Project acronym: # EuroBioRef

Project Title: EUROpean multilevel integrated BIOREFinery design for sustainable biomass processing

Instrument: Large Scale Collaborative Project

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SP7 – CONCEPTUAL PROCESS DESIGN AND INTEGRATION OF THE WHOLE PROCESS CHAIN/GRID INTO A BIOREFINERY

WP7.3 – PRELIMINARY FUNCTION TESTS

Deliverable report

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Deliverable Identification	
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Deliverable Title:	Pilot Plant TUDO: reactive distillation of 3HPA, 20 kg feed/day
Responsible Beneficiary:	MERCK
Contributing Beneficiaries:	TUDO, MERCK
To be Submitted to the EC:	Yes

History			
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V1	Alexander Niesbach, TUDO	First version	15/01/2013

Approval				
	Name	**Organization**	**Date**	**Visa**
Deliverable Responsible	Angela LENNERT	MERCK	16/01/2013	OK
Work Package Leader	An-Ping ZENG	TUHH	18/01/2013	OK
Sub-Project Leader	Wei ZHAO	PDC	21/02/2013	OK
Coordinator	Franck DUMEIGNIL	CNRS-UCCS	21/02/2013	OK

Dissemination level		
PU	Public	X
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Content

Executive summary

Description of the deliverable objective and content

Preliminary function tests in lab and bench scale units mean that all the tests done at the lab scale to validate the optimised catalyst, process conditions and raw materials are included in this WP. For example, catalyst life test or small academic demos are included here. This WP provides data to the integrated scenarios of WP7.1 and 7.2. EuroBioRef will locate in this WP all the process design and validation tests from the SP2 to SP6. Deliverables in this WP are grams to kg scale samples. Larger samples are produced by definition in SP8 (pilot demonstration).

Available or new lab/bench scale units for specific processes and/or process steps will be operated for preliminary tests. This will be done de-central in a non-integrated mode in each partners' facilities. The results will be used to prove or improve the performance within the process design and integration work (WP7.1, WP7.2). The results are inputs towards pilot demonstration (SP8).

Within Deliverable D7.3.2, a pilot plant on catalytic distillation will be investigated at TUDO with a feed flow of up to 20 kg per day for the production of *n*-butyl acrylate from *n*-butanol and acrylic acid. Both reactants are supposed to be synthesised from renewable resources.

Brief description of the state of the art

Thus far, RD is not applied for the production of *n*-butyl acrylate and only a few publications can be found on this topic. The reaction kinetics and the chemical equilibrium of the heterogeneously catalysed esterification of acrylic acid and *n*-butanol were experimentally investigated by Schwarzer and Hoffmann[1]. They theoretically studied an RD column using an equilibrium-stage model and a catalytic tube reactor using their own kinetic data. Zeng et al.[2] theoretically investigated the production of *n*-butyl acrylate with a single RD column. On the basis of kinetics measured by Schwarzer and Hoffmann, they studied the design and control of the column. Within their theoretical study, it was shown that the use of a reactive distillation column for the synthesis of *n*-butyl acrylate is beneficial, as *n*-butyl acrylate concentrations of more than 99.8 mol-% can be achieved in a single reactive distillation column. As a result, they provided a control strategy for an industrial RD column for the production of high purity *n*-butyl acrylate. Keller et al.[3] performed simulations with a non-equilibrium-stage model. Using the kinetic data of Schwarzer and Hoffmann, they simulated a pilot-scale RD column for the production of *n*-butyl acrylate to prove the feasibility of this process. Nevertheless, the production of *n*-butyl acrylate in an RD column was only studied on a theoretical basis by all of these publications.

The current production of the *n*-butyl acrylate synthesis is homogeneously catalysed and performed in a multistage process using two reactors and several distillation columns for the recovery of the purified product[4]. No investigations on the production of *n*-butyl acrylate from bio-based resources have been published so far and is therefore at first investigated within this work package.

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[1] Schwarzer, S.; Hoffmann, U. *Experimental Reaction Equilibrium and Kinetics of the Liquid-Phase Butyl Acrylate Synthesis Applied to Reactive Distillation Simulations*. Chem. Eng. Technol. 2002, 25, 975.

