EuroBioRef

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WP2 – Acetals Production

Deliverable report

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	Name	**Organization**	**Date**	**Visa**
Deliverable Responsible	Alexander NIESBACH	TUDO	16/09/2013	OK
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Dissemination level		
PU	Public	X
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Content

Description of the deliverable objective and content

Acetal context

Acetals will be synthesized by **direct oxidation** of alcohols on new catalysts tolerant to partially distilled loads or using new reactor technologies such as **Simulated Mobile Bed reactors and Catalytic Distillation.** Acetals will be synthesized from bio-resourced alcohols, namely ethanol (2nd generation supplied by BORREGAARD), glycerol (supplied by **NOVANCE**), butanol from WP4.2 or WP5.3 or WP6.3, fusel oils (by-products separated from 2nd generation ethanol, supplied by BORREGAARD), and other alcohols and diols (co-) generated *e.g.* in WP5.7, using single or mixed alcohols loads as reactant. This will enable the production of compounds with various properties according to the desired applications, the main one being aviation fuels. The types of acetals suited for this application will be defined in WP7.4 (blending).

For the synthesis, four strategies will be investigated:

(1) direct conversion of alcohols on new catalysts tolerant to partially distilled and thus cheaper loads;

(2) conventional and hybrid Simulated Moving Bed Reactor (SMBR) for combined complete conversion / products separation (recycling of mixtures to the SMBR unit will avoid the use of azeotrope-breaking solvents, which eliminates distillation costs);

(3) Reactive distillation as stand alone or combined with pervaporation and vapour permeation enables reaction shift towards products.

Catalytic distillation objectives

The concept of catalytic distillation for production of acetals in a column containing the catalyst immobilized within a gauze packing will be investigated in close collaboration with WP7.1 (PDC). The column configuration, operation parameters and product purities will be determined based on the models to be developed. The combination with membrane separation will also be investigated. This task will focus on acetals containing at least 10 carbon atoms which should be appropriate as aviation fuels. The most suitable type of acetals will be determined from initial screenings.

FEUP will develop reactive separation that will be hybridized by TUDO. Process engineers in ARKEMA will evaluate the industrial feasibility of the proposed solution.

Brief description of the state of the art

Although, the acetals of glycerol with heptanal and 2-octanone may gain an important role as additives to biodiesel, there has only been little investigation in this topic so far. In industry, acetals are mostly produced via inefficient and environmentally unfriendly homogeneous catalysis with strong mineral acids[1].

To overcome the environmental impact the research focuses on the development of a heterogeneous catalyst for these particular reactions. For the acetalisation of glycerol with heptanal, Umbarkar et al.[2] published promising results using mesoporous MoO3/SiO2 solid acid catalyst. Ruiz et al.[3] showed that tridimensional zeolites, Amberlyst-36 resin and gold catalyst are also suitable for this reaction. However, similar data is not available in literature for the acetalization of 2-octanone.

The inefficiencies in the production of acetals arise from thermodynamic limitations. The formation of acetals is a reversible reaction and is therefore limited by the chemical equilibrium. Silva et. al[4] studied the acetalisation of glycerol and found out that especially for longer aldehyde chains the equilibrium conversion is comparably low. Although, heptanal and 2-octanone have not been investigated in particular, the trend is assumed to be the same. Thus, the use of an RD will potentially enhance the

[1] Fristeri, F. et al., *Oxygenated additives production for diesel engine emission improvement*, Chemical Engineering Journal 134 (2007) 239-245

[2] Umbarkar, S. et al., *Acetalization of glycerol using mesoporous MoO₃/SiO₂ solid acid catalyst*, Journal of Molecular Catalysis A : Chemical 310 (2009) 150-158

[3] Ruiz, V. et al., *Gold catalysts and solid catalysts for biomass transformations: Valorization of glycerol and glycerol-water mixtures through formation of cyclic acetals*, Jorunal of Catalysis 271 (2010) 351-357

[4] Silva, P. et al., *Glycerol acetals as anti-freezing additives for biodiesel*, Bioresource Technology 101 (2010) 6225-6229

acetalisation of glycerol with heptanal and 2-octanone. By removal of the products from the RD column the reaction equilibrium is shifted towards the product side. The use of RD columns for acetalization has been investigated theoretically and practically for ethanol and ethylen glycol[5], ethanol and formaldehyde[6] and ethanol and butanal[7] and in the case of glycerol reactions, the acetalization of acetone and glycerol for the synthesis of solketal was experimentally studied in a reactive distillation process[8]. In all cases a higher conversion was achieved in an RD compared to the batch process.

