and the purity of the obtained hydrogen which is especially important for the use in hydrogen fuel cells. The main principle of the thermochemical-loop process is: the material first reduced by ethanol stream, and then reoxidized with water, in order to produce hydrogen and restore the original oxidation state of the material. As looping materials were chosen different mixed ferrites with a spinel structure: MeFe₂O₄ (Me = Fe, Co, Ni or Cu).

Introduction

Hydrogen production is based on the reforming of natural gas or naphtha. However, the industry is focused in searching of less energy intensive and more sustainable processes for hydrogen production. One highly attractive route is steam reforming of bio-alcohols which in principle are CO₂ neutral. One option for reforming is to split the reforming into two cycles (chemical-loop reforming), in the aim of achieving two separate streams for H₂ and CO. The main principle of the thermochemical-loop cycle is: the material is first reduced by ethanol stream, and then reoxidized with water, in order to produce hydrogen and restore the original oxidation state of the looping-material (Figure 1).

Results and Discussion

The initial experiments were carried out with ferrites – Fe₃O₄, CoFe₂O₄, NiFe₂O₄ and CuFe₂O₄, as electrons and O²⁻ vectors, prepared by co-precipitation method.

In order to understand the behavior of the different materials in the chemical-loop process of ethanol reforming, the four synthesized ferrites were tested on a laboratory-scale plant. Some representative data are plotted in Figure 2.

Characterization techniques used for studying the chemical-physical features of materials were: BET, TPR, XRD, Mössbauer spectroscopy, XPS, TEM and in-situ DRIFTS-MS, in order to investigate oxides modifications, occurring during the redox cycles.

Table 1: Surface area and crystallite size for the different ferrites synthesized.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area before heating, m²/g</th>
<th>Surface area after heating at 450°C, m²/g</th>
<th>Crystallite size after heating at 450°C, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>187</td>
<td>70</td>
<td>12</td>
</tr>
<tr>
<td>NF</td>
<td>197</td>
<td>94</td>
<td>7</td>
</tr>
<tr>
<td>PF</td>
<td>194</td>
<td>85</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 1 shows the surface area values for the fresh and calcined samples. Synthesized ferrites showed a high surface area even after the thermal treatment. Results indicate an inverse proportional relationship between the surface area and the crystallite size for the compounds (after thermal treatment), which may be caused by sintering phenomena. Compounds presented similar (although not identical) surface area and crystallite size, thus making it possible to study their chemical differences without contribution from these morphological features.

Products distribution during the reduction step with ethanol are shown in Figure 2. Differences between materials were small. For example, hydrogen and CO formation were higher over magnetite and copper ferrite. On other hand, nickel ferrite showed higher methane yields.
The study of the second step, the re-oxidation of the reduced spinel with water steam, showed that high yields for hydrogen formation were obtained over chosen mixed ferrites, Figure 3.

However, ethanol reduction led to coke deposition and metal carbides formation. This turned into the generation of CO and CO\textsubscript{2} during the re-oxidation step, because of the gasification of carbonaceous residues.

Conclusions

The redox properties of mixed ferrites MeFe\textsubscript{2}O\textsubscript{4} (Me = Fe, Co, Ni or Cu) have shown promising features for hydrogen production, which make them suitable to generate “pure” hydrogen by oxidation with water steam. Bio-ethanol can be used as the reactant for the reduction step. The main problem shown during the chemical-loop reforming of ferrites was the accumulation of carbon. Therefore, a deeper study of the coke formation mechanism together with solid state modifications of new loop-materials, will be necessary in order to improve the performance of the proposed process, that appears economically feasible and industrially attractive. Thus, the subsequent research will include the study of the solid-state chemistry of different mixed oxides during cycles. New materials will be prepared and tested, such as mixed Cu-Mn, Mn-Fe, Mn-Co spinels, and supported ferrites.

References

[1] Hurst, S., Production of hydrogen by the steam-iron method. Oil & Soap, 1939, 16(2), 29-35.
We present the design of a bifunctional catalyst involving the stabilization of metal NPs on a supported ionic liquid phase (SILP) for the deoxygenation of biomass substrates to tetrahydrofurans, alcanols and ethers as potential biofuels. Our catalyst design involved immobilization of an acid-functionalized ionic liquid (IL) on SiO\(_2\) to provide an acid catalyst and a stabilization medium for ruthenium nanoparticles (Ru NPs). Integration of an acid and metal catalyst onto a support allow for a single catalyst to carry out the dehydration, hydrogenation and hydrogenolysis reactions required to deoxygenate biomass substrates. Our bifunctional catalysts (RuNPs@SILPs) possess high catalytic activity, selectivity and recyclability in the deoxygenation of tetrahydrofuran substrates, derived from furfural (FUR) and 5-hydroxymethylfurfural (HMF), to 1-octanol (1-OL) and 1-nonanol (1-NL), respectively. Furthermore, RuNPs@SILPs provide a tunable catalytic system that allowed access to three different classes of biofuels, tetrahydrofurans, alcanols and ethers from a single starting material.

**Introduction**

Declining petrochemical resources and climate change are a significant challenge, but at the same time a remarkable opportunity for the chemical industry to develop and implement novel atom-economic and sustainable synthetic routes for the production of fine chemicals and fuels from renewable resources.\(^1\)\(^-\)\(^3\) Lignocellulosic materials, such as agricultural and forestry residues, are a viable feedstock for the chemical industry as they represent the largest and also the only source of terrestrial carbon which is renewable in short enough time frames useful for mankind. Our group has developed the concept of synthetic pathway design for platform chemicals derived from biomass in analogy to the retrosynthetic strategy developed by organic chemists.\(^4\) An analysis of 1-octanol shows how this value-added product can be produced from lignocellulose (Scheme 1): (1) lignocellulose fractionation into cellulose, lignin and soluble sugars;\(^5\) (2) catalytic dehydration of xylose into furfural;\(^6\) (3) aldol condensation of furfural with acetone to yield furfuralacetone;\(^7\) and (4) hydrogenation and hydrogenolysis of furfuralacetone to form 1-octanol.\(^8\)

**Scheme 1: Retrosynthetic analysis towards the synthesis of medium chain aliphatic alcanols, 1-octanol and 1-nonanol, from lignocellulosic biomass**

Herein, we present the design of bifunctional catalysts composed of ruthenium nanoparticles (Ru NPs) immobilized on a supported ionic liquid phase (SILP) for the deoxygenation of biomass substrates (Figure 1). An acid-functionalized SILP allowed for the immobilization of an acid and metal catalyst onto SiO\(_2\), which was capable of catalyzing the dehydration, hydrogenation and hydrogenolysis reactions required in Step 4 of Scheme 1. Catalytic results will be presented employing our bifunctional catalyst (RuNPs@SILP) in which FUR- and HMF-derived substrates are converted into three different classes of biofuels: tetrahydrofurans, alcanols and ethers.

**Figure 3: Bifunctional catalysts (RuNPs@SILP)** employed for the selective deoxygenation of biomass substrates (For R = -CH\(_2\)SO\(_3\)H, -CH\(_3\))

**Results**

Initial studies investigated the hydrogenolysis of 4-(2-tetrahydrofuryl)-2-butanol (THFA) to 1-octanol (1-OL) using RuNPs@SILP. Altering the quantity of sulfonic acid-functionalized IL employed in the synthesis of the SILP allowed for a control of the overall acidity of the bifunctional catalysts. Three acid-functionalized SILPs were synthesized having acidic IL loadings of 0.33, 0.66 and 1.00 of the total IL loading. RuNPs@SILP-0.33 reached a maximum yield of C\(_8\)-OLs (C\(_8\)-OLs = 1-OL and ethers) after 16h, while RuNPs@SILP-0.66 and RuNPs@SILP-1.00 obtained a maximum C\(_8\)-OL yield after only 4h (Table 1). Thus, increasing the SILP acidity provided an improved reaction rate...
toward the C₆-OLs, in which the quantity of ethers substrates, 1,1-dioctylether and ethylcloctylether, also increased with the bifunctional catalyst acidity. Moreover, the selectivity toward the C₆-OLs was preserved for RuNPs@SILP-0.66 and RuNPs@SILP-1.00 as only small quantities of the over-hydrogenation product OA were observed. The best catalytic conditions were obtained with RuNPs@SILP-1.00 at 150°C under 120 bar H₂(g) after 4h in which the total C₆-OL yield was 98%. The recyclability of RuNPs@SILP-1.00 was investigated under these reaction conditions, in which the bifunctional catalyst was successfully reused in three catalytic cycles (Table 1).

Subsequent catalytic studies explored the development of catalyst and reaction parameters that allowed for the selective formation of BTHF, 1-OL and DOE from THFA (Scheme 1). The catalyst acidity, reaction temperature and H₂(g) pressure were shown to significantly influence the formation of BTHF, by which decreasing these parameters allowed for the production of BTHF in high yield (83%). Selective formation of 1-OL was obtained through control of the reaction temperature, time and quantity of added water. A simple optimization of these parameters was conducted and provided a maximum 1-OL yield of 60%.

Finally, a two-step procedure was developed to obtain DOE in high yields (88%) and involved using Nafion® to catalyze the etherification of the deoxygenation of remaining 1-OL into DOE within the reaction mixture. RuNPs@SILP were active and recyclable bifunctional catalysts for the deoxygenation of tetrahydrofuran-based substrates in the production of the medium chain alcohols 1-octanol and 1-nonanol. Furthermore, RuNPs@SILPs were shown to be flexible catalysts in which the product selectivity could be tuned to provide high yields of tetrahydrofuran, alcohol and ether biofuel candidates. Future studies within our group involve the development of a continuous flow process using RuNPs@SILP toward the formation of tailor-made biofuels.

We also extended our deoxygenation strategy to the production of 1-nonanol (1-NL) from the lignocellulose platform chemical HMF (Scheme 1). A simplex optimization was used to investigate the reaction temperature, time and water content to determine the maximum yield of 1-NL. Under optimized conditions, a 1-NL yield of 56% was obtained at 155°C with 0.075 mL of added water after 20h.

**Summary and Outlook**

Supported ionic liquid phases were shown to be effective supports in the development of bifunctional catalysts for the selective deoxygenation of biomass substrates. RuNPs@SILP were active and recyclable bifunctional catalysts for the deoxygenation of tetrahydrofuran-based substrates in the production of medium chain alcohols 1-octanol and 1-nonanol. Furthermore, RuNPs@SILPs were shown to be flexible catalysts in which the product selectivity could be tuned to provide high yields of tetrahydrofuran, alcohol and ether biofuel candidates. Future studies within our group involve the development of a continuous flow process using RuNPs@SILP toward the formation of tailor-made biofuels.

