Bio-based production of crotonic acid from wastewater TEBE117004

Final report
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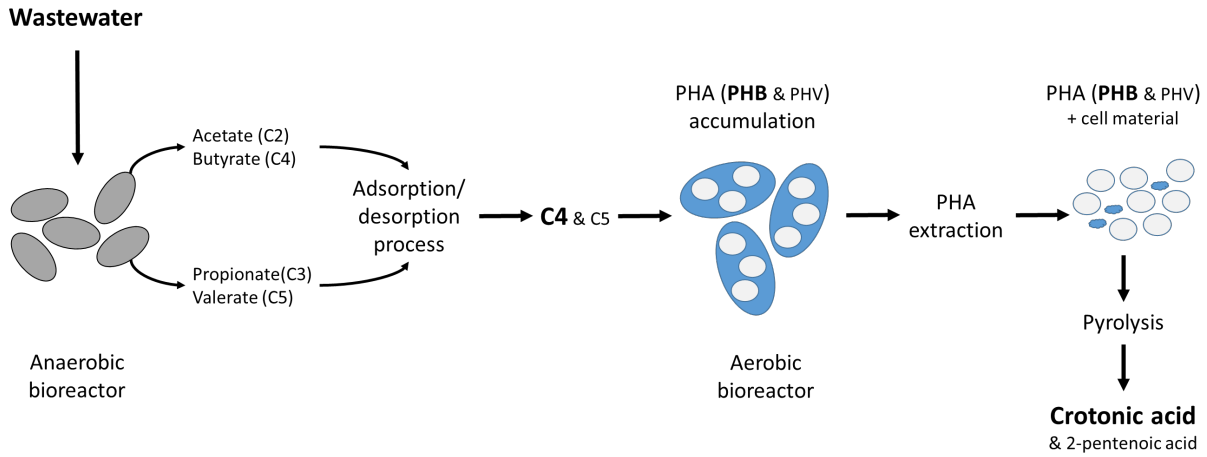

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Project partners:

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Summary

The production of polyhydroxybutyrate (PHB) from wastewater as was previously investigated by Paques BV was taken as a potential route towards valorization of wastewater. Considering that due to varying feed composition also the product composition varies, and typically not pure PHB is obtained, but a mixture known as polyhydroxyalkanoate (PHA), in which next to PHB, also polyhydroxyvalerate (PHV) co-polymers are present. Variations in composition of the PHA limit the market value, and an alternative valorization route through pyrolysis of the PHA was investigated to yield crotonic acid (2-butenoic acid) as the main product, and 2-pentenoic acid as the byproduct was investigated.
In this project, the entire chain including anaerobic digestion to form volatile fatty acids (VFAs), their adsorption and desorption for recovery from the broth, the aerobic conversion into PHA and the pyrolysis and fractionation of the acids 2-pentenoic acid and crotonic acid were investigated.

Activities regarding digestions were carried out at Paques (until 2021) and Paques Biomaterials (from 2021), adsorption & desorption of VFAs, extraction of PHA, PHA pyrolysis and distillation of the acids was researched by University of Twente. Eventually small batch of crotonic acid was sent to Bostik where application testing was carried out.
The main results obtained include:

WP1 – anaerobic VFA production
VFA production studies have been carried out at Paques, varying feedstock and nature of the feedstock.

WP2 – adsorption
The adsorption with desorption via magnetic hyperthemia technology was developed at the University of Twente. A small scale setup was constructed and used to show that water removal could be done very effectively using magnetic hyperthermia. Afterwards, the VFA could be obtained in a much higher amount at high concentration.

WP3 – aerobic PHA production
The activities have been shifted in 2021 from Paques to Paques Biomaterials, and during this period, a pilot plant facility has been constructed as well: PHA2USE in Dordrecht. Activities within this project have contributed to the PHA2USE facility, and have allowed research in the other work packages by producing enough PHA for further use.

WP4 – pyrolysis and fractionation of PHA

Next to pyrolysis, also work has been done on extraction of the PHA. For the pyrolysis process, we have compared direct pyrolysis of the biomass containing PHA, and on pyrolysis of PHA that was extracted and purified from the extraction solvent first. Both methods have been found suitable, where extraction followed by pyrolysis yields a cleaner pyrolysis mixture, while processing costs are obviously higher when an extra step is included.

For the downstream fractionation, we have developed a setup where pyrolysis was done with an integrated fractionation column of limited number of stages (Vigreux), while in collaboration with the Technical University of Dortmund, at their laboratories, a more detailed study on the fractionation via spinning band distillation (SBD) was carried out. This study yielded highly pure crotonic acid as distillate, and a sample of that product was shipped to Bostik for application testing.

