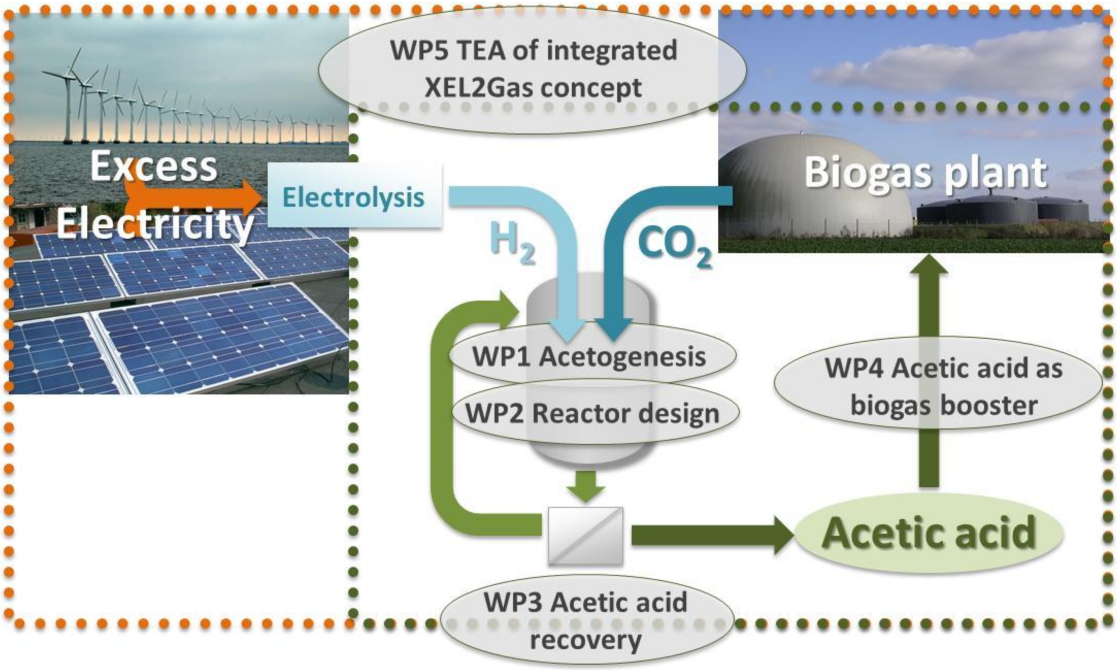
Final report

1.1 Project details

Project title	**XEL2Gas – Acetic acid as a storage molecule for excess electricity and its further conversion to biogas – proof of concept**
Project identification (program abbrev. and file)	ForskEL 2016-1-12437
Name of the programme which has funded the project	ForskEL
Project managing company/institution (name and address)	Aalborg University
Project partners	Aalborg University (AAU) Washington State University (WSU) BioVantage.dk ApS
CVR (central business register)	29102384
Date for submission	31-10-2018



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1.2 Short description of project objective and results

The XEL2Gas project investigated the potential of a new system for the storage of excess renewable electricity by biological conversion of electrolytically produced hydrogen (H_2) together with carbon dioxide (CO_2) into acetic acid, which could be used either as biochemical or as substrate for flexible biogas production. From a microbial screening a homoacetogenic bacterial strain APS was identified as the most robust and potential microorganism and a reactor system for the gas fermentation with a high gas transfer and immobilization of APS was developed in lab-scale. Separation of the produced acetic acid from the fermentation broth was successfully tested using ion exchange resins and biogas reactor studies showed instant conversion of acetic acid in pulse feeding regime.

1.2 Kort beskrivelse af projektets formal og resultater

XEL2Gas projektet undersøgte potentialet af en ny teknologi til lagring af overskudselektricitet fra fornybare energikilder i form af eddikesyre som fremstilles igennem en biologisk proces fra brint (H_2) produceret gennem elektrolyse og kuldioxid (CO_2). Eddikesyre kan benyttes enten som biokemikalie eller som substrat for fleksibel biogasproduktion. Efter en mikrobiel screening blev APS fundet at være den mest robuste og højeffektive mikroorganisme, og denne organisme blev testet i et nyt laboratorie-skala reaktordesign for gas fermentering med høj gas overførsel og immobilisering af APS. Ionbytte viste sig som en effektiv separeringsmetode for eddikesyre fra fermenteringen og en hurtig omsætning af eddikesyre til biogas kunne eftervises i reaktorforsøg.