**References**

Session: Combustion Chemistry 2
Continuing Upgrades of Detailed Chemical Kinetic Reaction Mechanisms of Large Hydrocarbon and Bio-derived Fuels

Charles K. Westbrook
Lawrence Livermore National Laboratory

Summary

When a detailed chemical kinetic reaction mechanism is developed, validated to whatever level of confidence is possible, and then submitted to a journal or website for general use, there is a great temptation to consider that project, that chapter in kinetic evolution, to be complete. Several such mechanisms have been provided to the general kinetics public by this author, including two of the most downloaded, used, and cited mechanisms in the entire literature, specifically the \( n \)-heptane mechanism (Curran et al., Combustion and Flame, 1998) and the related mechanism for iso-octane (Curran et al., Combustion and Flame, 2002). These mechanisms, in addition to their wide range of applicability, also introduced the use of 25-30 reaction classes to help keep the mechanisms well organized, a practice that has become widely used ever since. In addition, the mechanisms provided quite reliable estimates of autoignition delay times and other integrated properties. A more recent large kinetic mechanism for soy and rapeseed biodiesel fuels (Westbrook et al., Combustion and Flame, 2011) used most of the same reaction classes to model the C16 and C18 methyl esters that are in most biodiesel fuel, and the mechanisms for these biodiesel components were built using much the same rules as those for the large hydrocarbon fuels.

Over time, the details of these kinetic mechanisms have been studied by the original authors of the models, as well as by others using new diagnostic facilities, and numerous errors and other reasons for correction of the mechanisms have been identified. Some researchers continue to use the original mechanisms, because they are unaware of the growing lists of errors and applicability limits of these mechanisms, or sometimes because they feel comfortable using a known kinetic models, no matter how serious the errors.

This is a common situation, and most useful kinetic mechanisms are revised periodically, attempting to keep available a useful mechanism for such practical and widely interesting fuels. But in the cases noted above, there are so many shortcomings to these mechanisms, and the upgrades being made are so fundamental and wide-ranging, that we want to provide the kinetic modeling discipline with a thorough summary of the problems and errors we have identified and how they are being corrected, and what better model performance users of the upgraded mechanism are likely to expect.
Optical study of hydrogen and biofuels autoignition kernel growth at an “over-tailored” shock tube

S. P. Medvedev\(^1\), H. Olivier\(^2\), S. V. Khomik\(^1\), O. G. Maximova\(^1\), G. L. Agafonov\(^1\)

\(^1\)Heterogeneous Combustion Laboratory, Semenov Institute of Chemical Physics, RAS, Moscow, Russia
\(^2\)Shock Wave Laboratory, RWTH Aachen University, Aachen, Germany

Dynamics of reaction front propagation after autoignition event determines an efficiency of burning in engines and combustors. Optical investigation of the autoignited combustion at low temperature and high pressure represents an appropriate technique of collection of experimental data for theoretical models validation. The paper reports the results of schlieren visualization of autoignition of experimental data for theoretical models validation. The paper reports the results of schlieren visualization of autoignition of hydrogen – air, ethanol – air and 2,5DMF – air mixtures in a shock tube operated under the over-tailored conditions. Comparative study of hydrogen and biofuels autoignition kernel growth is presented.

* Corresponding author: podwal_ac@yahoo.com

Introduction

Autoignition phenomenon is one of the most intriguing issues of gaseous combustion studies. Dynamics of autoignition is generally expressed in terms of ignition delay. The experimental data on ignition delay play a key role in validation of reaction mechanisms describing the reactive processes in internal combustion engines, gas turbines and other machines that use heat release upon fuel oxidation. For hydrogen and typical biofuels, a classical concept of homogeneous autoignition is failed at the low-temperature range when \( T < 1100-1200 \) K. Under these conditions, autoignition starts locally in a hot spot(s). Thus, delay time before the onset of the hot-spot ignition becomes a parameter of practical importance. Another question to be resolved is dynamics of reaction front propagation from a hot spot. The appropriate way to perform a detailed study of the above mentioned phenomena is an optical investigation of the autoignited combustion at low temperature and high pressure. The results of such investigation can be useful for theoretical models validation.

Test set-up

Shock tube represents one of the convenient tools for the self-ignition study. In many cases the conditions of the low-temperature ignition requires an observation time of more than 10 ms. To achieve these parameters we employ an over-tailored mode of shock tube operation instead of standard reflected shock procedure (tailored or under-tailored cases) [1]. The experiments were performed in a shock tube of Shock Wave Laboratory (RWTH Aachen University) with the total length of 11.4 m. The high-pressure section features the length of 5.1 m and circular cross-section of 100 mm in diameter. The 6.3 m long low pressure section has rectangular cross-section of 54 x 54 mm\(^2\). The sidewalls of the low-pressure section are equipped with quartz windows. The ignition dynamics behind a reflected shock wave was monitored by schlieren visualization along with pressure recording. Besides, the onset of ignition was detected by a germanium photodiode (with amplifier) mounted in the end wall. The parameters of the shock wave were measured by means of standard transducers (Kistler 603B, Kulite XCQ-080-35). Schlieren images were recorded by a high-speed Shimadzu HPV-1 camera. The mixtures under investigation (different lean hydrogen-air mixtures as well as stoichiometric biofuel-air mixtures) were prepared in a separate mixer by the partial pressure technique.

It was achieved an observation time of 35 ms at temperature range of 650-950 K and pressure up to 12 bar. Specific feature of the used technique is relatively smooth pressure/temperature rise at the initial stage that simulates compression dynamics in a piston engine. The details of pressure/temperature measurements and data processing technique are presented in [1].

Results

The experiments revealed the spot nature of the low-temperature autoignition and enable to compare directly an efficiency of hydrogen and biofuel combustion under conditions relevant to prospective engines and gas turbines. First, one can demonstrate an example of the influence of concentration of hydrogen in air on the structure and dynamics of ignition kernel. Figure 1 represents autoignition of 12%H\(_2\) and 6%H\(_2\) in air mixtures under the same conditions. Each frame in Fig.1

![Figure 1 – Hydrogen autoignition. P=10 bar, T=860K. a - 12%H\(_2\) in air, b - 6%H\(_2\) in air](image)

was made approx. 1.5 ms after autoignition start. Physical linear size of a frame is 33 mm.
As seen from Fig.1, the autoignition kernel of 12%H₂-air mixture spreads more rapidly than that of 6%H₂-air mixture. Quantitative analysis of a speed of reaction front propagation \( V_R \) was performed by calculation of instantaneous equivalent radii of a visible region occupied by combustion products. For 12%H₂-air mixture \( V_R = 9-10 \) m/s while for 6%H₂-air mixture the value of \( V_R \) appeared to be twice lower. Finally, it should be noted that passing from 12% to 6% of hydrogen the reaction front is transformed from a cellular to a highly wrinkled shape.

Visualization results of autoignition of biofuels are represented in Fig.2. Again the photos are made at approx. 1.5 ms since ignition start, and horizontal scale is 33 mm. This enables direct comparison between autoignition of lean hydrogen–air and stoichiometric biofuel–air mixtures under similar pressure/temperature conditions.

As seen, ignition kernel of ethanol–air mixture (Fig.2a) has much in common with that of 12%H₂-air (Fig.1a). Less sensitive 2,5-Dimethylfuran (2,5-DMF)–air mixture (Fig.2b) exhibits the same autoignition behavior as 6%H₂-air mixture (Fig.1b). Note that the ignition kernel of 2,5-DMF becomes similar to that of 12%H₂-air when temperature increases up to 960K (Fig.2c).

The suggested analysis demonstrates that, in general, dynamics of autoignition kernel growth of a given biofuels can be simulated by taking proper lean hydrogen-air mixture. The performed experiments confirmed a conclusion of [2] on the less sensitivity of 2,5-DMF in comparison with ethanol.

The nature of spot autoignition is still not fully understood. Normally, at a relatively low temperature after a local autoignition event the reaction front propagates with speed close to laminar flame velocity [3]. Nevertheless, measurement of turbulence intensity under the over-tailored conditions is a subject of a further research that can help to refine dynamics of an autoignition kernel growth.

Concluding remarks
A novel the “over-tailored”-shock tube technique was applied to study hydrogen and biofuels low-temperature autoignition. The shadow/schlieren visualization makes possible to compare directly an autoignition dynamics of different fuels under conditions relevant to piston engines and gas turbines.

Acknowledgments
The authors thank the Cluster of Excellence "Tailor-Made Fuels from Biomass", which is funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities. Partial support by the Russian Foundation for Basic Research (project no. 12-03-00963-a) and State contract no H.4x.44.90.13.1106 is gratefully acknowledged.

References
Experimental and kinetic investigation of \textit{n}-octanol

L. Cai\textsuperscript{1,}\\ A. Sudholt\textsuperscript{1,} Y. Uygun\textsuperscript{2,} W. Kopp\textsuperscript{3,} P. Parab\textsuperscript{4,} S. Kruse\textsuperscript{1,} J. Beeckmann\textsuperscript{1,}\\ R. Tripathi\textsuperscript{5,} M. Döntgen\textsuperscript{3,} H. Olivier\textsuperscript{2,} K. Leonard\textsuperscript{3,} A. Heuler\textsuperscript{4,} S.M. Sarathy\textsuperscript{1,} H. Pitsch\textsuperscript{1,}\!

\textsuperscript{1}Institute of Combustion Technology \hspace{1em} \textsuperscript{2}Shock Wave Laboratory
\textsuperscript{3}Institute of Technical Thermodynamics \hspace{1em} \textsuperscript{4}Physico Chemical Fundamentals of Combustion
\textsuperscript{5}Clean Combustion Research Center, King Abdullah University of Science and Technology, Kingdom of Saudi Arabia

The combustion chemistry of \textit{n}-octanol was investigated in this study. Ignition delay times were determined experimentally in a high-pressure shock tube for a range of initial conditions. A detailed kinetic model was developed to describe the oxidation of \textit{n}-octanol at both low and high temperatures. The model shows good agreement with the presented experimental dataset. A comparison between the C\textsubscript{8}-fuels, \textit{n}-octanol, \textit{n}-octane, and di-\textit{n}-butylether (DBE), which have similar elementary compositions, but different molecular structures, was conducted to analyze the impact of fuel structure and group functionality on ignition propensity.

\textsuperscript{*}Corresponding author: lcai@itv.rwth-aachen.de

\textbf{Introduction}

Short chain alcohols are widely applied as alternative sustainable fuels and blending fuel components for internal combustion engines. Recently, the longer chain alcohol \textit{n}-octanol has been identified as a biofuel candidate that can be obtained from biomass-derived platform chemicals. While the shorter chain ethanol is a well-established alternative fuel for spark-ignition engines, \textit{n}-octanol can be applied in diesel engines due to its higher cetane number. Furthermore, it was shown experimentally \cite{1} that \textit{n}-octanol allows for an almost soot and NO\textsubscript{x}-free combustion over a wide range of engine loads. For a better understanding of its global oxidation behavior, knowing its fundamental combustion characteristics is of particular importance. In addition, the chemical reaction model of \textit{n}-octanol is required in computational fluid dynamics (CFD) calculations to simulate its combustion performance in research and in engine development.