No investigation on the acetalization of glycol with heptanal and 2-octanone was published so far and are therefore for the first time studied in this work.

Deviation from objectives and corrective actions

FEUP will develop reactive separation that will be hybridized by TUDO. Process engineers in ARKEMA will evaluate the industrial feasibility of the proposed solution.

In the project, it was agreed, that this collaboration will be done in a way, that FEUP will develop reactive separations in task 5.2.4 (Simulated Moving Bed Reactor and new technology, developed and patented by FEUP, that integrates water selective membranes and SMBR) for 1,1-dibutoxyethane (1,1-DBE, C10H22O2) and glycerol acetal (GEA). The experimental data obtained in this task will be provided to task 5.2.6.

Therefore, FEUP's 52 person months will be mainly in task 5.2.4.

TUDO worked on a theoretical study for the production of acetals in a reactive distillation column. In the beginning of the project, two acetalisations, namely heptanal + glycerol and 2-octanone + glycerol were chosen by ARK and TUDO as case-studies for this investigation. As the investigated reactions are different to the reactions investigated by FEUP, estimation methods were used and compared to gain data for the reaction kinetics and property data was determined and compared to literature data prior to performing the simulations.

Innovation brought and technological progress

The concept of catalytic distillation for the production of acetals in a column containing the catalyst immobilized within a gauze packing was investigated by TUDO. At first, two reaction systems were identified, that were investigated in more detail in this task. The reactions of heptanal and 2-octanone with glycerol to glycerol acetals were chosen as reaction systems. The acetalisation of glycerol with heptanal leads to the formation of two main products (2-hexyl-1,3-dioxolan-4-yl)methanol (HDM) and 2-hexyl-1,3-dioxan-5-ol (HDO) and the co-product water. For both products (HDM & HDO) the cis and the trans isomer can be formed, resulting in a total of 4 different products for the first reaction. The reaction scheme can be found in fig. 1:
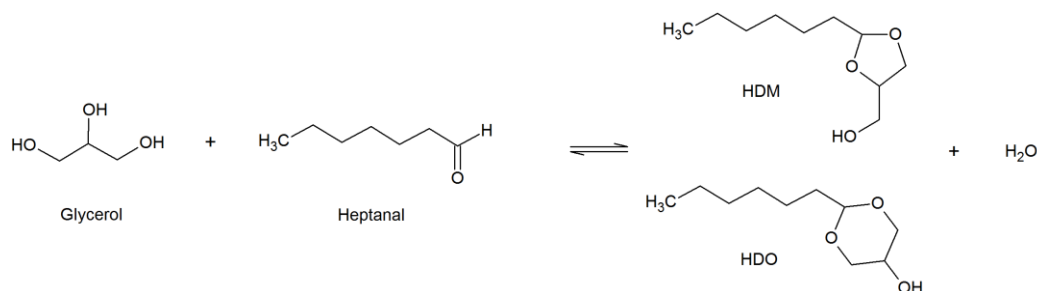

Figure 1: Reaction scheme of the acetalisation of glycerol with heptanal

[5] Chopade, S. and Sharma, M., *Acetalization of ethylene glycol with formaldehyde using cation-exchange resins as catalysts : batch versus reactive distillation*, Reactive & Functional Polymers 34 (1997) 37-45

[6] Chopade, S. et al., *Reaction of ethanol and formaldehyde: use of versatile cation-exchange resins as catalyst in batch reactors and reactive distillation columns*, Reactive & Functional Polymers 32 (1997) 53-64

[7] Agirre, I. et al., *Catalytic reactive distillation process development for 1,1 dethoxy butane production from renewable sources*, Bioresource Technology 102 (2011) 1289-1297

[8] Clarkson, J.S. et al., *Continuous Reactor Technology for Ketal Formation: An Improved Synthesis of Solketal*, Organic Process Research & Development 5 (2001) 630-635