WP5 – application testing

At Bostik, the produced crotonic acid was applied in a few different formulations, and the performances were studied.

1. Introduction

Overall aim:

The overall aim of the project was to develop a competitive route towards crotonic acid. This route consists of the anaerobic biotechnological conversion of waste into volatile fatty acids (VFAs), the recovery of these VFAs from the broth, and use as feedstock for the aerobic biotechnological conversion into PHA. In the final stage, the PHA is depolymerized via thermal depolymerization (pyrolysis). By improving the selectivity of the VFA production towards more butyric acid, and the recovery with fractionation, it is possible to feed butyric acid enriched VFA to the aerobic PHA production. As a result a higher fraction PHB is obtained, and less polyhydroxyvalerate (PHV). In the final stage we aim to extract the PHA from the biomass and integrate the solvent recovery with the pyrolysis in a molecular distillation derived approach. If needed, this will be combined with a fractionation to obtain highly pure and highly valuable (5 – 10 €/kg) crotonic acid. This approach matches perfectly with the aim of the biotechnological conversion line in the BBEG program.

Approach

In this project, we have combined fundamental new research at the University of Twente on several separation steps and the pyrolysis of PHA to make crotonic acid with pilot scaled biotechnological conversions of wastewaters into VFAs and PHA at Paques and Paques Biomaterials. At Bostik application studies were performed.

2. Results

WP1 – anaerobic VFA production
Controlling the type of VFA produced during the fermentation of carbohydrates in waste streams is a key starting step for the stability of the whole crotonic acid production process. In this project we evaluate the growth of granular biomass capable of VFA production and a better steering of the type of VFA produced (see Figure 1).

Figure 1. – Granulation process of VFA producing biomass (white-yellow color) over time.

WP2 – adsorption
The adsorption with desorption via magnetic hyperthemia technology was developed at the University of Twente. A small scale setup was constructed and used to show that water removal could be done very effectively using magnetic hyperthermia. Afterwards, the VFA could be obtained in a much higher amount at high concentration.

The results are more elaboratively described in the PhD Thesis of Vahideh Elhami. This chapter has also been submitted for publication in a scientific journal.

WP3 – aerobic PHA production
The main goal of this work package was to produce PHA materials to be used in WP4 activities. We used PHA biomass batches produced in the PHA pilot plant in Lelystad (FABULOUS project) and from a larger pilot trial in Leeuwarden (part of the PHA2USE project).
The activities have been shifted in 2021 from Paques to Paques Biomaterials, and during this period, a pilot plant facility has been constructed as well: PHA2USE in Dordrecht. Activities within this project have contributed to the PHA2USE facility, and have allowed research in the other work packages by producing enough PHA for further use.

WP4 – pyrolysis and fractionation of PHA
Next to pyrolysis, also work has been done on extraction of the PHA. For the pyrolysis process, we have compared direct pyrolysis of the biomass containing PHA, and on pyrolysis of PHA that was extracted and purified from the extraction solvent first. Both methods have been found suitable, where extraction followed by pyrolysis yields a cleaner pyrolysis mixture, while processing costs are obviously higher when an extra step is included.

The results are more elaboratively described in the PhD Thesis of Vahideh Elhami. The extraction of the PHA was published
https://www.sciencedirect.com/science/article/pii/S1383586622013296

also the pyrolysis and partial fractionation was published:
https://pubs.acs.org/doi/full/10.1021/acs.iecr.2c03791

For the downstream fractionation, we have developed a setup where pyrolysis was done with an integrated fractionation column of limited number of stages (Vigreux), while in collaboration with the Technical University of Dortmund, at their laboratories, a more detailed study on the fractionation via spinning band distillation (SBD) was carried out.
This chapter from the Thesis of Vahideh Elhami has also been accepted for publication (ACS Sustainable Chemistry and Engineering).

This study yielded highly pure crotonic acid as distillate, and a sample of that product was shipped to Bostik for application testing.

WP5 – application testing
At Bostik, the produced crotonic acid was applied in a few different formulations, and the performances were studied.
for certain applications, the addition of CA seems interesting and could lead to further studies and the companies Bostik and Paques Biomaterials are currently in orientation stage for future activities.