\textbf{Kinetic modeling of \textit{n}-octanol}

In order to gain a first insight into the oxidation reactivity of \textit{n}-octanol, the \textit{C-H} bond dissociation energies (BDE) are first computed using quantum chemistry calculations with the CBS-QB3 composite method. Consistent with the literature studies of short alcohols, a structure conformer with a C-C-C-O dihedral angle of 60° (gauche arrangement) is found to be more stable than the one with a trans (180°) arrangement. As depicted in Figure 1, the dissociation energy of \textit{C-H} bonds are highly sensitive to their position relative to the \textit{OH} functional group. While the existence of the hydroxyl moiety enhances \textit{H} atom abstraction from the alpha carbon sites and inhibits the \textit{H}-abstraction at beta sites, the effect of \textit{OH} group on other \textit{C-H} bonds is minor. In general, the computed values are consistent to the BDE’s reported for the shorter-chain alcohols \textit{n}-butanol and \textit{n}-pentanol at the same carbon sites. Therefore, reaction classes and rate rules considered in \textit{n}-butanol \cite{2} and \textit{n}-pentanol \cite{3} mechanisms are employed to construct the detailed chemical kinetic mechanism for \textit{n}-octanol oxidation. The model includes the reaction classes of elementary reactions to describe both high and low temperature pathways of alcohols.

\textbf{Fig. 1: C-H bond dissociation energies for \textit{n}-octanol in [kcal/mol].}

At high temperatures, fuel decomposition reactions are important. These dissociation reactions are affected not only by the thermal energy, but also by the nature of the inert collision partners. To investigate the influence of collision partners on the thermal decomposition of \textit{n}-octanol at elevated temperatures, reactive molecular dynamics simulations were conducted. These atomistic simulations yield insight into the thermal decomposition and determine the branching ratio of the dissociation products as well as the collider efficiencies. Ignition delay times of stoichiometric \textit{n}-octanol/air mixtures have been experimentally investigated in a shock tube at 20 and 40 bar. The results obtained are compared to the computed ignition delay times using the proposed model in Figure 2. It can be seen immediately that \textit{n}-octanol shows a clear negative temperature coefficient (NTC) behavior, which is not observed for the shorter chain alcohols, such as \textit{n}-butanol and \textit{n}-pentanol.
Using the present model, ignition delay times of stoichiometric n-octanol/air mixtures are predicted fairly well over the entire range experimentally investigated. The observed deviations between simulations and experiments are within experimental uncertainties.

Comparison of C₈ fuels

In order to deepen the understanding of group functionality effect on the ignition propensity, ignition delay times of the C₈-fuels n-octanol, DBE, and n-octane, which are similar species representing alcohol, ether, and alkane, are numerically calculated using the proposed reaction mechanism and mechanisms from the literature [4,5]. The calculations are performed at a pressure of 40 bar and Φ = 1.4, reflecting local conditions, at which compression ignition engines typically ignite. The computed results are presented in Figure 2. It is clearly shown that DBE ignites with the shortest induction time at all temperatures. As reported by Cai et al. [4], the central O atom in the ether group causes a lower C-H bond dissociation energy at the alpha site compared to a secondary C-H bond in an n-alkane. This results in a facile H atom abstraction site in DBE, which propels low temperature chain branching via H atom migrations across the central O atom. Furthermore, the peroxides derived from DBE are highly unstable [6] and decompose faster than those derived from alkanes, which leads to a fast second OH abstraction at the low to intermediate temperatures and thus accelerates the ignition. For the conditions considered here, n-octanol exhibits a similar ignition performance as n-octane besides the reduced reactivity in the low temperature regime. The major differences between linear alcohols and alkanes with the same carbon chain length were revealed in a reaction pathway analysis. The presence of the hydroxyl moiety enhances H atom abstraction from the alpha carbon site, and the subsequent alpha hydroxyalkyl radical's reaction with O₂ yields an aldehyde. This reaction sequence inhibits low to intermediate temperature chain branching for alcohol fuels. However, this inhibitory effect of the hydroxyl moiety on the ignition propensity is reduced for the longer chain n-octanol, because the greater number of carbon sites in the molecule decreases the branching fraction of the alpha fuel radical production.

Summary

This paper presents a chemical kinetic investigation on the oxidation of n-octanol. A detailed kinetic model for n-octanol combustion was developed by applying methods recently developed for n-butanol and n-pentanol combustion models. Ignition delay times were experimentally obtained for n-octanol oxidation in a shock tube. Good agreement between simulations and experiments was presented over a wide range of initial conditions. 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.

References

Keynote Lecture

A. Faaij, Energy Academy Europe, A.P.C.Faaij@uu.nl

--------------------------------------------------------------------------------------------------

Keynote Lecture:
Ethanol/Gasoline engines, status and prospect

W. Cheng, Massachusetts Institute of Technology, wkcheng@MIT.EDU

--------------------------------------------------------------------------------------------------
Session: Biomass Processing
Catalytic Biomass Processing Enhanced Using High Throughput Experimentation

Florian Huber, Claudia Liebold, Tilman Sauer, Jochen Berg, Christopher Federsel, Alfred Haas
hte GmbH, -the high throughput experimentation company-
Kurpfalzring 104, 69123 Heidelberg, Germany

Contact e-mail: christopher.federsel@hte-company.de | florian.huber@hte-company.de

The increasing demands for biofuels have led to an increasing demand for efficient catalysts testing capacity. High throughput catalyst testing is a time-efficient approach for meeting such a demand. We present the latest developments of High Throughput Technology and case studies showing the effectiveness of parallel testing and data quality for catalytic biomass processing.

Rapeseed oil as feedstock for biofuel applications offers advantages in terms of its low costs and good flow characteristics at low temperatures. High Throughput Technology can efficiently be used for the hydrotreating of rapeseed oil to study different catalyst samples at a variation of temperatures. In one of the case studies we present, rapeseed oil is hydrogenated in a parallel trickle-bed unit over non-sulfided and sulfided catalysts for demonstrating hydroprocessing of bio oils.

The samples were characterized by infrared spectroscopy (IR) and gas chromatography (GC). By using simulated distillation (SimDist) the reaction progress was followed as higher degree of hydrodeoxygenation (HDO) show a decrease in boiling points of the processed oil. By using an autosampler a continuous liquid sampling was realized whereby heating up to 140 °C liquefaction of the reaction products during sampling. Depending on reaction conditions, different products resulted from the processing of rapeseed oil, whereby the reaction temperature affected the product composition most.

The processing of bio oil using hte’s parallel testing technology was successfully demonstrated by means of hydrotreating rapeseed oil. Other examples of catalytic biomass conversion enhanced by high throughput technology will be presented in detail as well.
“Assessment of regional lignocellulosic residue and waste availability”

S. Möhring, H. Wulfhorst, J. Roth, R. Ulber, N. Tippkötter*
Junior Research Group BioSats, Institute of Bioprocess Engineering,
University of Kaiserslautern, Kaiserslautern, Germany

The aim of this study was an acquisition of renewable feedstocks for a potential use in an exemplary lignocellulose-based biorefinery in the area of Kaiserslautern, Germany. The area regarded in this study comprises approximately 780,000 hectares and includes parts of the Palatinate Forest. Further, impacts of mechanical pretreatment on the transport volume were determined. Selected raw materials were analyzed regarding their potential sugar yields from enzymatic hydrolysis. Finally, the profitability of local supply for an exemplary lignocellulosic biorefinery was evaluated according to the results of an in silico simulation of the biorefinery process.

* Corresponding author: tippkoetter@mv.uni-kl.de

Introduction

The established “first-generation” biorefineries based on starch and similar sugars come with the disadvantage of competing with food production. In an attempt to create sustainable systems for the biofuel production while avoiding said competition “second-generation” biorefineries have been developed. These plants have by now reached a pilot-scale stage. Instead of starch they convert cellulose extracted mostly from lignocellulosic biomass, such as wastes from forestry, agriculture, or private gardens, or also from craft, such as sawmills.

For the successful establishment of lignocellulosic biorefineries the amount of available and transportable feedstock has to be considered in concern to economic and ecologic aspects. Since wooden plant biomass does not provide as much energy as equal amounts of conventional energy crops, relatively large quantities have to be provided.

Approach

Regarding the environs of Kaiserslautern, a town enclosed by the German Palatinate Forest, the abundance of potential feedstock for an exemplary lignocellulose-based biorefinery was acquired and evaluated using official records and personal interviews. The effect of mechanical pretreatment on selected feedstocks were studied by exposing samples of grass and hedge clippings to a pressure of 200 or 400 bar prior to the enzymatic hydrolysis. All enzymatic hydrolysates were conducted at 50 °C in an overhead rotator for 24 hours with a solids concentration of 100 g/L, 6 % (w/w) Cellulase (NS-22086, Novozymes) and 6 % (w/w) Xylanase (NS-22083, Novozymes). The sugar content was quantified using HPLC. Additionally, samples of abundant feedstocks were analysed regarding their total structural carbohydrate content using the protocol published by the National Renewable Energy Laboratory (NREL). [1] Ecologic and economic impact of transport and processing including pretreatment, transportation, enzymatic hydrolysis of the biomass and the fermentation of the resulting sugars were simulated using the Intelligen software SuperPro Designer. The significance of on-site pre-treatment and systematic boundaries of local biomass pre-processing and parameter significance have been evaluated with the biorefinery simulation.

Results

The area regarded in this study comprises approximately 780,000 hectares, including the town of Kaiserslautern, Germany. The amount of wood, straw, grass and garden residues existing in this area has been determined. The biomass considered was composed of waste from forestry as well as spent wood, straw, grass and private garden residues (see Fig. 1).

Fig. 1: Theoretically available biomass residues in 2010 (in tons dry matter).

Considering the portion of biomass that is already being utilized, about 30,000 tons of wood and 13,500 tons of straw could be ascertained for a potential use in a biorefinery to date (see Fig. 2).
The amounts of fermentable sugars available in these biomass types have been evaluated in a laboratory scale before being transferred to pilot scale in silico. Finally, the effects of biomass densification leading to a reduced transport volume have been considered for the simulation of this biorefinery concept.

**Summary**

In this study potential feedstock for a possible lignocellulose-based biorefinery in the environs of Kaiserslautern, Germany, was recorded. Taking into account the amount of residues already being utilized by other means, about 30,000 tons dry matter of wood and 13,500 tons dry matter of straw could be ascertained for a potential use in an exemplary biorefinery annually. Mechanical pretreatment of that biomass after harvest, such as chopping and briquetting, leads to a significantly decreased transport volume and therefore leads to decreased transportation costs. However, a simulation of the biorefinery concept led to the conclusion that a complete biorefinery in the area of Kaiserslautern is likely to be economically inefficient.

**Acknowledgement**

This research is supported by the BMEL/FNR e.V. in the framework of the Junior Research Group BioSats (FKZ 22028411).

**References**

Two pre-treatment techniques of lignocellulosic biomass have been investigated for their effects on enzymatic hydrolysis, namely the laccase-mediator-system (LMS) and the organocat pretreatment. In comparison to previous results on solvent-based pretreatments, namely ionic liquid-pretreatment, both pretreatments exploit mainly the inhibition by lignin, but not sufficiently the change in cellulose structure, thus only slightly improving enzymatic activity.