1.3 Executive summary

As Denmark is aiming at developing a share of renewable energy for electricity production of 50% wind energy by 2020 and 100% renewable energy production in 2050, the energy supply will face increasing shares of fluctuating electricity production. During peak production periods it is expected that the electricity price will become low or even negative to such an extent that rapid deployment of technical facilities capable of absorbing the electricity and turning it into a storable intermediate product will make economic sense. The aim of the XEL2Gas project was therefore to develop an economically viable and robust process concept capable for long-term storage of fluctuating renewable electricity production from e.g. wind power and large-scale photovoltaic plants (PV). The core process to be developed in the project is the conversion of H_2, generated from excess electricity by electrolysis of water, and CO_2 derived from industrial production or biogas production into acetic acid (CH_3COOH), a high-value platform chemical that can easily be stored and also used as substrate for the biogas process. In order to perform a techno-economic analysis (TEA) of the new concept (WP5), the XEL2Gas project was testing the different unit processes in the following work packages (figure 1.3.1):

- WP 1 Biocatalyst development for acetogenesis (AAU)
- WP 2 Reactor design for acetogenesis (AAU, BioVantage)
- WP 3 Separation and recovery of acetic acid (WSU, AAU)
- WP 4 Using acetic acid as biogas booster (AAU)

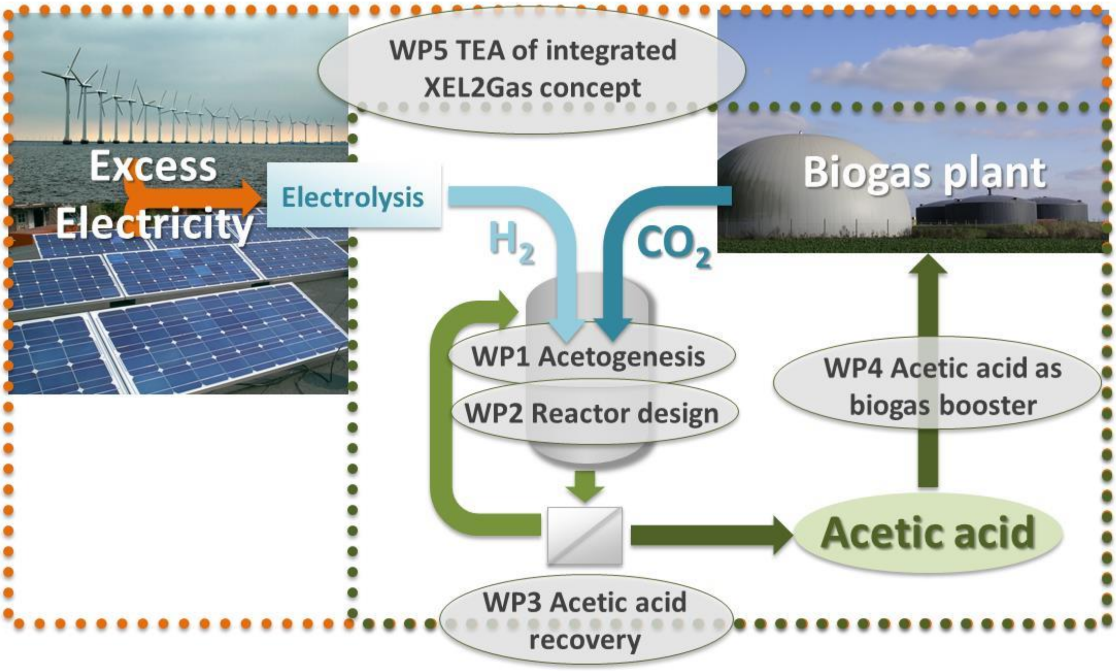

Figure 1.3.1: Overview of the processes and WPs involved in the XEL2Gas project.