[2] Zeng, K.-L.; Kuo, C.-L.; Chien, I.-L. *Design and Control of Butyl Acrylate Reactive Distillation Column System*. Chem. Eng. Sci. 2006, 61, 4417.

[3] Keller, T.; Tretjak, S.; Lacroix, C. et al. *Process Intensification of n-Butyl Acrylate Synthesis Using Catalytic Distillation - A Theoretical Study*. Proceedings of the 19th International Congress of Chemical and Process Engineering, Prague, Aug 28−Sept 1, 2010.

[4] Bell, S. L. Acrylic Acids and Esters; *Process Economics Program 6D*, SRI Consulting, CA, 2003

Deviation from objectives and corrective actions

Within the EuroBioRef project it was found, that the dehydration and esterification take place under different conditions. Therefore, it is not possible to integrate both reaction steps in one reactive distillation column. The reaction has to take place in two steps, the dehydration reaction in a pre-reactor and the esterification in a reactive distillation column subsequently. Therefore, only the esterification of *n*-butanol with acrylic acid will be investigated experimentally in the project in a reactive distillation column.

So far, no bio-based acrylic acid and *n*-butanol was provided to TUDO. Hence, the experimental investigations in the pilot-scale reactive distillation unit were only performed with conventional *n*-butanol and acrylic acid. Hereby, the technical feasibility of this synthesis could be proved and the pilot-scale reactive distillation column could be prepared. The technical feasibility of this process was shown with the results listed below and the pilot-scale reactive distillation column is ready to perform experiments using bio-based raw materials as soon as they become available. The nonequilibrium-stage model was already validated using the two performed experiments with conventional raw materials. The validation will be checked with experiments using bio-based raw materials.

The validated model will be used (in WP5.5) to determine the influence of the different sets of impurities in bio-based raw materials and their influence on the process performance.

Innovation brought and technological progress

In preparation of the pilot-scale reactive distillation experiments, batch experiments were performed at TUDO to define the polymerisation behaviour of the system and the influence of polymerisation inhibitors. Two different inhibitors, phenothiazine and hydroquinone monomethyl ether were investigated. Using the results of the batch experiments, the limits of the operation window for the experiments in the reactive distillation column were determined. As the polymerisation risk increases with increasing temperature, an upper temperature limit was defined. Below this temperature limit, the necessary amount and composition of the inhibitor was investigated to ensure a total inhibition of the polymerisation in the reactive distillation column. Hereby, the required amount of inhibitor for upcoming experiments in pilot plant scale was established.

At first, the column had to be prepared for the upcoming experimental study. Therefore several modifications were performed. As the pilot plant experiments will take place under reduced pressure to ensure a safe operation by reducing the polymerisation risk, a vacuum pump had to be attached and put into operation. Additionally several hoses and flange assemblies were replaced to allow operation under reduced pressure.

Based on the knowledge gained by the batch experiments, an inhibitor addition concept was developed and implemented. Through the implementation of this concept, the polymerisation risk was minimized and the synthesis of *n*-butyl acrylate by reactive distillation in our pilot plant reactive distillation column can be further investigated. The pilot plant reactive distillation experiments will be used to validate the modelling results.

Two pilot plant reactive distillation experiments were successfully performed. Within these experiments, a total feed flow of 3.6 kg per hour was fed with an excess of *n*-butanol, to increase the acrylic acid conversion and hereby decrease the risk of polymerisation. The experiments show the technical feasibility of the process and were used to perform a model validation. Therefore, the experiments were not aiming at producing *n*-butyl acrylate with a high purity, but to provide experimental data for the model validation. The validated model will be used for further simulation studies investigating an industrial RD process for the production of *n*-butyl acrylate using bio-based feedstocks.

