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Production of electricity from Formic Acid – Catalytic decomposition and fuel cell integration

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Zusammenfassung

In naher Zukunft wird die Energieerzeugung aus erneuerbaren Quellen durch dezentrale Speichertechnologien ergänzt werden müssen, um Fluktuationen in der Produktion abzufangen. Wasserstoff wird in diesem zusammenhang eine wichtige Rolle als Energievektor spielen – sei es in seiner molekularen Form, sei es als wasserstoffreiches Trägermolekül. Ameisensäure ist aufgrund ihres Wasserstoffgehalts von 53g/l ein vielversprechender Kandidat für ein solches Trägermolekül

Dieses Forschungsprojekt befasst sich mit der Kombination eines Ameisensäurereformers mit einer industriellen PEM-Brennstoffzelle. Der resultierende Prototyp hat eine elektrische Ausgangsleistung von 1kW$_{el}$ und kann zu einem UPS-System ausgebaut werden. Das Hauptaugenmerk der Forschungsaktivitäten lag dabei auf den Details der Integration, sowohl was Konstruktion und Verschaltung als auch die Prozesskontrolle betrifft.

Résumé

Dans le futur, la production d'énergie des sources renouvelables sera complémenté par des technologies de stockage décentralisé d'énergie, afin de compenser des fluctuations de production. L'hydrogène va jouer un rôle important comme vecteur d'énergie ainsi que matériel de stockage, soit sous forme moléculaire, soit faisant partie d'une molécule secondaire riche en hydrogène. L'acide formique avec ses 53 g/l d'hydrogène est un candidat promettant pour une telle molécule porteuse.

Ce projet était dédié à la combinaison d'un réformateur acide formique avec une pile à combustible PEM industrielle. Le prototype résultant a une puissance électrique de 1kW$_{el}$ et a le potentiel d'être développé en système UPS. L'essentiel des activités était concentré sur les détails de l'intégration des deux procédés sur le niveau de construction et contrôle, mais aussi sur l'intégration énergétique. L'opération du système et sa stabilité sous conditions steady-state autant que sa performance pendant start-up et shut-down étaient caractérisés.

Le potentiel synergétique de ces deux technologies promet d'aboutir à un procédé industriel compétitif et efficient.

Abstract

In the future, production of energy from renewable sources will have to be complemented by different technologies of decentralized energy storage, as fluctuations in production will have to be compensated for. Hydrogen will play an important role both as energy vector and storage material, either in its molecular form or as part of hydrogen rich secondary molecules. Formic acid, containing 53 g/l of hydrogen is a promising candidate for such a secondary storage molecule.

This project was dedicated to the combination of a formic acid-to-hydrogen generator with an industrial PEM fuel cell system. The main focus lays on the integrational details, concerning both the constructive and the process control level as well as the energetic integration of the two processes. System operation and stability using the primary 50/50 H_2/CO_2 reformate gas under steady state conditions, as well as its dynamic performance during start-up and shut-down were characterized.

The synergetic potential of these two technologies promises to result in a competitive and efficient industrial process.

1 Initial position

This work was based on the technology “HyForm”, allowing the production of a hydrogen rich refor-mate gas from formic acid as base material. This technology offers the possibility to supply hydrogen while avoiding the well-known problems related to its storage at high pressure and/or low tempera-tures.[1-4] It was developed at EPFL (group of Prof. Laurenczy) and has been patented in 2008.

The technology is based on a ruthenium-based homogeneous catalyst in aqueous solution that allows the dissociation of formic acid into H_2 and CO_2 by the following reaction:

$$HCOOH_{aq} \rightarrow H_2 + CO_2$$

Formic acid contains 53 g/l of hydrogen, a storage density superior to that of other high-performance storage technologies – notably the storage of pure hydrogen under high pressure or cryogenic and liquefied storage systems.[3-6]. Under ambient conditions formic acid is a non-flammable liquid (flash-point at 69°C) of moderate toxicity. In combination with the ready decomposition into CO_2 and H_2 un-der mild conditions, these properties make formic acid a promising material for the chemical storage of hydrogen.

The volumetric productivity of such a formic acid based hydrogen generator becomes interesting at temperatures as low as 80°C – a detail that simplifies the process engineering and opens the possibility to use a low temperature / low value heat source to supply the necessary reaction heat (ΔH_R = 31.5kJ/mol).