Ten different microbial strains capable of the conversion of hydrogen and CO_2 into acetate (homoacetogens) were screened in WP1 to identify the most robust and high yielding strain. The strain showing the highest growth rate and acetate production was APS using 3% corn steep liquor and 0.5% digested manure as low cost nutrient medium. The new reactor design to be developed in WP2 was mainly targeting to overcome the gas-liquid transfer limitations of hydrogen. The final new design in lab-scale showed promising production rates in continuous operation. For the recovery of acetic acid from the fermentation broth of WP2 different resins were tested in WP3 for binding acetic acid by ion exchange. Finally, the addition of acetic acid to the biogas process was tested in pulse feeding to evaluate the suitability of acetic acid for instant biogas production to counterbalance periods of low energy production by fluctuating renewable resources.

1.4 Project objectives

The overall objective of the 2-year XEL2Gas project was to develop a proof-of-concept solution for the conversion of excess electricity into acetic acid and its further use as substrate for flexible biogas production. The different unit processes – the acetogenesis in a gas fermentation process, the recovery of acetic acid by ion exchange resins and the use of acetate as substrate for instant biogas production – were each developed and tested in lab-scale. Based on the results of the different processes and on economic values found in literature, a techno-economic analysis (TEA) was performed to calculate the overall economy of the new concept and identify the main bottlenecks and potentials for the development of the concept for full-scale implementation. This will form the basis for the roadmap of a follow-up project to mature the unit processes and test them in an integrated set-up in large-scale.

1.5 Project results and dissemination of results

The experiments performed and technical results achieved in the different work packages are described in the following. As the 2-year XEL2Gas project was meant as a proof-of-concept project, the main outcome of the project is the feasibility of the different unit processes of the XEL2Gas concept in lab-scale.

WP 1 Biocatalyst development for acetogenesis (AAU)

During the first project period the screening of different potential acetogenic strains for the production of acetic acid from hydrogen and CO_2 was performed. A total of 10 acetogenic strains known to perform the desired reaction were tested, namely:

- *Clostridium autoethanogenum* DSM-10061
- *Clostridium ljungdahlii* DSM-13528
- *Clostridium aceticum* DSM-1496
- *Acetobacterium woodii* DSM-1030
- *Blautia producta* DSM-2950
- *Clostridium ragsdalei* DSM-15248
- *Moorella thermoacetica* DSM-521
- *Sporomusa ovata* DSM-2662
- *Clostridium drakei* DSM-12750
- *Acetobacterium sp.* DSM-2396

The strain selected (strain APS) showed high pH tolerance with an optimal range of pH 6.5-7.5, a low product inhibition, its tolerance towards oxygen and the highest acetate productivity.

Experiments were conducted to investigate the influence of trace metal addition and of hydrogen partial pressure on the fermentation.

First, the development of a low-cost fermentation medium containing all essential nutrients required for cell growth and product formation was examined. As such the effect of using corn steep liquor and digested manure from a biogas reactor was considered to cover the needs for micro- and macronutrients of the strains.

Similar controlled batch fermentations were performed while increasing the hydrogen partial pressure to optimize the fermentation conditions. Hydrogen partial pressure was found to have significant influence on both formate and acetate production.

WP 2 Reactor design for acetogenesis (BioVantage)

In the preliminary design two different reactor concepts were initially developed and evaluated based on the ability to maximize mass transfer between the gas and liquid interphase under anaerobic conditions. A variety of construction materials for the reactor concepts were evaluated based on the desired functionality including positive operational pressure, transparency, and safety. Thick plexi glass and thick safety glass were found to provide most of the desired functionality and also the most flexible design solution. Screen mesh and polyethylene foam were found as promising materials for bacteria immobilization.

A new reactor set-up was developed that improves the gas to liquid mass transfer coefficient for H_2 in water.

The highest acetate production was 3.7 g L^{-1} d^{-1} in combination with an ion exchange module, which removes the acetate directly from the media (WP3).

WP 3 Separation of acetic acid (WSU)

Several ion exchange resins for extraction of acetic acid from the fermentation broth were tested.

Six different types of ion exchange resins, were assessed for their acetic acid adsorption capacities across five different concentrations of acetic acid; 5 g/L, 10 g/L, 15 g/L, 25 g/L and 40 g/L at two different pH conditions of pH 5 and 6.

Screening experiments were done to select the ideal ion exchange resin that has highest affinity towards acetic acid.

Two of the tested ion exchange resins showed best acetate adsorption capacity for an initial acetate concentration in the feed solution of about 40g/L. Effect of temperature and pH was found to be significant between gel-type and macroporous resins, especially at high initial concentrations of acetate in the feed.