Introduction
The targeted synthesis of tailored (pure) products such as fuel components or chemicals from lignocellulosic biomass requires specific conversions as provided by biocatalysts such as enzymes or cells. To make biomass available for specific enzymatic degradation, it is typically pretreated in order to 1) separate the main polymers fractions lignin, hemicellulose, and cellulose, thereby specifically addressing the unspecific adsorption of enzymes, and 2) to increase the surface area and reduce the crystallinity. Recently, we have explored the effect of two potential pretreatments on enzymatic activity in more detail. These are the laccase-mediator pretreatment [1] that addresses specifically the lignin removal from lignocellulose and the organocat-pretreatment [2] that facilitates mainly the separation of the polymer fractions, and thereby, also removes lignin from the cellulosic fibres to be enzymatically degraded.

Methods
For the LMS-pretreatment, the lignocellulosic material was milled in a lab blender and sized by a hand sieve with 0.8 mm mash width. 50 g/L beech powder in 100 mM NaAc buffer pH 4.5 was subjected to 60 UABTS/gDW laccase (T. versicolor) treatment with 5 mM ABTS at 40°C for 48 h. After LMS pretreatment, the solid was washed freeze dried. Organocat-pretreated substrate was kindly provided by ITMC. The subsequent hydrolysis was performed by desalted Celluclast at a load of 0.1 g/gDW, at 40°C, 800 rpm, 6 mL, 1% DW substrate (10 g/L), NaAc buffer (0.1 M, pH 4.5) or itaconic acid buffer.

Results
Within a biorefining process enzymatic hydrolysis for cellulose degradation is embedded into the sequence of processing and recycling operations. The pretreatment solvents have to be compatible with enzymatic degradation, should provide an easy access to the enzyme and finally, be easily recyclable.

The LMS pretreatment of beech wood powder using the mediator HBT increases the sugar yields obtained by a subsequent enzymatic hydrolysis, nearly doubling the sugar concentrations after hydrolysis in comparison to the untreated reference. ABTS and syringaldehyde (SA) did not exhibit positive effects on the hydrolysis yields, eventually due to polymerisation reactions of this compound at the lignocellulose surface.

The Organocat-pretreatment resulted in a approx. 8fold improvement of glucose release in comparison to untreated beech wood powder. A significant dependence on particle size could be
shown, suggesting that the Organocat pretreatment does not support the disintegration of the wooden raw material [3]. Interestingly, it was shown that enzymatic degradation could be made compatible with the subsequent fermentation potentially allowing for recycle of the fermentation media.

In comparison to ionic liquid pretreatments, both approaches could not increase lignocellulose particle surface, thereby, the increase in glucose release is too low. The enhanced enzymatic accessibility to the cellulosic portion within the LC biomass seems to be one of the key advantages in IL pretreatment and has been exploited for an integrated process w/o residue removal [3]. However, LMS which is the lowest is considered to be fully compatible w.r.t to the subsequent fermentation process, whereas the organocat’s solvent recycling is considered to be simpler than the ionic liquid recycling exploited for the ionic liquid EMIM Ac [4].

Summary
Of the pre-treatments exploited within TMFB until now, the pretreatments’ compatibility with enzymatic degradation is LMS >> Organocat > ionic liquid, whereas the lignin removal is LMS < IL << organocat. However, the structural impact of IL >> Organocat ~ LMS.

Outlook
In future, the biomass fractionation processes have to be evaluated w.r.t the overall process energy demand. In future we will address the impact of a range of pre-treatment solvents and conditions onto the enzymatic degradation of lignocellulosic biomass. In particular, MTHF- and EtOH-based treatments incorporating also alkaline components will be in the centre of interest.

References
Session: Biofuel Application 1
The purpose of this paper is to show examples of what could be gained by optimizing engines for paraffinic fuels. It is not in the scope of this paper to explain in detail about all possibilities for engine optimization, but rather arouse the interest to this topic. Several studies have shown that HVO (Hydrotreated Vegetable Oil) and GTL (Gas-To-Liquid) diesel fuels and their blends offer significant potential for either very low emission and/or low fuel consumption engine optimization. The production volumes of these fuels are constantly increasing, which make them an attractive alternative to conventional fuels. On-board fuel detection in combination with engine optimization would bring significant benefits for all stakeholders.

**Corresponding author:** Tuukka.hartikka@nesteoil.com

### Introduction

HVO (Hydrotreated Vegetable Oil) and GTL (Gas-To-Liquid) diesel fuels could be described as advanced fuels, due to their physical and chemical properties. Today, more than 15 million tons of paraffinic fuels are produced annually worldwide: approximately 13 million tons of GTL and 2 million tons of HVO [1, 2]. The chemical and physical properties of HVO and GTL are very similar, so the combustion behavior is practically the same with both fuels [3].

Paraffinic fuels are known to reduce tailpipe emissions when used as neat or in blends [3], but they also offer significant potential for specific engine calibration. Specific fuel consumption could be lowered remarkably when taking the full advantage of HVO’s and GTL’s very low level of aromatic hydrocarbons, high cetane number and high hydrogen to carbon ratio.

### Properties of paraffinic fuels

HVO diesel is produced from vegetable oils and/or animal fats by hydrotreatment, whereas GTL is produced from natural gas by using Fischer-Tropsch (F-T) process. The final product from both of the processes is purely paraffinic diesel. The main differences are in the carbon chain length, the amount of ring structures (napthenes) and the ratio of normal- and iso-paraffins.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>EN590 B0 (summer grade)*</th>
<th>HVO*</th>
<th>GTL**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>≈835</td>
<td>≈780</td>
<td>≈765-790</td>
</tr>
<tr>
<td>Viscosity at 40 °C</td>
<td>mm²/s</td>
<td>≈3.5</td>
<td>≈2.5-3.5</td>
<td>≈2.5-3.5</td>
</tr>
<tr>
<td>Cetane number</td>
<td></td>
<td>≈53</td>
<td>&gt;70</td>
<td>&gt;70</td>
</tr>
<tr>
<td>Distillation range</td>
<td>°C</td>
<td>≈180-360</td>
<td>≈180-320</td>
<td>≈160-340</td>
</tr>
<tr>
<td>Total aromatics</td>
<td>wt-%</td>
<td>≈30</td>
<td>≈0</td>
<td>≈0</td>
</tr>
<tr>
<td>Oxygen content</td>
<td>wt-%</td>
<td>≈0</td>
<td>≈0</td>
<td>≈0</td>
</tr>
<tr>
<td>Typical carbon chain length</td>
<td></td>
<td>C8-C23</td>
<td>C10-C20</td>
<td>C8-C24</td>
</tr>
<tr>
<td>Lower heating value</td>
<td>MJ/kg</td>
<td>≈43</td>
<td>≈44</td>
<td>≈44</td>
</tr>
</tbody>
</table>

Source: * Neste Oil, ** Various

### Optimizing engines for paraffinic fuels

The paraffinic composition of GTL and HVO offer simultaneous reduction of NOₓ and PM emissions, which in turn allow better trade-off between specific fuel consumption and emissions [4]. By adjusting the main injection timing Aatola et al. [5] and Sugiyama et al. [6] were able to increase the engine efficiency by 4-5%, at the same time keeping the same engine out NOₓ level than with petroleum diesel. Including optimization of pilot injection(s), further advantages could be achieved [6].

High cetane number of GTL and HVO shortens the ignition delay at low and medium loads and improves combustion [6]. The high cetane number also allows higher EGR rates to be used, without making the combustion unstable [7]. Aakko-Saksa et al. showed that optimizing an engine for HVO by adjusting the injection pressure and timing, EGR rate and applying Miller timing, the NOₓ emissions could be lowered as much as 60% without a penalty in the PM emissions in all the tested load points. At the same time the specific fuel consumption was lowered on average by 5% [8].

---

*Corresponding author: Tuukka.hartikka@nesteoil.com

**Figure 1.** Selected fuel properties of different fuels.

**Figure 2.** Trade-off between NOₓ emissions and specific fuel consumption with varying injection timing. [4]
Since HVO and GTL fuels do not contain any aromatic hydrocarbons and the hydrogen to carbon ratio is high, the soot emissions are lower compared to traditional diesel fuel. Additionally, if the injection timing is adjusted for lower soot output and better fuel economy, the DPF (diesel particulate filter) could be regenerated less frequently [9]. This in turn would reduce on-road fuel consumption and engine oil dilution.

Kind et al. showed that by optimizing injection timings (pirots + main injection), rail pressure and air mass flow for GTL, passenger car tailpipe CO2 emissions were lowered as much as 10% compared to petroleum diesel [10].

Opportunities for all stakeholders

On-board fuel detection and calibration optimization could be done by using technology already available in modern diesel cars: e.g. cylinder pressure sensors, NOx sensors and fuel quality sensor. With advanced algorithms, the ECU could recognize the used fuel quality and change the engine operating parameters accordingly [11].

Detecting the fuel quality would bring significant benefits for all stakeholders. Possibility to improve engine performance and durability, minimize damages caused by misfueling and improved emission performance could sales arguments to be quantified.

Bringing value for all stakeholders

<table>
<thead>
<tr>
<th>SOCIETY</th>
<th>ENGINE MANUFACTURERS</th>
<th>CONSUMER</th>
</tr>
</thead>
<tbody>
<tr>
<td>GHG reduction</td>
<td>Improved real-life fuel consumption</td>
<td>Lower fuel consumption</td>
</tr>
<tr>
<td>Improved local air quality</td>
<td>Better engine and emissions durability</td>
<td>Increased reliability</td>
</tr>
<tr>
<td>No biofuel blending</td>
<td>Increased service interval</td>
<td>Minimized damages caused by misfueling</td>
</tr>
</tbody>
</table>

Picture 3. Benefits of fuel detection and engine optimization for different stakeholders.

Conclusions

Paraffinic fuels offer significant opportunities for optimized engine calibration. When taking the full advantage of the sensors used in the modern vehicles, the engine calibration could be adjusted according to the actual fuel quality. This in turn would increase customer satisfaction by lower fuel consumption, better durability and fuel flexibility.

Today, engines and fuels are regulated separately in the legislation: regulation No 443/2009 (CO2 limits for passenger cars) and 2009/28/EC
Due to the decreasing amount of fossil oil, ethanol is already blended in gasoline, as seen in E5 or E10 to E85. For this paper the effect of Butanol as an alternative fuel was investigated. Therefore n-, sec- and Isobutanol were tested in a single cylinder research DISI engine and the gaseous and particulate emissions were measured and compared to the emissions of 98-octane gasoline. Some characteristic emissions for Butanol are shown and explained in this paper.

Introduction
A worldwide increasing demand for energy and the finite nature of fossil fuel compromise the security of supply. In order to solve this problem, a responsible handling of primary energy sources is required and additional alternatives have to be obtained. Therefore especially Ethanol has found its way for the use in gasoline engines by adding it to the common gasoline made from petroleum. In this paper, the results obtained with Butanols are described, which might be a substitute for gasoline as well due to the higher lower heating value (LHV). In addition to that, Butanol is less aggressive to plastics than Ethanol. The fuels tested are n-, sec- and Isobutanol.