Prior to the present project, the feasibility of the technology was proven in a prototype with a continu-ous production capacity of 15slpm of hydrogen, using a 5L reactor vessel charged with 2.5L of catalyst solution heated by 2 electric surface heating elements with a maximum heating power of $0.75kW_{el}$. This prototype was used to test different process control concepts and characterize the system productivity, stability and efficiency as well as to define bottlenecks and limitations of the chosen sys-tem design. The basic process structure is shown in Figure 1:

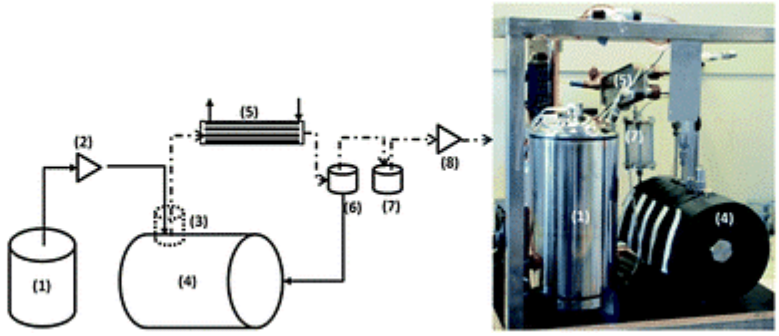

Figure 1 Representation of the first HyForm prototype. (1) FA reservoir, (2) FA feed pump, (3) FA preheating, (4) reactor, (5) reformate cooling, (6/7) condensate separator, (8) reformate MFC

Operation of this first prototype showed that the production of a constant flow of hydrogen using the HyForm technology is straightforward. The system shows promising dynamic properties and the catalyst displayed no sign of deactivation even after 12 months of intermittent use, despite unfavorable conditions (frequent exposure to air and high temperatures). However, it also became clear that several pitfalls needed to be avoided for the design of a viable and efficient industrial process:

- **Solvent management**
  While the concentration of solvent vapor in the reformate gas can be greatly reduced by a cooling step with condensate recycling to the reactor, losses during prolonged operation cannot be neglected.
- **PEM fuel cell compatibility/adaptation**

Tests performed with an industrial PEM fuel cell stack using HyForm product gas as feed showed the necessity to adapt the fuel cell to the dilute hydrogen quality on two levels:

1. The Pt catalyst used by default in fuel cells optimized for pure hydrogen is not directly applicable for use with dilute reformate. A Pt/Ru catalyst is usually used for these feed qualities
2. The channel geometry of the graphite distribution plates needs to be optimized to ensure even distribution of feed gas over the full anode catalyst surface. Using standard plates results in local starving of the catalyst, i.e. a decrease of local hydrogen concentration below safe levels, causing damage to the membrane electrode assemblies

+ **Formic acid supply**
  Refilling of the formic acid reservoir installed in the prototype turned out to be highly impractical as it required opening the lid and manual pouring from 2.5L bottles. The FA vapors being released during this process required the use of breathing and eye protection as well as subsequent ventilation of the lab environment
+ **Reactor heating**
  Using electric surface heating elements turned out to be an effective but highly inefficient way of maintaining a constant reaction temperature. Experiments showed that the process requires an overall heat input of ~3.2 kJ/nL$_{H2}$, which is mostly due to the large amount of water vapor contained in the primary product gas (~20vol% at 5bar and 100°C). Electrically heated, this amounts to around 75% of the electricity produced when the reformate is fed to a PEM fuel cell. This effect brings the overall efficiency of a combined HyForm – fuel cell process down to around 12%, mostly independent of process scale.

2 Goal of the project

Starting with the experiences made with the first prototype capable of producing 15slpm of hydrogen, the next logical step was to improve the process efficiency and to prove its suitability as hydrogen source for an industrial PEM fuel cell. The goal of this project was therefore to design and build a combined and fully integrated HyForm reformer / PEM FC system, using and exploiting its full synergetic potential to reach competitive efficiency levels.

The central improvement to be implemented was the use of a combustion system using the fuel cell anode off-gas (AOG) as fuel. For reasons of process safety, a catalytic combustion at low temperatures was chosen over a thermal combustion step. This change should theoretically push the overall process efficiency to values close to those attainable in standard PEM-fuel cells using pure H_2. Design work was based on a commercial PEM fuel cell system specifically optimized for HyForm reformate feed compositions.