WP 4 Acetic acid as biogas booster (AAU)

Batch and reactor tests were carried under thermophilic (52°C) and mesophilic (37°C) conditions with addition of acetic acid (HAc) in different concentrations and increasing loading, respectively, to investigate the degree and limitations of the conversion of HAc for pulse feeding.

Thermophilic digestion trials

Biomethane potential batch tests (BPM) were performed for screening the effect of increasing dosage of acetic acid added to thermophilic inoculum (52°C). Acetic acid (HAc) was added in 5 different dosages, 0.1, 0.25, 0.5, 0.75 and 1 g HAc, respectively. At the dosage of 0.1 g HAc, a methane yield of 0.314 L-CH_4/g was reached, while for the 0.25 g dosage the final methane yield decreased to 0.136 L-CH_4/g HAc. At the dosage of 0.5 g Hac and higher, no significant methane production was detected. At the end of the BMP experiments the pH in the vials of different HAc dosages was 7.76, 7.34, 5.98, 5.31 and 4.66 for the dosage 0.1, 0.25, 0.5, 0.75 and 1.0 g-HAc, respectively. The decreasing pH in the vials with higher additions of acetic acid showed low buffer capacity of the inoculum used, leading to unfavorable conditions for the methanogenic microorganisms of the biogas conversion process.

The continuous thermophilic biogas reactor experiment was carried out using a laboratory scale reactor with a working volume of 4 L. Process trials with different loadings of acetic acid were performed to determine the process adaptation time and maximal load for full acetic acid conversion when added to the biogas process. The reactor was started with feeding of cow manure alone at a hydraulic retention time (HRT) of 20 days, reaching steady state condition for 3 HRT with an average SGP of 270 mL (61% CH_4) at an OLR of 2.7 g-VS L^{-1} d^{-1}. During this start-up period volatile fatty acids (VFA) concentration was 1.30 ± 0.19 g-COD/L and the pH was stable at 8.08.

After the start-up phase, acetic acid was dosed to the manure once a day in increasing concentrations. The HAc loading was increased every 2-3 weeks from 0.06 g $L^{-1}d^{-1}$ to 0.11, 0.21, 0.41 and 0.81 g $L^{-1}d^{-1}$ HAc. The standard gas production (SGP) decreased in the beginning from 289 to 205 mL/g-VS, then increased to 457 ml/g-VS, but decreased to 344 mL/g-VS for the highest HAc loading. The average methane content of the trials was 63 % CH_4.

VFA analyses showed that the concentration of Hac in the reactor was constantly below 1 g/L with an average concentration of 0.588 g/L, giving no indication for inhibition of the AD process. HAc concentration was highest and with high variations in the first phase, lowering and more stabilizing throughout the 2nd and 3rd phase and rising again in the 4th and 5th phase. Especially a significant increase of the HAc concentration in the final phase of the highest HAc loading is correlated to, the lower specific biogas yield in this phase. pH analysis shows only a minor decline of the pH below pH 8 in the first phases, but a significant decline down to pH 7 during the 4th and 5th phase.

Mesophilic digestion trials

The effect of acetic acid addition was also tested for mesophilic anaerobic digestion. Initial batch tests were conducted in an experimental set-up equal to the thermophilic batch tests described above, only differing by the used inoculum and the incubation temperature (37°C). These batch tests showed a similar response to increasing acetic acid concentrations as observed in the thermophilic tests. The methane production for batches with 0.1 g HAc and 0.25 g HAc dosage resulted in methane yields of 0.27 L-CH_4/g HAc and 0.11 L-CH_4/g HAc, respectively, corresponding to 72% and 29% of the theoretical maximum yield. The batches with higher HAc dosage did not produce significant amounts of methane. As described above, it is assumed that the inoculum could not sufficiently buffer the acid addition at higher dosage. Consequently, the pH decreased and methanogenesis was inhibited.

A continuous reactor test was also carried out at mesophilic temperature. As for the batch tests, the experimental design was equal to the thermophilic set-up. However, the pattern of increasing HAc pulses was changed. After a reference phase of feeding manure only, the daily HAc addition was stepwise increased from 0.08 g $L^{-1}d^{-1}$ to 0.88 g $L^{-1}d^{-1}$. The methane yield first increased with increasing the HAc dosage from 0.08 to 0.22 g $L^{-1}d^{-1}$, suggesting that the HAc pulses had a stimulating effect on the process, improving the overall digestion of the substrate mixture. With a further increase of the HAc dosage the methane yield decreased, reaching between 74% and 89% of the full methane potential.