Approach / Test set-up
The investigations were performed on a single cylinder research DISI engine. The particulate matter was determined by using a Scanning Mobility Particle Sizer (SMPS) from TSI. The exhaust gas was diluted with an ejector diluter from Dekati. The sample is heated up to 350°C to vaporize volatile components. To determine gaseous emissions a Motor Exhaust Gas Analyzer (MEXA) from Horiba was used.

The three investigated Butanols were not blended to gasoline but were used undiluted. So the characteristic emissions become more obvious. The engine was run at 1500 rpm and IMEP 6.6 bar. In this operating point, the Start of Injection (SOI) was varied from 180°C ATDC to 370°C ATDC and the intake valve timing (position of maximum lift) was varied from 80°C ATDC to 130°C ATDC to vary the internal EGR ratio. The timing of the exhaust cam shaft was kept constant. The engine was run stoichiometrically (λ = 1).

Results
As investigated in other works with alcohol fuels [1, 2], the emissions of nitrogen oxides are lower compared to gasoline due to the significantly higher (about two times) heat of vaporization of alcohol and the resulting lower combustion temperature.

The emissions of carbon monoxide do not increase with late SOI, like they do significantly when using gasoline. For Butanol the CO emissions stay at a similar level, except for a conspicuous peak for n- and Isobutanol at a SOI between 290°C and 330°C BTDC.

The exact opposite is observable for unburned THC. The amount of hydro carbons emitted increases for all Butanols when the injection takes place later, while they stay nearly constant for gasoline. Over all, the amount of THC emitted decreases when the ratio of internal EGR increases. This is because of the higher temperature before ignition due to the remaining exhaust gas in the combustion chamber and the better vaporization of the fuel. The THC emissions from all Butanols fall below the emissions of gasoline, when SOI is adjusted earlier. That is caused by the oxygen which comes with the Butanol and improves the combustion. This was also observed for Ethanol blends [3]. The reasons for the increase of THC at late SOI are the different boiling points. The investigated Butanols have boiling points of 100°C (sec-Butanol), 113°C (Isobutanol) and 117°C (n-Butanol), while 98-octane gasoline is completely vaporized at a temperature of about 210°C. According to DIN EN 228 it is necessary for 98-octane gasoline to vaporize to 20-52 vol.-% at a temperature of 70°C. That means that a higher percentage of gasoline is vaporized and participates in the combustion which results in higher carbon monoxide emissions caused by the short time for homogenization and consequently diffusion combustion. For Butanol, the time to vaporize completely is too short, so a high amount of unburned Butanol leaves the combustion chamber.

Regarding the particulate matter, it becomes obvious that the number of small particles, with a diameter smaller than 23 nm, which are not restricted by law, increases strongly when using
Butanol as fuel, see Fig. 10. The number of the small particles rises with a higher ratio of internal EGR. This tendency can also be seen with gasoline, but the number of small particles is significantly lower compared to Butanol. A possible reason for this phenomenon can be the number of aromatic hydrocarbons, which are part of gasoline (up to 35%) and have a significant influence on the particulate emissions [2]. Since no aromatics are included in the Butanol, they have to be formed during the combustion, which takes time. This might be the reason why the number of small particulates in the nucleation mode for late SOI is much higher for Butanol than for gasoline. Due to the lack of time, the formed nanoparticles have no possibility to agglomerate and build larger particles.

![Fig. 10: Total concentration of particles for different SOI and earliest Intake Valve Opening (IVO)](image)

Over all, the level of the particulate concentration for Butanol is nearly the same as for gasoline. Advantages can be taken for very early SOI, where the concentration is lower. For all fuels and valve timings, a minimum of the particulate emissions becomes obvious at SOI 290°CA to 340°CA BTDC. In this range, the piston and intake valve are wetted as little as possible.

![Fig. 11: Particle size distribution SOI 180° BTDC latest IVO](image)

Looking at the particle size distribution, Fig. 11, the large number of small particles emitted when using Butanol compared to gasoline becomes obvious again. Especially with a higher ratio of EGR, the number of small particles increases for late SOI. The difference between the total concentration and the total concentration of particles above 23 nm gets smaller the earlier the injection takes place. The difference in efficiency becomes obvious when looking at the indicated specific fuel consumption. The efficiency with Butanol is worse than with gasoline for late SOI but gets better than gasoline when the SOI becomes earlier. This applies for all tested valve timings and agrees with the high number of hydrocarbons emitted at late SOI for Butanol.

One can also observe a specific behavior for the different kinds of Butanol, which are, over all, similar. The differences can be explained through the different boiling points, higher heat of vaporization and maybe the different molecule structure.

**Summary**

In this paper, characteristic emissions for Butanol were shown and compared to those of 98-octane gasoline. The emissions of all kinds of Butanol are similar but not identical. Butanol-specific emissions can be observed for the level of particles, the particle size distribution and the level of emitted THC at late SOI. The emissions of nitrogen oxides decrease due to the lower combustion temperature because of the higher heat of vaporization of Butanol. CO emissions stay nearly constant for all SOI and are about 50% lower than for gasoline. Butanol is a possible substitute for gasoline, and can be used in blends, like it is done with Ethanol already. The higher heating value makes it more desirable than Ethanol.

**Outlook**

More experiments with Butanol should be made with regard to the potential of lower emissions. Therefore, multiple injections will be investigated. Further, blends with Butanol and gasoline will be investigated with different volume percentages in order to find a realistic scenario to use Butanol as a blending component instead of ethanol.

**References**


In this study the ignition and combustion behavior of Di-n-Butylether and 1-Octanol is compared in three test bench setups under conditions relevant for a part load operation point in a mid-size diesel engine passenger car. Both fuels have the same molecular formula but differ in their molecular structure. The thermodynamic single-cylinder engine results showed an almost soot free combustion at EU6 NOx-levels. The further optical measurements revealed that while Di-n-Butylether forms soot during combustion, 1-Octanol burns virtually soot free.

Introduction

With the aim to increase the local air/fuel ratio and therefore inhibit soot formation diesel engine related surrogate fuels with high oxygenation and/or decreased cetane number are in the focus of investigations [1,2]. Within the cluster of excellence pathways have been discovered to synthesize two such fuels, 1-Octanol [3] and Di-n-Butylether (DNBE).

Both fuels have the identical molecular formula however have the oxygen atom at a differing position: for DNBE the oxygen atom is in the middle of the molecule, while for 1-Octanol it is at the end of the carbon chain. In result both fuels have different properties as well as a different combustion behavior. The combustion was investigated for the two fuels at three test benches and is compared against that of diesel fuel. The used test benches were a thermodynamic single-cylinder diesel engine (TSCE), an optical single-cylinder diesel engine (OSCE) and a high pressure chamber (HPC).

Test set-up

The experiments at the TSCE were carried out at load points typical for state-of-the-art mid-size diesel engine passenger cars. The main focuses of the measurements were the combustion behavior and exhaust gas emissions. In order to get comparable conditions for all three test benches, the chosen load point for this study was 1500 min⁻¹ with 6.8 bar IMEP. The EGR-rate was adjusted in order to reach EU6 emission legislation NOx level. [4]

The HPC is a continuously scavenged high pressure and high temperature chamber. In the present investigations steady-state boundary conditions of 50 bar and 800 K were chosen, which represent the boundary conditions of the TSCE for the chosen load point at time of injection. The sprays hydrodynamic as well as ignition behavior was characterized using the simultaneous visualization of shadowgraphy and OH⁺-chemiluminescence. [5]

The OSCE features the same injection system and similar combustion chamber geometry as the TSCE. The differences are due to the optical accessibility of the engine and result i.a. in a lowered compression ratio [6]. As compensation the intake temperature and pressure were adjusted to match the conditions of the TSCE at time of injection. Start of injection and injection pressure were used from the TSCE in order to have the same combustion phasing for all fuels. To investigate the ignition and the soot formation the OH⁺-chemiluminescence and the soot luminosity were visualized with a high speed imaging system.

Results

In Figure 1 the lift-off length is depicted versus the ignition delay of the three fuels as a result from the OH⁺-chemiluminescence visualization [7]. With lower cetane number – the derived cetane numbers for DNBE and 1-Octanol are 115 and 34, compared to Diesel with a cetane number of 56 – the ignition delay of the fuels increase. Furthermore under the given boundary conditions the ignition of 1-Octanol is more instable resulting in a higher standard deviation. The lift-off length vastly depends on the ignition delay: the shorter the ignition delay of the fuel, the closer the ignition takes place to the nozzle.

![Fig. 1: Average lift-off length versus average ignition delay from HPC measurement](image-url)
chemiluminescence visualization. Similar to the HPC results the ignition delay increases with decreasing cetane number. However the absolute ignition delay times are decreased overall compared to the HPC results. This can be attributed to the charge motion. The lift-off length is significantly reduced with regard to the charge motion but is as well limited by the inner radius of the piston bowl, which is 24 cm. Due to the long ignition delay for 1-Octanol the ignition takes place after end of injection. This contributes to a higher degree of homogenization resulting in a higher premixed burn peak which can be seen in the spatial OH\* signal distribution (not depicted).

Using the same intake CO\(_2\) concentration as needed at the TSCE to reach an indicated specific NO\(_x\) level of 0.2 g/kWh, one can see that the ignition delay significantly increases for the three fuels. For DNBE the ignition still takes place shortly before injector closing. In result an ignition further downstream of the nozzle can be seen, while the other two fuels practically ignite somewhere in the combustion chamber, leading to a higher standard deviation. The soot luminosity visualization showed a signal for Diesel as well as DNBE, while for 1-Octanol almost no signal was detected.

Moving on to the TSCE results, Figure 4 compiles the relevant combustion and emission data from the measurements. As expected from the HPC and OSCE results the pressure trace analysis confirms that DNBE has the shortest ignition delay, while 1-Octanol takes the most time. Furthermore the heat release rate of 1-Octanol shows a higher maximum revealing the higher premixed burn peak, while DNBE burns mostly diffusion controlled resulting in a maximum more than three times as low. The standard deviation of the IMEP is slightly higher for 1-Octanol than for Diesel and DNBE which conforms to the trend of the HPC results. The exhaust gas emissions of soot both for DNBE and 1-Octanol are significantly lower than for Diesel.

**Summary**

The present study compared measurements of Diesel, DNBE and 1-Octanol at the HPC, OSCE and TSCE. It was shown that:

- A higher cetane number leads to a shorter ignition delay and a higher lift-off.
- A less stable ignition for 1-Octanol in the HPC measurements resulted in a less stable combustion in the TSCE measurements.
- The addition of charge motion shortens the ignition delay significantly while the further addition of EGR prolongs the ignition delay.
- Besides the oxygen content the long time for mixture formation helps in creating a virtually soot free combustion for 1-Octanol.
- Its isomer DNBE forms soot during the combustion, however the oxygen content helps in significantly reducing the exhaust gas soot emissions compared to Diesel.
Outlook
In future measurements at the HPC the influence of EGR on ignition and combustion behavior will be investigated using N₂. For the OSCE a further look on the soot formation is planned for the investigated fuels.