3. Opportunities for spin-off and future activities

At Paques Biomaterials, a pilot facility is under construction to do the extraction of PHA from biomass also at pilot scale. This enables a much larger stream of PHA to become available in the near future. Together with project partners, we will now also look for new opportunities to apply the pyrolysis and fractionation at larger scale so that more work on the application testing can be done at Bostik. For larger scale testing at Bostik, 5-6kg per batch would be needed, resulting in order of magnitude 100g per batch crotonic acid. It is anticipated that this would be well-possible at the PHA extraction plant of Paques Biomaterials.

Another activity that has spun out is a project proposal that is currently under evaluation at NWO, in which Paques (thus the company Paques that was initially involved in the project, and is now more in the VFA still, and not PHA) is one of the users. In this proposal, we evaluate an alternative route from butyric acid to crotonic acid. Also there, when we get funded, Bostik is one of the users in the community and looking for applications.

4. Execution of the project

Over the course of the project, one major change has taken place, and that is that Paques BV has been changed ownership and that a small company, Paques Biomaterials BV has been carved out. Since this company continues the PHA-related developments, a contract change has taken place in 2021, and from that point on Paques Biomaterials BV was project partner. This had technically no impact at all on the execution of the project, as the team members remained the same.

Several other events have changed the end-date: first, we had to find the right doctoral candidate, which was not easy since knowledge on polymer synthesis, process engineering and the physics of magnetism should be combined. Eventually we did find with Vahideh Elhami a very good candidate. She started six months after the initial anticipated starting date, and therefore the project start and end dates were requested to be changed.
As integral part of the learning process to develop understanding of the magnetic hyperthermia, a research visit to the USA was anticipated. Unfortunately, the native

country of the PhD candidate (Iran) was not a good match with the USA presidential policy (Trump administration) regarding admitting citizens of Iran. Therefore, instead of a longer stay by the PhD-student, only the supervisor could spend one week in the laboratory of the University of Arkansas to do some initial magnetic hyperthermia measurements in preparation of the construction of our own setup. As a result the travel budget remained partly unused.

Another event, the Covid-19 pandemic did impact on the project. The research at the University of Twente has been delayed several months due to the labs being closed. Eventually, we have requested another 3 month extension for the project. This was enough to finalize all foreseen activities, and overall, we can look back at a project where the goals were met.

While the end goal, testing crotonic acid from fermented waste water in formulations, was done at Bostik, at the other end-user Wacker Chemie, there was a change in the composition of the team, and due to the current (end 2022) situation, it was not possible to do application testing there.

Considering all the planned activities, we have seen at University of Twente, that due to the behavior of the crotonic acid (melting point at 72˚C), it was necessary to build a new equilibrium cell for measurements on the vapor liquid equilibria (VLE). The regular VLE equipment, an ebulliometer, suffered from crystallization at cold spots, and operation was compromised at high crotonic acid concentrations. At lower concentrations the equipment could still be used, and it was shown in these regions that there was a good agreement between the results in the new equilibrium cell and in the ebulliometer. This was not anticipated, and also the building of the magnetic heating equipment costed significant time (not so high investment money wise, but many man hours to discuss and study how the equipment should be constructed). As a result, there was still some budget left, but no manpower, and since at the same time at TU Dortmund a new spinning band distillation column had been developed, we have reached out to that party and agreed that they could perform for us several distillation experiments in close collaboration with the Twente team. The end result is that in these experiments we were able to isolate enough material at high purity to do the application testing at Bostik.

The combined changes in execution has led to a change in the budget (overall-budget neutral, only a shift in allocation), which was formally requested in May 2022.

5. **PR**
   However, for the first steps of VFA production and PHA production, we have presented our work in several academic and industrial events, highlighting mostly our new capacity to generate PHBVs with better controlled molecular weight.
   A key event along this project was the opening of the PHA2USE Demo plant in Dordrecht, a key infrastructure to scale up PHA production and application technologies.

6. **Conclusions and recommendations**

For the production of larger amounts of crotonic acid, we have seen that all investigated steps are technically possible, and especially the biotechnological conversions that have been developed at Paques and Paques Biomaterials are already in an advanced state. The separation steps are now much better understood and also at Paques Biomaterials in collaboration with an external party, the extraction of PHA from the biomass is being piloted (part of PHA2USE project). With this project, the technical feasibility of the pyrolysis followed by further purification by distillation has also been shown. This can in the future generate a route towards commercialization that is for Paques Biomaterials certainly a highly interesting alternative to the direct marketing of the PHA at smaller production scales. Further design of a pilot distillation setup to obtain higher quantities of high purity crotonic acid are recommended. If properly designed, the 2-pentenoic acid can also be obtained in pure form as a highly valuable byproduct.