The second reaction is the acetalisation of glycerol with 2-octanone. It leads to the main product (2-hexyl-2-methyl-1,3-dioxolan-4-yl)methanol (HMDM) and the co-product water. For this reaction, comparably to the solketal formation in a reactive distillation column[9], only the 5 atom cycle ring is formed. Again, the cis and the trans isomer can be produced. The reaction scheme can be found in fig. 2:
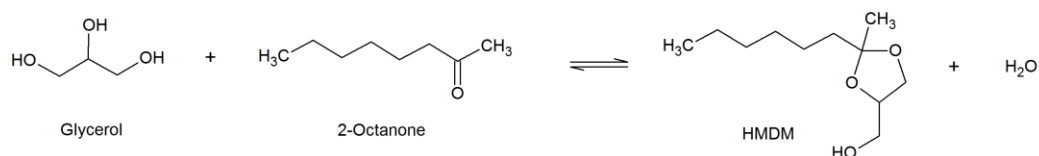
Figure 2: Reaction scheme of the acetalisation of glycerol with 2-octanone

A feasibility study on the production of glycerol acetals by reactive distillation was carried out. To define the content of such a feasibility study, a meeting with Process Design Center (PDC) was arranged and it was agreed on, that a first draft was made by PDC and the detailed content was discussed by both, TUDO and PDC. The division of work between FEUP and TUDO in this task was discussed in a conference call.

Predictive simulations depend largely on the quality of the used thermodynamic and kinetic properties. Before the simulations were performed, a characterisation of the required thermo-physical properties was done by TUDO. Required parameters for the prediction of the property data were taken from the Aspen Properties[®] database, if available. A literature research was done and available literature data was used to validate the predicted property data. Property data that could not be found in literature were identified and the missing thermodynamic data were estimated using group contribution methods.

For the simulation studies it was agreed on, that the feasibility will be proven by taking only the formation of the 5 ring atom cycle form (HDM) into account for the heptanal acetalization to simplify the simulation and to show the feasibility of the technology. For the two possible products of the heptanal-glycerol acetalization, a comparison of the thermodynamic and physical property data was performed. The boiling point of HDM at atmospheric pressure was estimated by Aspen Properties™ to 585 K and the boiling point of the HDO was estimated to 532 K. The boiling point of glycerol at this pressure is 560 K and is therefore in between HDO and HDM. Both products can be easily separated from water and heptanal (large boiling point differences, no azeotropes) and both, HDO and HDM, form a light-boiling azeotrope with glycerol. As from now on only HDM was taken into account, a comparison to HDO was performed at the end of the study.

As there is no information on kinetic data and the reaction equilibrium available in literature and the system investigated by FEUP (acetaldehyde + glycerol) is different to the systems investigated for this study, an estimation of the reaction equilibrium is necessary for both reactions. The estimation of the equilibrium constant at standard conditions was done using the standard free energy change for the reaction. The temperature dependency of the equilibrium constant was calculated using the Van't Hoff equation.

After both models were set up completely, they were used for performing several simulation studies. The dependency of the reactant conversions on crucial operating parameters (reflux ratio, distillate-to-feed ratio and pressure) was studied an operating conditions for a maximisation of the product purity were suggested. Based on these results, a general feasibility of the acetals production using a reactive distillation process was shown.

FEUP determined physical-chemical, thermodynamic and kinetic data for GEA system, which were not available in the open literature.

Analysis of the results

After the two reaction systems were selected, the estimation of the equilibrium constant had to be performed by TUDO, to allow for a simulation of the two processes. As no information on kinetic data and the reaction equilibrium was available in literature, the different group contribution methods,

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[9] Clarkson, J.S. et al., *Continuous Reactor Technology for Ketal Formation: An Improved Synthesis of Solketal*, Organic Process Research & Development 5 (2001) 630-635

available in Aspen Plus™, were used for the estimations. The resulting reaction equilibrium constants for a temperature of 298 K are summarised in Table 1:

Table 1: Reaction equilibrium constants at 298 K

Reaction	Group contribution method	K_{eq}
Heptanal + Glycerol	Joback	$7.46*10^{-12}$
	Benson	8.95
	Gani	$9.30*10^{-4}$
Octanone + Glycerol	Joback	$3.35*10^{-16}$
	Benson	2.69