References
Session: Biofuel Refinery and Reference Process
Methanation studies with a high pressure fixed bed tube reactor, 
Effect of nitrogen dilution on the hydrogenation of carbon monoxide

M. Schütze, 1 I. Kiendl, 2 M. Klemm 1
1 Deutsches Biomasseforschungszentrum gGmbH, Torgauer Str. 116, 04347 Leipzig, Germany
2 Linde AG – Engineering Division, Dr.-Carl-von-Linde-Str. 6-14, 82049 Pullach, Germany

Methanation, the reaction of synthesis gas (CO + H₂) to methane and water, is a key step on the way from biomass to synthetic natural gas (SNG). The highly exothermic methanation reaction makes the temperature management in an adiabatic fixed bed reactor a lot challenging. Synthesis gas gained by air gasification is highly diluted by nitrogen. The high nitrogen content in feed gas makes the temperature management a lot easier. This paper presents first investigations on the influence of a high nitrogen dilution on the methanation reaction in an adiabatic fixed bed tube reactor under different reaction conditions.

Introduction
Synthetic natural gas (SNG) based on biomass is a secondary energy carrier with several advantages. One of the most important is that the already existing natural gas infrastructure can be used for storage, distribution and application. The SNG-process chain consists of biomass pretreatment, biomass gasification, gas cleaning, methanation, and raw-SNG treatment. The methanation, a key step on the way from biomass to SNG, is the catalytic conversion of synthesis gas (CO + H₂) to methane and water (eq. (1)). Side reactions are the water-gas-shift-reaction (eq. (2)) and the Boudouard-reaction (eq. (3)).

\[
\begin{align*}
\text{CO} + 3 \text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H_{\text{R}}^{\circ} = -206 \text{ kJ/mol} \quad (1) \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_{\text{R}}^{\circ} = -41 \text{ kJ/mol} \quad (2) \\
2 \text{CO} & = \text{CO}_2 + \text{C} \quad \Delta H_{\text{R}}^{\circ} = -173 \text{ kJ/mol} \quad (3)
\end{align*}
\]

The methanation can be catalyzed by different kinds of active metals, typically Ruthenium (Ru), Nickel (Ni), Platinum (Pt), Iron (Fe) or Cobalt (Co), or by metal compounds. Due to methanation activity, availability and price, Nickel is most frequently utilized for methanation catalysts by now [1,2].

The synthesis gas which is used in the methanation reaction can be provided through different gasification techniques of the pretreated biomass. Synthesis gas gained by air gasification, which is already state-of-the-art for small-scale electricity and heat production, is highly diluted with nitrogen. By now there are no studies dealing with nitrogen dilution in the methanation unit. The paper by Kiendl et al. presents first results in this field [3].

Different dilution levels from 30-60 Vol.-% nitrogen have been carried out in an adiabatic fixed bed tube reactor at different temperature levels using a commercial 20 wt.-% nickel catalyst. Nitrogen dilution helps to limit the temperature increase by the strongly exothermic methanation reaction. However, full carbon monoxide conversion and high methane selectivity was observed. It can also be shown, that the methane selectivity is independent of the nitrogen dilution up to 50 Vol.-% of nitrogen in the feed gas.

Reactor set-up
With the methanation reactor used for these experiments (Figure 1) it is possible to analyze heterogeneous catalyzed gas reactions at temperatures up to 1123 K and pressures up to 6 MPa using flow rates of about 400 l/h. Different H₂/CO-ratios, N₂-dilution, H₂O-feeding, H₂S-poisoning, and even the change of flow direction are possible. The gas can be recycled and the product gas is finally analyzed by gas chromatography and FTIR-spectroscopy.

Figure 1: Flow sheet of the methanation unit.

The feed gas can be mixed as requested and is heated by two stages (heater and superheater) to the desired inlet temperature. The reactor oven has five independently controlled heating sections (Figure 2). The tube reactor has an axial protective tube for inner thermocouples which makes it possible to measure the temperature in each heating section and even in the middle of the catalytic bed material. The flow direction can be varied from the bottom up or from the top down. For a better temperature management of the strongly exothermic methanation reaction the product gas or parts of it can be recycled.

* Corresponding author: michael.schlueter@dbfz.de

© DBFZ, 2014
Experimental
For the experiments 36.2 g of 2-3.15 mm catalyst particles were used. The catalyst bed is about 9 cm high located in the fourth heating section due to stable temperature conditions. That equals, with a constant flow rate of 417 l/h, a residence time of around 3 s. The nitrogen content was varied between 30 Vol.-% and 60 Vol.-%, and the reaction temperature between 533 K and 623 K. The synthesis gas ratio was always stoichiometric at $\text{H}_2/\text{CO} = 3.0$. The pressure was constant at 2 MPa.

Results
In all experiments a CO conversion close to 100% can be reached. Despite of that complete CO conversion and the stoichiometric ratio of hydrogen and carbon monoxide, a methane selectivity of only 90% is observed. A reason could be the occurrence of the side reactions (2) and (3) which means CO$_2$ and carbon are produced as undesirable byproducts.[4]

The relatively high nitrogen content in feed gas has a cooling effect. A higher nitrogen dilution results in a lower reaction temperature. That leads to a lower methane and CO$_2$ concentration in product gas. Nevertheless the methane selectivity is constant at 90% until the nitrogen dilution reaches 60%. At this level the methane selectivity decreases from 90% to 80% (Figure 3). Reason for that could be the fact, that a lower reaction temperature favours the methanation reaction. That keeps the methane selectivity constant until the highest tested N$_2$ dilution of 60% is reached and the methane selectivity decreases. The experiments for 623 K initial temperature show comparable results.

![Figure 2: Adiabatic fixed bed tube reactor in the reactor oven.](image)

Figure 2: Adiabatic fixed bed tube reactor in the reactor oven.

**Summary**
The results show that the methane selectivity is independent of the nitrogen dilution up to a value of 60%. Furthermore the cooling effect of the high nitrogen content investigated in these experiments makes the complicated temperature management of the highly exothermic methanation reaction, especially in a fixed bed reactor, a lot easier.

**Outlook**
These results could help to expand the applications of the air gasification technology. Due to the easier temperature management the process control of the fixed bed methanation reactor can be simplified. With the combination of air gasification and methanation energy can be stored chemically and will be available for later usage.

**References**
Catalytic biorefining of lignocelluloses to useful lignin oils and hydrolysable holocelluloses

P. Ferrini, X. Wang, R. Rinaldi
Max-Planck-Institut für Kohlenforschung
Mülheim an der Ruhr, Germany

The first step for the transformation of lignocellulosic biomass into fuels or fuel additives is its fractionation into the main components: phenolic fraction (lignin) and carbohydrate fraction (pulp or holocellulose, i.e. hemicellulose and cellulose). Herein, we demonstrate a new catalytic fractionation method that exploits H-transfer reactions for the production of non-pyrolytic lignin bio-oil and pulps hydrolysable by cellulases. The lignin bio-oils are highly depolymerized, highly stable and easier to upgrade than organosolv lignin. The pulps can easily undergo enzymatic hydrolysis, producing yields of fermentable sugars comparable to those obtained from organosolv pulp. The mixture of phenols poses some technical challenges for the separation of the components, due to their high boiling points. Through a catalytic tandem reaction, it is possible to transform phenols into arenes, obtaining a mixture of compounds with low boiling points and low oxygen contents.

Introduction
Among the components of lignocellulosic biomass, lignin is the only one containing aromatic structures. Unfortunately, due to the high complexity of the polymer and condensation of lignin fragments occurring within the fractionation process, obstacles still exist for the use of lignin on large scale applications. The depolymerization and liquefaction of lignin to obtain aromatics often require high temperatures and high H₂ pressures. Herein, we report a fractionation process that can lead to the separation of lignin as a highly-depolymerized bio-oil. This product offers new opportunities for the production of aromatics. However, lignin depolymerization leads often to complex mixtures of phenols with high boiling points and with high oxygen contents. These characteristics make these bio-oils unsuitable fuels or fuel additives. Accordingly, the hydrodeoxygenation of the non-pyrolytic bio-oil rendering arenes with low boiling points is needed. A new method for the hydrodeoxygenation of phenols is also presented here.

Catalytic fractionation
The organosolv process is one of the main fractionation methods under investigation as an entry-point into biorefinery schemes. By “cooking” wood in organic solvents (e.g. alcohols) at temperatures around 180-200 °C, pulps suitable for enzymatic hydrolysis in addition to sulfur-free lignin are obtained. Unfortunately, the organosolv process forms reactive lignin fragments that also undergo condensation forming strong C-C bonds. As a result, the reactivity of organosolv lignin is a considerable low, compared to that of native lignin. Our work shows a new catalytic fractionation method that produces highly-depolymerized lignin bio-oils, together with pulps amenable to enzymatic hydrolysis. In this approach, lignocellullosic biomass is cooked in solvent mixtures containing 2-propanol (H-donor) in the presence of Raney Ni (hydrogenation catalyst). This procedure results in the transfer hydrogenation of phenols, aldehydes and ketones in addition to the hydrogenolysis of aryl alkyl and diaryl ethers under mild conditions. This system is thus capable of cleaving the ether bonds and reducing the reactive groups of lignin fragments, generated in the fractionation process. Consequently, this feature prevents condensation of the lignin fragments. As a result, the lignin product is a non-pyrolytic bio-oil (Figure 1 B). Gel Permeation Chromatography (GPC) shows the molecular weight distribution of a non-pyrolytic lignin bio-oil sample, compared to that of organosolv lignin (Figure 1A). The prominent peaks below 500 Da (i.e. monomers and dimers) demonstrate that high depolymerization is achieved by the catalytic biorefining by H-transfer reactions.

Figure 4. GPC analysis and pictures (right side) of (A) organosolv lignin and (B) non-pyrolytic bio-oil. Reaction condition: poplar wood (17 g), 140 mL mixture 2-ProOH:H₂O (7:3), 10 g Raney Ni (just for B), 180 °C, 3 h.

Enzymatic hydrolysis of the pulps using a commercial cellulase preparation (Celluclast) proves that the conversion of the pulps, obtained from the catalytic biorefining, into fermentable
sugars are similar to those from organosolv pulp (84-87 wt% yield of glucose after 72 h).
To examine the reactivity of bio-oil, further H-transfer reactions on non-pyrolytic bio-oil and, for comparison, on organosolv lignin were performed. The non-pyrolytic bio-oil undergoes full conversion in the presence of Raney Ni and 2-propanol (solvent and H-donor) at 160 °C for 18 h, leading to highly volatile products, such as alkanes and aliphatic alcohols. For comparison, a conversion of 56 wt% of organosolv lignin into a mixture of aromatic and aliphatic compounds is achieved under the same conditions.

From phenols to arenes
H-transfer reactions, in combination with acid-catalyzed dehydration, proved to be a unique system to transform phenols into arenes. As shown in Scheme 1 for dehydroxylation of phenol, the reaction proceeds through three main steps, where the first one is the initiation step and the second and third are the propagation steps of the tandem conversion.