The pH in the reactor varied within a range of pH 7.3 to 7.5 in the course of the experiment. These fluctuations did not correlate with the HAc dosage increase, suggesting that the process had sufficient buffer capacity to maintain a stable and favourable pH.

VFA analysis revealed elevated acetic acid concentrations during HAc pulsing. This rise is rather correlated to incomplete conversion of additional HAc than indicating process imbalance as the digestion process performed stable with respect to yield and production rate.

Overall, the experiments performed in WP4 indicate that while addition of acetate in higher concentrations in batch test can cause inhibition, this effect cannot be seen in continuous reactor operation. This means that acetate can be used as substrate for instant biogas production in a continuous process.

WP 5 TEA for acetic acid production from excess electricity and utilization as biogas booster (BioVantage, AAU)

Data input from WP1, WP2, WP3 and WP4 on the yield and productivity together with costs and prices from literature were used for the techno-economic analysis of the XEL2Gas concept in WP 5. The TEA of the whole concept was calculated as a sum of the TEA of the unit processes, using the output of each previous process as input to the subsequent process, all based on kg of hydrogen produced in the electrolysis and identifying the overall production price per kg-acetate. The economic analysis was done for 3 different scenarios, (1) applying the current prices and process efficiencies, (2) with prospected prices and efficiencies achieved after 3 years of further development and (3) with prospected prices and efficiencies achieved after 5 years of further development. Additionally, the revenue of biogas production from the produced acetate was calculated to compare this with the acetate production price.

For the **electrolysis**, the efficiency of the process is expected to increase from currently 66.7 kWh used for producing one kg of H_2 to 51.9 kWh/kg-H_2. Furthermore, it is projected that oxygen, which is produced as by-product in the electrolysis process can be sold with a price of 0.07 DKK/kg. With a constant electricity price of 0.30 DKK/kWh the hydrogen production costs would decrease in a prospected 5 year period of further development from 39.45 to 24.40 DKK/kg-H_2.

Using the hydrogen production prices as input for the costs of **acetate fermentation,** and a revenue from simultaneous biogas upgrading when using CO_2 from biogas as input, acetate could be currently produced with a 60% efficiency of the fermentation process for a price of 7.38 DKK/kg-acetate. Increasing the fermentation efficiency to 80% through further development combined with lower H_2 production costs, the acetate production costs could be lowered to 2.91 DKK/kg-acetate.

Including the costs for the **acetate recovery** with a prospective increase of the NaOH re-use in the process and of the separation efficiency from 80% to 90% and 95%, respectively, the overall production price for the separated acetate would currently be 8.28 DKK/kg-acetate and 3.40 DKK/kg-acetate after the prospective process improvements. This would mean that the XEL2Gas concept could produce acetate at the current market price of 3.75 -4.25 DKK/kg after further process optimization. In comparison, the production price would be without a revenue for biogas upgrading be currently 10.14 DKK/kg-acetate and 4.80 DKK/kg-acetate after further improvements. Finally, the significance of the electricity price for the final production price can be seen in the drop to 5.74 DKK/kg-acetate and 2.23 DKK/kg-acetate for the same scenarios as the latter, but without electricity costs. In this perspective, the production of acetate by the XEL2Gas concept would be very competitive in periods of excess electricity production, when electricity prices would approximate 0.00 DKK.

Using acetate for biogas would, on the other hand, only give a revenue of 1.17 DKK per kg of acetate. This means that unless the biogas price would be much higher for periods of low electricity production by renewables, selling acetate as final product on the market would give the higher revenue.

1.6 Utilization of project results

The project results of the XEL2Gas project will be used as a baseline for the design of an integrated XEL2Gas concept, which should be tested and further optimized in pilot-scale in a follow-up project.

1.7 Project conclusion and perspective

The results of the lab-scale tests of the XEL2Gas project indicate that the technology could after further process optimization in a follow-up project be very competitive for valorisation of excess electricity by production of acetic acid- and the process might be competitive compared to the current acetate production based on fossil resources. Using acetate as substrate for instant biogas production has, on the other hand, a much lower economic value.