As shown in Table 1, three group contribution methods were used for the heptanal and glycerol reaction (Joback, Benson and Gani) and two methods were used for the 2-octanone and glycerol reaction (Joback and Benson). As no experimental data is available for the reaction kinetics and except for the Benson method, all other methods result in infeasible chemical equilibrium constants, the Benson method was used for the simulation using the equilibrium stage model in Aspen Plus™, ending up in equilibrium constants of 8.95 for the reaction of heptanal and glycerol at 298 K, leading to an equilibrium conversion of 58 % at this temperature and 2.69 for the reaction of 2-octanone and glycerol at 298 K. leading to an equilibrium conversion of 43 % at this temperature. After implementation of the reaction equilibrium, initial simulations were performed. For these simulation studies, an equilibrium stage model was used and a height of 30 equilibrium stages was applied. A total condenser was used and the feeds were fed between the 10th and 11th stage (glycerol) and the 20th and 21st stage (heptanal/2-octanone). The reactive section was chosen to be between the 20th and 30th stage. This set-up was used, as glycerol is the heavy boiling component and an increased contact time between light- and heavy boiling component can be expected, when the heavy-boiler is fed above and the light-boiling component is fed below the reactive section. **First simulations showed conversions of more than 40 % for both reactants of both reaction systems.** Further simulations studies identified **possible conversions of more than 80 % for the heptanal system** at higher reflux ratios, while the **maximum conversions achieved with the octanone system are still in the range of 40 %**.

After the initial simulations were performed, more detailed simulation studies were done and the conversion of glycerol was monitored while the operating parameters distillate-to-feed ratio, reflux ratio and column top pressure were varied. Figure 1 shows the results of the variation of the reflux ratio for the reaction of glycerol and heptanal.
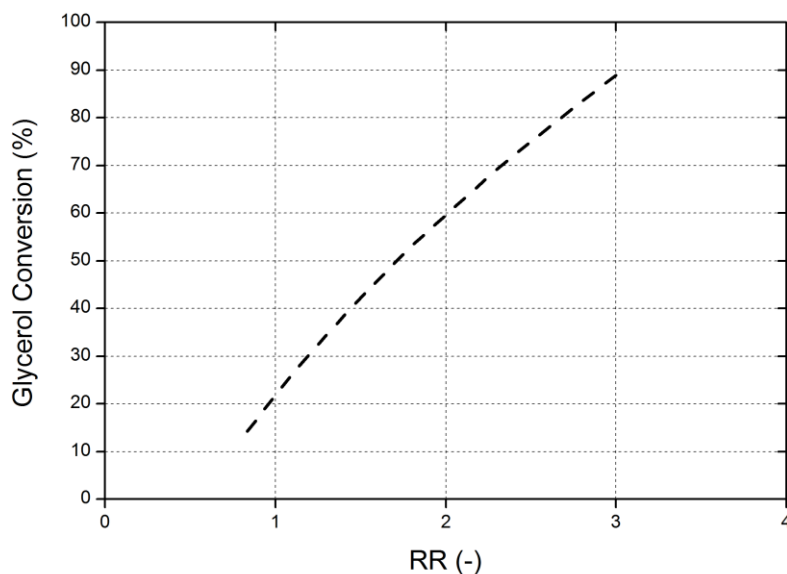
As shown in the diagram, an **increasing reflux ratio significantly increases the conversion in the column**. For this study, the distillate-to-feed ratio was set to 0.5 and the pressure was set to 1.013 bar. For the whole investigation, the reflux ratio was varied between 0.8 and 3, for the maximisation of the conversion up to 3.2; the distillate-to-feed ratio was varied between 0.2 and 0.4 and the pressure was varied between 200 and 1013 mbar, while keeping the other operational parameters constant. For the pressure it was found, that **decreasing the pressure leads to an increased conversion**, which results from the exothermic nature of both reactions investigated in this section. For the distillate-to-feed ratio it was found, that for the investigated range an **increase in the distillate-to-feed ratio leads to a significant increase in the conversion**. Therefore, a low pressure, a high reflux ratio and a high distillate-to-feed ratio is advantageous for a high conversion of the investigated glycerol + heptanal/2-octanone reactions. **The results shown above were also found for 2-octanone process, demonstrating the technical feasibility of the production of both acetals in a reactive distillation process**.

Based on these simulations, the maximum conversions were identified by TUDO, that can be achieved within the investigated range of the operating parameters. **For the 2-octanone process, a maximum conversion of 77.3 % for both reactants was achieved at a pressure of 0.2 bar, a reflux ratio of 3.2 and a distillate to feed ratio of 0.45. For the reaction of heptanal and glycerol in the reactive distillation column a maximum conversion of 88.8 % was achieved at a distillate-to-feed ratio of 0.5, a pressure of 1.013 bar and a reflux ratio of 3. Both conversions were therefore increased in comparison to the equilibrium conversion.** If the 6 ring cycle form (HDO) is primarily formed by the heptanal-glycerol reaction, the effort for the separation of the product from glycerol increases, as glycerol becomes the heavy boiling component of the system. As the reaction to HDO is also exothermic, a decrease of the operating pressure leads to an increased conversion. In order to purify HDO in a single reactive distillation process, glycerol needs to be almost completely consumed, which could be achieved by feeding an excess of heptanal.