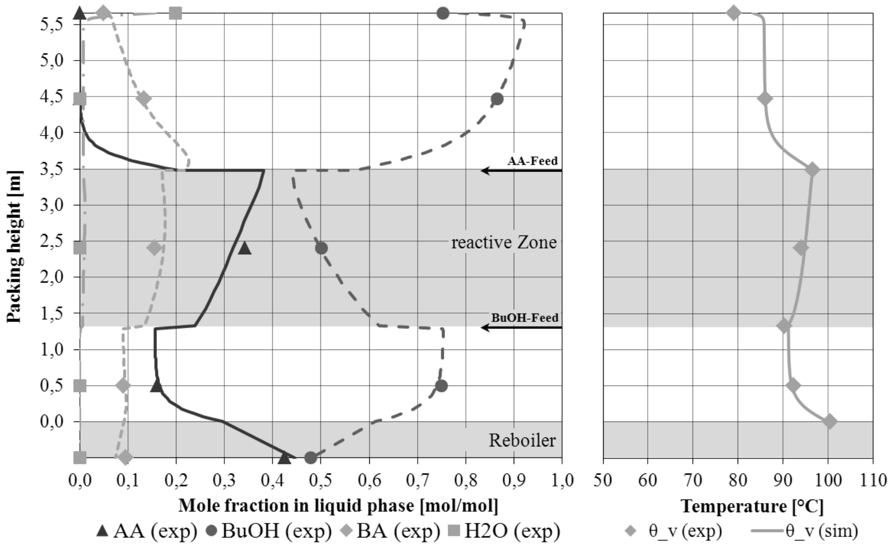

Figure 1: Experimental (symbols) and simulation (lines) results of a column profile used for the model validation.

Analysis of the results

Due to the lack of bio-based raw materials, some reactive distillation experiments were already performed using conventional raw materials. Hereby, the technical feasibility of the reactive distillation technology for the synthesis of *n*-butyl acrylate in a reactive distillation column was shown. A feed flow of 3.6 kg per hour was used, which successfully fulfils the desired 20 kg per day. As shown in Figure 1, *n*-butyl acrylate could successfully be synthesised and the model that was set-up is able to predict the experimental results. Due to experimental constraints, a bottom product with purified *n*-butyl acrylate could not be achieved within the experimental investigation. This will be investigated in more detail using the validated nonequilibrium-stage model implemented in Aspen Custom Modeler.

During the experimental investigation, the polymerisation could successfully be prevented in the pilot-scale column, so that the developed concept will also help to avoid the polymerisation in industrial columns.

Impact of the results

Within the project, the technical feasibility of the reactive distillation process for the synthesis of *n*-butyl acrylate from acrylic acid and *n*-butanol was shown and therefore, further investigations on this process using bio-based raw materials should be performed. A reactive distillation process for the further processing of components with a high tendency to polymerise was developed and the polymerisation inhibition concept was validated by two pilot-scale reactive distillation experiments. These experiments were used to validate a nonequilibrium-stage model, that can be used for an analysis of the process, e.g. in respect to the impact of impurities resulting from bio-based raw materials. Impacts of the experimental investigation using bio-based raw materials will be generated, as soon as the necessary raw materials become available.

As soon as bio-based raw materials can be used for this process, the first investigation for this reaction will be performed in a pilot-scale reactive distillation column. The feasibility of the reactive distillation concept for the further processing of bio-based chemicals (at the example of the *n*-butyl acrylate synthesis) will be shown, potentially enhancing the industrial application of this concept for the *n*-butyl acrylate synthesis and comparable reactions. The gained knowledge can be used to develop reactive distillation processes for the further processing of bio-based raw materials and hence to provoke the use of bio-based raw materials for the production of speciality or bulk chemicals.

Related IPR

The current results are not patentable. The further experimental investigations using bio-based raw materials and the theoretical investigations about the impact of bio-based impurities on the process could be published.

Publishable information

As soon as further investigations on the esterification in a reactive distillation column using bio-based raw materials are performed, these results can be published.

Conclusion

The polymerisation of acrylic acid and *n*-butyl acrylate could be prevented in a pilot-scale reactive distillation unit and the technical feasibility of the reactive distillation concept for the production of *n*-butyl acrylate from acrylic acid and *n*-butanol was shown with a feed flow of up to 3.6 kg per hour. In this experiment, 0.31 kg/h n-butyl acrylate was produced. A non-equilibrium-stage model was validated, which can be used for analyses of the process.