Main reactions involved in the one-pot tandem conversion:

\[
\begin{align*}
\text{OH} + \text{Raney Ni} & \rightarrow \text{OH} + \text{H}_2 \text{O} \quad (I) \\
\beta\text{-Zelite (H-BEA)} & \rightarrow \text{H}_2 \text{O} \quad (II) \\
\text{OH} + \text{Raney Ni} & \rightarrow \text{H}_2 \text{O} \quad (III)
\end{align*}
\]

Overall reaction:

\[
\text{OH} + \text{Raney Ni plus H-BEA-35} \rightarrow \text{H}_2 \text{O} + \text{H}_2 \text{O} \quad (IV)
\]

Scheme 1. Reaction pathway proposed for the tandem dehydroxylation of phenol.[6]

Firstly, the phenol is reduced to cyclohexanols via H-transfer from 2-propanol to the aromatic ring (Scheme 1-I). Then, the solid acid catalyst (H-BEA-35) catalyzes the dehydration reaction to form cyclohexene (Scheme 1-II). This product is a better hydrogen donor than 2-propanol, thus, in the last step, the hydrogenation of the aromatic ring of phenol proceeds through H-transfer from cyclohexene, that is then transformed into the benzene (Scheme 1-III).

This reaction was performed on organosolv lignin, leading to a product mixture with a low oxygen content. The conversion proceeds under mild conditions and leads to high conversion (70 – 80 % C yield) and high selectivity for arenes (71 – 78 wt% from GCxGC analysis, Figure 2).

Figure 5. GCxGC analysis of products from dehydroxylation of organosolv lignin. Reaction conditions: Raney Ni (0.6 g), H-BEA-35 (50 mg), substrate (0.1 g), 2-ProH (0.50 g), n-C6H12 (7 mL) 160 °C for 2 h and sequentially at 220 °C (bio-oil) or 240 °C (lignin) for additional 2 h.

Conclusion
We demonstrated two new methods for lignocellulosic biomass valorization for the production of fuels and fuel additives. The catalytic biorefining leads to highly-depolymerized and highly stable non-pyrolytic lignin bio-ols that are more amenable to be upgraded, compared with lignin. The catalytic tandem reaction for dehydroxylation of phenols leads to arenes with low boiling points. In both cases, exploiting H-transfer reactions, it is possible to perform the reactions under low-severity condition in absence of gaseous hydrogen.

Acknowledgements
R.R. is thankful to the Alexander von Humboldt Foundation for the funds provided by the Sofja Kovalevskaia Award 2010 endowed by the Federal Ministry of Education and Research. This work was performed as part of the Cluster of Excellence “Tailor-Made Fuels from Biomass”, which is funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities.

References
The cluster of excellence “Tailor-Made Fuels from Biomass” (TMFB) aims at the development of efficient and sustainable processes for the production of next generation biofuels from lignocellulosic biomass. The identified bottlenecks in the reference process in terms of the energy demand of the pretreatment and the downstream processing are addressed using systematic process design. An increase by a factor of 1.3 in the process yield, a 30% reduction of the heat and 19% reduction of the electricity demand is demonstrated. Nevertheless, an improvement of the overall efficiency is required for viable processing in competition to fossil fuels.

Introduction
The objective of a tailor-made fuel as a substantial contribution to the development of third generation biofuels is not only an efficient combustion without emissions, but also an efficient and sustainable process. The TMFB process is based on the conversion of lignocellulosic biomass and competes with fossil-based fuels as well as established biofuels. Hence, the tailor-made fuel requires a continuous assessment and improvement in order to enable viable production. The current flow diagram of the TMFB reference process is depicted in Figure 1. In the first step, the lignocellulosic biomass is comminuted and fractionated into its main constituent’s cellulose, hemicellulose and lignin, which is conducted using the biphasic Organocat process. 2-methyltetrahydrofuran (MTHF) is used for the extraction of lignin while oxalic acid catalyzes biomass depolymerization in the aqueous phase. The lignin-rich stream is utilized as an internal energy supply. The xylose- and cellulose-rich streams are hydrolyzed yielding C5- or C6-sugars respectively. The C5 sugar fraction is fermented into itaconic acid and the cellulose fraction is fed to an acid hydrolysis, known as the commercial Biofine process. After conversion, itaconic and levulinic acid are recovered, purified and further hydrogenated yielding either 2- or 3-MTHF.

![Fig. 1: TMFB reference process for the conversion of lignocellulosic biomass into methyltetrahydrofuran](image)

The thermodynamic properties which could not be simulated in Aspen Plus®. Mass and energy balances were simulated in Aspen Plus®. The thermodynamic properties which could not be found in the literature were estimated using Cosmo RS. A spreadsheet-based assessment of the process efficiency enabled to compare the processing alternatives in terms of yield, heat and electricity demand. While the values for the Biofine process are taken from literature and hence the levulinic acid pathway was not further investigated, the analysis and improvement of the pretreatment...
and the itaconic acid pathway are subsequently described. First, the pretreatment is investigated with four times solvent utilization before it is recycled via costly distillation. Second, the performance of the fermentation is investigated with the two microorganisms Ustilago maydis and Aspergillus terreus. The latter is an industrial strain, which does not require pH control with sodium hydroxide. As a third step, the separation of itaconic acid from water is explored in three different concepts. In the evaporative crystallization concept the water is evaporated, while the itaconic acid concentration exceeds the solubility limit and solid itaconic acid is obtained. Vapor recompression is applied in order to reduce the energy demand. The second process consists of a reverse osmosis to increase the concentration of itaconic acid at 40°C and a cooling crystallization as depicted in Figure 2. This concept is based on the temperature-dependent solubility of itaconic acid in water.

The third concept also includes a reverse osmosis step but applied an extraction into 2-MTHF (Figure 3). Due to biocompatibility problems the recycle of the aqueous phase is not fed back into the fermenter but is closed prior to the reverse osmosis.

**Results**

The successful reutilization of the solvent translates into a reduction of the heat and electricity demand along with a reduction of the oxalic acid loss compared to the previous case. For the itaconic acid pathway the utilization of A. terreus yields a higher product stream resulting in an overall increase of the process yield by a factor of 1.3. While the fermentation using U. maydis requires a pH adaptation, this is not necessary using A. terreus hence simplifying the downstream processing.

Comparing the two microorganisms as well as the different downstream processing concepts, the fermentation using A. terreus coupled with cooling crystallization or extraction shows the most promising results. Reasons are a higher yield and titer compared to U. maydis, a reduced electricity requirement for electrodialysis and the development of efficient downstream processing concepts. However, the effect of uncertainties in the thermodynamic properties as well of impurities needs to be investigated.

**Conclusions**

The identified bottlenecks, namely the solvent recovery in the Organocat, the fermentation yield as well as the downstream processing of the itaconic acid pathway were investigated to explore possible improvements in efficiency. A major reduction of the heat demand of 30% and the electricity demand of 19% as well as an increase in the overall process yield by a factor of 1.3 was achieved. Nevertheless benchmarking the results against state-of-the-art fuel production demonstrates that there is still need for further improvement.

**References**


Session: Biofuel Application 2
Impact of HVO on Emission Performance and DPF Regeneration Behavior of a High Efficiency Diesel Combustion System

O. P. Bhardwaj1*, B. Lüers1, B. Holderbaum1, Th. Koerfer1, M. Honkanen2
1 FEV GmbH Aachen, Germany
2 Neste Oil Oyj, Finland

The “Department of Advanced Diesel Engine Development” at FEV GmbH Aachen in cooperation with Neste Oil Oyj, Finland, carried out a detailed investigation program to explore the potential of Hydrogenated Vegetable Oil (HVO) as a biofuel candidate for future compression ignition engines. The engine results for pure HVO are compared to the petroleum based diesel fuel (B0) and FAME (RME / B100) at different load points with respect to the combustion behavior, emission performance and soot particle characteristics. To ensure that the findings are relevant for future automotive business, the testing program was carried out on a EURO 6 compliant High Efficiency Combustion System (FEV-HECS) designed for passenger car applications.

*Corresponding author: bhardwaj@fev.com

Introduction

The production of bio-based diesel fuels from vegetable oils is commonly accomplished using a process known as Trans-esterification. The product of Trans-esterification is Fatty Acid Methyl Ester (FAME), also known as “Biodiesel”. An alternative process is Hydro-treatment of seed oils or animal waste fats to produce highly paraffinic renewable diesel fuel called Hydrogenated Vegetable Oil (HVO). HVOs are straight and branched chain paraffinic hydrocarbon fuels with high Cetane Number and high Hydrogen to Carbon ratio (H/C Ratio) compared to petroleum based diesel fuel (B0).

The characteristics of the emitted soot, is a function of in-cylinder formation conditions, where the thermal decomposition chemistry of the fuel molecules play a significant role. The previous studies have reported a significant variation in the microstructure and oxidative reactivity of soot derived from different petroleum based diesel fuels and biofuels. Thus, apart from the detailed combustion and emission analysis, the present work fundamentally focusses the influence of fuel properties on particulate matter reactivity and, thereby, the regeneration behavior of a Diesel Particulate Filter (DPF).

Methodology and Approach

Figure 1 depicts the methodology and approach adopted for the present research. The soot samples were collected from a High Efficiency diesel Combustion System (HECS), exceeding the requirements set for EU 6 emission limits for passenger cars. The soot loaded DPF samples were subjected to a Temperature Programmed Oxidation (TPO) in an innovative Laboratory Gas Test Bench (LGB), to determine the kinetic parameters of the soot oxidation behavior. Furthermore, the soot extracted from DPF was used for microstructure studies using X-Ray Diffraction (XRD) technique.

Microstructure Analysis using XRD

The microstructure of soot particle can influence its degree of graphitization as well as the optical properties and the ease with which it can be oxidized in the DPF. The XRD is a classical technique to examine the structure of carbonaceous materials such as coal, graphite, carbon black and soot. The study of these structures can be described by a set of crystal lattice parameters as illustrated in Figure 2. The distance between the planes along the c axis (d002 planes), its stacking distance Lc and the length La (d100 plane) of the crystallite have been measured to find a correlation with its oxidation, thereby the soot reactivity can be determined. The values of La can be calculated from the plane d100 and Lc from d002 (where 100 and 002 are the miller indices of the corresponding planes) using Scherrer formula that connects the particle size with reflection width. These parameters reveal corresponding particle
size along c-axis and corresponding length along a-axis.

![Diagram](image)

**Figure 2**: A flake cut out of a graphite slab (upper left), a perspective 3D view of the graphite structure (upper right) and key lattice parameters defining a crystal structure (below)

**Soot Oxidation Analysis**

From the previous experience of soot oxidation studies using TGA (thermogravimetric analyzer), we know, that due to the soluble organic fractions (SOF) and volatiles, a small portion of the soot in the initial phase of the experiment can be oxidized with lower activation energy (at lower temperatures), taking this into consideration, ~20% of the soot was oxidized before the test starts.