The resulting HyForm-FC system was then to be tested and its performance characterized under steady state conditions and its dynamic performance was to be optimized.

3 Procedures / methods / experimental

3.1 Adapted PEM fuel cell

The fuel cell used in this project was procured from Inhouse Engineering GmbH, Berlin. The design is based on a water-cooled 16-cell stack with a total nominal output power of 1kW$_{el}$ The Pt/Ru catalyst as well as the anode gas distribution plates were specially adapted to the use of 50/50 HyForm reformate. The characteristics of the fuel cell are summarized in Table :

Table 1

Characteristics	**Symbol [Units]**	**Value**
Nominal output power	P_{el} [W]	1000
Cell number	-	16
Active area / cell	A_{cell} [cm^2]	200
Total active are	A_{tot} [cm^2]	3200
Catalyst type	-	Pt/Ru
Nominal H_2 excess	-	0.4
H_2 flow at P_{el}	$V_{H2,max}$ [NL/min]	30

The fuel cell is operated in current control mode, all cell voltages are monitored to guard against cell damage due to insufficient feed flow or quality. As a precaution against CO poisoning an air bleed system with a stoichiometric capacity of 5% (rel. to reformate H_2 feed flow) is installed at the reformate/ feed gas entrance line.

A backfeed DC/AC converter (EA Elektronik Automation) with a maximum power input of 800W was supplied by Inhouse Engineering and used as variable load during the operation of the fuel cell. Initial tests of the adapted 1kW stack conducted by the manufacturer showed an optimum hydrogen excess of 40%, which can be safely decreased to 35% for short periods of time.
The flow diagram of the fuel cell module including all interfaces with the HyForm reformer module can be found in Annex 1.

3.2 Pressure drop measurements

Pressure drop experiments were conducted using stainless steel tubes cut to the length of the actual tube bundle used in the reactor (290mm). This length was determined based on the estimated heat transfer characteristics between combustion gas and FA decomposition catalyst solution bulk. Pressure difference was measured by a water-filled U-tube connected to inlet and outlet of the packed bed, gas flow rates were determined by bubble gas flow meter.

3.3 Combustion catalyst bed design

Combustion experiments were conducted using a 100mm reaction tube (6x4.5mm stainless steel) immersed in heating oil maintained at the set temperature using a thermostat bath. This setup was chosen to simulate as closely as possible the conditions found in the actual reactor under operation. The three components of the combustion gas – hydrogen, CO_2 and air – were separately controlled by mass flow controller (Brooks) and sent through a static mixer element and a flame arrestor before entering the combustion catalyst bed. Inlet and outlet temperature were measured using thermocouple sensors (Type K, Thermocoax SA) placed before the first and after the last catalyst pellet.
Figure 2 shows the catalyst bed geometry used for the combustion tests in a dummy tube: The single catalyst pellets are fixed in a tubular wire mesh cage that is inserted into the tube. Thus, the position of each pellet can be chosen freely and fixed by pinching the cage.

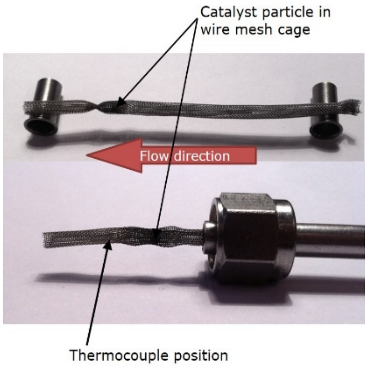

Figure 2 combustion catalyst bed setup - Wire cage with one catalyst pellet

The AOG composition and flow rate just prior to FC stack start-up (start of electricity production) was identified as critical in terms of H_2 concentration (50vol% in CO_2), while the maximum overall hydrogen flow rate occurs under normal operation at full capacity. Therefore, combustion tests were carried out for both start-up and steady state conditions, varying total flow to account for gas flow mal-distribution over the different tubes. A first set of experiments used only one catalyst pellet (Ø 1.8mm) placed at 50mm from the tube entrance. In a second set of experiments, the behavior of a 3-pellet string of the same size, placed at even distances of 25mm was tested.