As no experimental thermodynamic and physical data is available for some of the VLEs and an indication for a light-boiling azeotrope with water was found, a hybridization of the reactive distillation column would be advantageous in order to obtain pure products and to achieve high conversions of both reactants. Most likely the light-boiling azeotrope will occur at the top of the column, hence the integration with a membrane process, such as a hydrophilic vapour permeation or a hydrophilic pervaporation, to remove the water would be a suitable process option.

FEUP performed a thermodynamic and kinetic study of the acetalization reaction between acetaldehyde and glycerol to produce glycerol ethyl acetal (GEA).

Amberlyst-15 wet (A15) resin was selected as the most suitable catalyst for this reaction. Through the study of the reaction thermodynamic equilibrium it was possible to determine the value of the equilibrium constant as a function of temperature, $\ln(K) = 1.419 + 1055/T$, and the corresponding thermodynamic parameters $\Delta H^0_{298K} = -8.77 \, kJ \cdot mol^{-1}$ and $\Delta G^0_{298K} = -12.3 \, kJ \cdot mol^{-1}$. Additionally, the standard enthalpy and free Gibbs energy of formation of GEA were also obtained, being -584.4kJ·mol^{-1} and -387.0kJ·mol^{-1}, respectively. The Langmuir-Hinshelwood-Hougen-Watson model considering internal mass transfer limitations presented the best fitting of the reaction kinetic behaviour. The parameters estimated for this model were $k_c \left(mol \cdot g_{cat}^{-1} \cdot s^{-1}\right) = 3.13 \times 10^9 - 6223/T$ and $K_{S,W} = 1.82 \times 10^{-3} \exp\left(2361/T\right)$. The acetalization of glycerol with acetaldehyde presents an activation energy of 51.7kJ·mol-1.

Some unavailable physical-chemical properties of GEA as a function of temperature, as density ($\rho\left(g \cdot cm^{-3}\right) = -7.723 \times 10^{-4} T + 1.355$) and viscosity ($\log\left[\mu(cP)\right] = \dfrac{1255}{T} - 4.286$) were also determined.

Impact of the results

In this project, the technical feasibility of the reactive distillation process for the synthesis of glycerol acetals from heptanal and 2-octanone was shown on a theoretical basis. Nevertheless, the reaction equilibria and some of the thermodynamic and physical property data of the products had to be estimated and are crucial for the presented results. Therefore, experimental studies identifying the reaction equilibria and reaction kinetics should be performed to validate the shown results. Furthermore, an experimental investigation to identify the synthesized products and the ratio between the two possible acetals for the heptanal reaction needs to be performed to allow a more detailed process analysis. As soon as the experimental kinetic data is obtained, lab- or pilot-scale experiments with a reactive distillation column could be performed to experimentally validate the feasibility of this process.

Related IPR

The current results are not patentable and no publications are planned.

Publishable information

No publications for the presented results are planned.

Conclusion

The two acetalisation reactions shown above were studied in more detail in this investigation by TUDO. Thermodynamic physical and property data was generated using Aspen Plus™ and validated using literature data, if available. The reaction equilibrium was estimated and implemented in the model. An equilibrium-stage reactive distillation model was set up and simulation studies were performed, to identify the impact of crucial operational parameters on the conversion of the reactants. The technical feasibility of the acetalisation reactions in a reactive distillation column was shown on a theoretical basis. The maximum conversions, achievable in the investigated operating window were determined, when equimolar feed compositions are used. For the 2-octanone + glycerol reaction, a maximum conversion of 77.3 % can be achieved and for the heptanal + glycerol reaction, only taking the five atom cycle acetal into account, a maximum conversion of 88.3 % was achieved.

With regard to GEA system, the study conducted required the determination of relevant physical-chemical properties for GEA that were inexistent so far (for instance, the dependence of the density and viscosity of this compound with temperature). Furthermore, a mathematical model was developed describing the kinetics of the acetalization of glycerol. This model may be used as the basis for the development of any process for the synthesis of GEA using the same renewable raw materials and catalyst (A15, which was identified as the most effective for this reaction).