The detailed methodology used at Laboratory Gas Test Bench (LGB) is described in refs. [2, 3]. To make a close approximation with the real DPF applications, soot loaded DPF samples were used for the analysis as depicted in Figure 3

![Microscopic View](image)

**Figure 3**: A microscopic view and specifications of soot loaded DPF segments used for oxidation studies

**Relationship of Soot Structure and Oxidation**

Figure 4 shows relationship of the soot microstructure and its oxidation behavior in DPF. The lower values of \( L_a \) as well as \( L_c/d_{002} \) indicates smaller crystallite size, and hence, should lead to higher reactivity, however, the behavior of soot samples is observed anomalous as compared to oxidation behavior. Some other researchers have also observed a similar behavior. This suggests that carbon structures in the soot vary from highly structured graphic sites to the highly disordered amorphous hydrocarbons. To regard the impact of background generated by amorphous hydrocarbons, in addition to the evaluation of the lattice spacing and crystallite size using Scherrer formula, a new parameter named as “Peak to Amorphous Ratio” abbreviated as “PtA” was evaluated in the present work\(^3\). The lowest PtA ratio value of HVO indicates higher disorder in the microstructure of HVO soot. This parameter, corresponds well with soot oxidation behavior in DPF, where the thermal regeneration temperature and passive regeneration temperature of soot from HVO was reduced by ~ 43 °C and ~ 37 °C respectively, compared to petroleum diesel (B0) soot.

![Graph](image)

**Figure 4**: Relationship: soot structure and oxidation

**Key Conclusions and Outlook**

The PM emission result indicates that HVO fuelling resulted in ~ 50 % reduction in smoke emissions and ~ 43 % reduction in PM flow, while the reduction with RME was ~78 % and ~ 62 % respectively. Due to lower activation energy, the thermal regeneration and passive regeneration temperature of soot from HVO was reduced by ~ 43 °C and ~ 37 °C respectively, compared to B0 soot. It is observed, that the oxidation behavior of soot is not contributed by one parameter, rather, it’s a combined effect of several physico-chemical properties such as optical properties, microstructure, metal content and elemental composition of soot (i.e H/C ratio, oxygen content).

A further validation of these laboratory findings is recommended on the vehicle applications under real world driving conditions.

**References**


Influences of HVO and FAME on Combustion and Emissions in EURO-VI Diesel Engines

B. Stengel¹*, T. Sadlowski¹, V. Wichmann¹, H. Harndorf¹

¹Institute of Piston Machines and Internal Combustion Engines
Rostock University, Rostock, Germany

Current European legislation demands the use of renewable energy in the transport sector. To achieve this goal biofuels are used as blend components. Due to different fuel properties of biofuels the engine operation can directly be affected. This study investigated the use of HVO and FAME as straight diesel substitutes in a modern passenger car diesel engine and their impacts on the combustion and the emissions. Results showed that the combustion was positively affected in terms of a shortened ignition delay. Furthermore raw exhaust emissions were clearly reduced when operating with HVO and FAME.

* Corresponding author: benjamin.stengel@uni-rostock.de

Introduction
The variety of powering vehicles has widened and deepened during the last decades as fuel costs have increased and upcoming emission limits must be met. Nevertheless gasoline and diesel engines will persist for passenger car, heavy duty truck and ship applications for the upcoming decades. Besides the improvements of combustion control and exhaust aftertreatment systems biofuels can help to further reduce emissions [1] and to decrease the dependency on fossil fuels. Biofuels based on vegetable oil can be produced in two established ways (Figure 1), by esterification (fatty acid methyl ester, FAME) or by hydrotreating (hydrotreated vegetable oil, HVO). Biofuel blends are commonly used as blend components. However the use of straight FAME and HVO in modern passenger car diesel engines is hardly investigated.

Experimental setup
In the framework of this study engine tests were performed with FAME and HVO as straight fuels using a EURO-VI passenger car diesel engine with a state-of-the-art exhaust aftertreatment system. Standard diesel fuel (EN 590) was used as reference. Analysis of the fuels showed higher cetane numbers for FAME and HVO. The heating value of HVO was similar to EN 590 diesel while the heating value of FAME was slightly lower. To analyze the impacts of the biofuels on the combustion process the heat release rates were calculated from in-cylinder pressure measurements using a single-zone model. Sampling points upstream and downstream of each component of the exhaust aftertreatment system were applied to determine effects of the fuels on emissions as well as on exhaust aftertreatment efficiency (Figure 2). Furthermore, data from the engine control unit (ECU) allowed investigation of fuel effects on engine control settings like EGR rate or fuel rail pressure.

Results
Results from engine tests showed that HVO positively affects the combustion by a decreased ignition delay due to its significantly higher cetane number [2] (Figure 3). Raw exhaust emissions of NOx and soot were clearly reduced. FAME also showed a decreased ignition delay compared to EN 590 diesel. This effect may also be reasoned
by its increased cetane number [3]. However, the lower heating value of FAME [2] leads to shifted engine control settings when using standard ECU calibration.

Raw exhaust emissions of FAME showed even higher reductions of soot compared to HVO which is caused by the fuel’s oxygen content [4] while NOx emissions where slightly increased (Figure 4). Furthermore, FAME reduced high CO emissions during low load operation significantly.

**Conclusions**

The study showed that HVO is very suitable as diesel substitute for modern passenger car diesel engines. The properties of HVO lead to a better combustion and reduced raw exhaust emissions. A fuel adapted ECU setting could reduce fuel consumption without exceeding exhaust emission limits. Operation with FAME showed enormous potential in terms of reducing soot and CO emissions. However engine control settings need to be adapted for FAME to ensure a safe and optimal engine operation.

**References**


Microbial contamination of biogenic fuels

Bernd Leuchtle¹*, Wei Xie¹, Thiem Zambanini³, Simon Eiden², Winfried Koch², Heide vom Schloß³, Martin Zimmermann¹, Lars M. Blank¹

¹Institute of Applied Microbiology - iAMB, ABBt - Aachen Biology and Biotechnology, RWTH Aachen University, 52074 Aachen, Germany
²Oel-Waerme-Institut - OWI - Affiliated institute RWTH Aachen, 52134 Herzogenrath, Germany

Fatty acid methyl ester (FAME), a first generation renewable fuel is the mainly used biosubstitution for blending Diesel and domestic heating oil (DHO). Its use on the one hand reduces the carbon dioxide output, but is seen critical, on the other hand, for its possible positive effect on microbial contaminations. This research project is aimed to point out factors that influence microbial growth in DHO-storage tanks and to describe its influence on storage tanks and the distribution system. It could be shown that a free water phase is essential for microbial growth, which is enhanced if FAME is added to the fuel. Once started, the microbes, which grow in strong biofilms, produce acids and can harm metal parts used as storage tank building material. Also, water transportation from the initial point of contamination to other parts of the distribution system was detected.

Introduction

Microbial contamination of fuels and lubricants and the subsequent fouling of tanks, pipes, filters, as well as pumps can occur [1]. Microbial contamination of jet fuel and (ship) diesel has been studied in detail [2]. In contrast, the microbial contamination of Domestic Heating Oil (DHO), a fuel chemically comparable to diesel, as well as the impact of such contaminations on DHO-storage tanks, has not been investigated. Domestic heating oil is generally stored significantly longer (up to years) than other fuels and fewer controls are conducted by users and regulatory bodies. The enormous consumption of about 40 billion liters per year worldwide [3], the decentralized storage of domestic heating oil, e.g., in private households, and the long storage times demand the investigation of microbial contamination of domestic heating oil. To lower the CO₂-output from fossil fuel combustion, biofuels are added to fossil fuels. For Diesel Fatty Acid Methyl Ester (FAME) is used in recent years as biosubstitution. Since FAME is easier degraded by microbes than fossil fuels [4], its addition in DHO may increase microbial growth in storage tanks.

Within this research project, factors that influence microbial growth within a domestic heating oil storage tank and the effect of growing microbes on tanks and the distribution system (e.g., filters and pumps) were investigated. The results can help to develop prevention strategies for microbial growth and in the long-run the reduction of equipment malfunction.

Test set-up

The test set-up included long time storage experiments and a pump testbench. In storage experiments domestic heating oil was filled in glass bottles. Depending on the experiment, different conditions, such as water volumes, were set. The used tank materials were two different kinds of polyethylene (PE) polymers, zinc diecast nozzles and Nitrile Butadiene Rubber (NBR) rings. The batches were inoculated with a mixed culture of yeast, bacteria, and fungi and were stored open at 20°C. The pump test bench used a standard pump and a standard sinter filter (70 μm) to pump heating oil from an inoculated storage bottle in circles.

Results

Water is essential for microbial growth. The water has to be available as a free water phase and not only dissolved in the heating oil. No minimum amount of water could be determined, which microbes require for growth. Further experiments suggest that the cell concentration is critical for microbial growth (Figure 1), rather than the total cell number present in the fuel.

In all experiments, the addition of FAME led to an increased rate of growth and a higher amount of microbial biomass. Notably, the initial cell concentration required for effective growth was reduced if FAME was present (Figure 1).

While the addition of PE or NBR had no effect on microbial growth, the batches containing zinc showed different Cell Dry Weight (CDW) and pH-trends compared to references without added materials (Figure 2).
In addition, the microbes corroded the zinc-parts. This corrosion was higher in batches containing FAME (20% (v/v), assigned B20) compared to batches, which contained only DHO (assigned B0) (Figure 3).

By using a pump test bench, water transportation through the heating oil distribution system was observed after microbial contamination. The water accumulated in the filter casing, leading to new microbial growth in this area (Figure 4). This accumulation of water was observed after microbial growth. Since the test bench was not operated sterile, microbes grew in both, inoculated and not inoculated batches. Although growth was observed, the amount of microbes and hence the transported water was lower in not inoculated batches (Figure 4).

Summary
Microbial contamination of domestic heating oil was observed. Growth was only observed if a free water phase was present. The addition of FAME resulted in enhanced microbial contamination. The addition of polyethylene parts used to build DHO-storage tanks neither did nor were influenced by microbial growth. Added zinc was corroded as a result of microbial growth. Using a pump test bench, a transportation of water through the system could be observed after microbial growth within the water phase in the DHO storage bottle was observed.

Outlook
The formation of emulsions through microbial contaminations and also the production of biofilms and corrosion promoting substances, such as acids, have to be investigated further. The gained knowledge can help producers and users of DHO and storage tanks to reduce microbial contamination and thereby avoid equipment malfunction.

References
[1] Zimmer, A., Cazarolli, J., Teixeira, R.M., Viscardi, S.L.C., Cavalcanti, E.S.H., Gerbase, A.E., Ferrao, M.F., Piatnicki, C.M.S., Bento, F.M., Monitoring of efficacy of antimicrobial products during 60 days storage simulation of diesel (B0), biodiesel (B100) and blends (B7 and B10), Fuel, 112 (2013) 153-162.
Keynote Lecture:
Biomass beyond bioenergy: creating sustainable value

L. van der Wielen, Delft University of Technology, L.A.M.vanderWielen@tudelft.nl
// Tailor-Made Fuels from Biomass

Contact:
Fuel Design Center
c/o Institute for Combustion Engines (VKA)
RWTH Aachen University
Schinkelstraße 8
52062 Aachen
exc@vka.rwth-aachen.de
www.fuelcenter.rwth-aachen.de
Tel.: +49 241 80-95352
Fax: +49 241 80-92630

Publisher: Florian Kremer
Layout: Anja Zöß; Anna Wilhelmi