3.4 Initial fuel cell compatibility tests

Initial tests to ascertain the compatibility of the HyForm reformate gas with the adapted fuel were con-

ducted using the electrically heated first prototype as hydrogen source. Communication between the two process control systems was set up in such a way that the system would automatically react to a change in fuel cell set point (output current): The fuel cell controller converts the new current set point into a hydrogen and reformate flow rate, which is then passed on to the reformer module as new gas production set point. As soon as the gas flow has stabilized on the requested level (criterion: actual flow rate inside ±5% of set point for 10 seconds) the fuel cell controller adjusts current output to the new level.
Experiments included the verification of start-up and shut-down procedures, the optimization of control parameters under normal operation as well as a performance and stability test.

4 *Results / findings*

4.1 Catalytic anode off-gas (AOG) combustion system design

The catalytic combustion of the hydrogen rich anode off-gas (AOG) coming from the fuel cell is a key element of the combined reformer-FC system. For a standard hydrogen excess in the anode feed of 40% (λ_{H_2} = 1.4) its LHV is still 2.4 kJ/Nl – enough to supply the heat needed to maintain stable reaction temperatures under normal operation, where the heat of reaction of the FA decomposition ((ΔH_R = 31.5 kJ/mol FA) as well as heat losses due to solvent evaporation, product gas and combustion off gas enthalpies as well as heat dissipation to ambient need to be balanced.

The catalytic combustion system had to be designed to fulfill three different key requirements:

1. The overall amount of catalyst loaded into each tube needs to be sufficient to reach full hydrogen conversion
2. Even for maximum hydrogen concentrations in the combustion feed the combustion temperature must stay below the ignition temperature of the combustion mix at any point inside the tubes. (T<535°)
3. The maximum pressure drop through the catalyst bed under normal operating conditions was limited by the maximum pressure at the outlet of the FC anode of 250mbar. As a consequence, all components installed downstream from that point, i.e. all components of the catalytic AOG combustion had to be chosen and/or designed to cause minimum pressure drop

Based on these requirements, a commercial combustion Pt catalyst (Johnson Matthey Type 0.5R73C, 0.5wt% Pt on Al_2O_3 spheres) was chosen as base material for the AOG combustion. Its Pt loading is sufficient to achieve full hydrogen conversion while its particle size distribution (1.8mm < d_p < 3.5mm) is in the right range to optimize both pressure drop and combustion behavior.

To meet both requirements using only one type of catalyst the packing density of catalyst pellets needed to be varied over the tube length from single pellets at the tube inlet to a fully packed bed at the outlet. In this way, the hydrogen conversion is spread out over the full tube length and overheating and ignition of the combustion mixture can be avoided.
In terms of overheating and ignition, the inlet of the catalyst bed is the most critical region, as the hydrogen and oxygen concentration are not yet reduced by partial conversion. Experiments therefore focused on this region of the catalyst bed, using wire mesh support cages charged with single catalyst pellets at defined distances.

4.1.1 Pressure drop

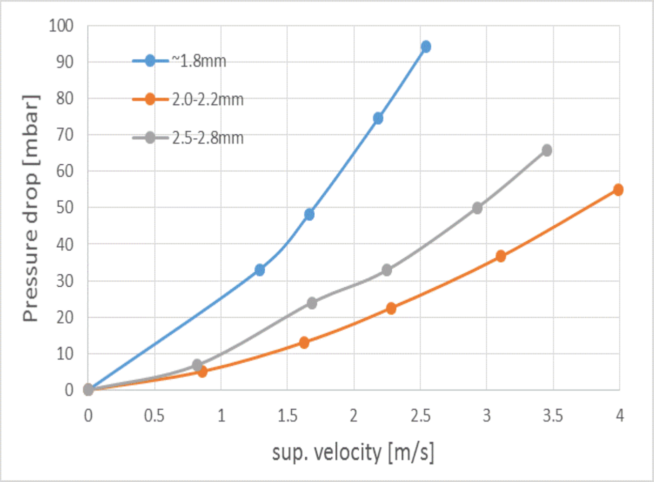

Figure 4 Pressure drop through a packed bed, for different pellet sizes. Tube int. diameter. 3mm, test fluid: air @ 1024mbar, 294K

Special attention was given to the combustion catalyst bed inside the tube bundle, i.e. to the combination of catalyst particle size and internal tube diameter. To determine the optimum bed geometry for minimum pressure drop, experiments with various tube / particle size combinations were conducted. The results obtained for 3mm tubes and air at ambient conditions shown in figure 4 indicate that the pressure drop passes through a minimum for a tube to particle diameter ratio of ~0.7. This was explained by the opposing effect of the particle diameter on packing density and tube obstruction by single pellets. As can be expected from the decreased superficial velocity, experiments also showed a largely decreased pressure drop when the tube diameter was increased from 3mm to 4.5mm (Figure 3). It is interesting to note that for the smaller pellet size pressure drop seems to be solely depend on gas velocity, while variations in packing geometry only becomes important once pellet size approaches tube size.

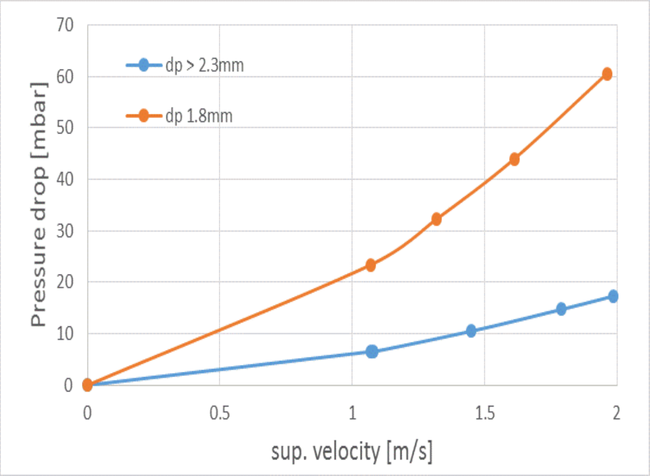

Figure 3 Pressure drop through a packed bed for different pellet sizes, Tube int. diameter. 3mm, test fluid: air @ 1024mbar, 294K

Based on these results, 6 x 4.5mm tubes were used as heat transfer / combustion tubes and the catalyst particle fraction d_p > 2.5mm was used for the packed part of the catalytic combustion bed

4.1.2 Catalyst concentration profile

Figure 5 shows the combustion temperatures measured down-steam from the single catalyst pellet arrangement for a H_2 fuel concentration of 50vol% and two different air/fuel ratios. It can be seen that the temperature remains comfortably below the ignition point for a stoichiometric H_2/air mixture. The used inlet bed geometry is therefore suitable for use in the multi-tube combustion system. It is interesting to note that an increased overall flow rate results in increased combustion temperature. This might be caused by increased catalyst activity but can also be assigned to the decreased temperature loss through radial heat transfer between pellet and temperature sensor.

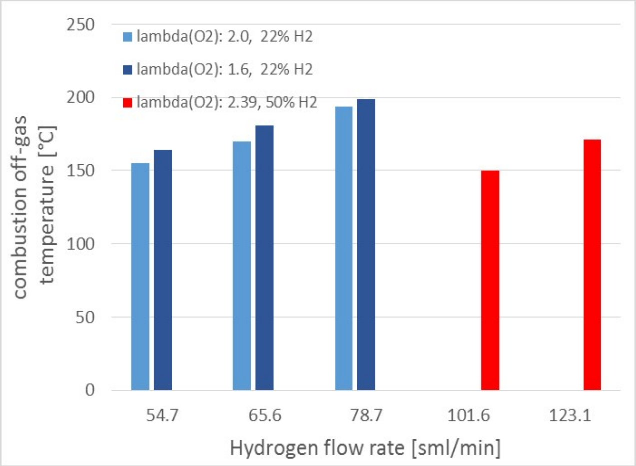

Figure 5 Combustion temperatures in a single-tube test with one catalyst pellet for different H2 feed flows and air ratios

Based on these results, the radial catalyst concentration profile was defined as follows: A first wire mesh cage, 80mm long and containing 3 single catalyst pellets (Ø ≤ 1.8mm) at distances of 25mm is placed at the tube inlet. In a following, second cage the catalyst concentration is increased to 5 pellets (Ø ≤ 1.8mm) of 15mm distance. The remaining tube length downstream of the cages contains a packed bed of catalyst pellets of larger diameter (d_p > 2.5mm) to ensure full hydrogen conversion.

4.2 Fuel cell tests with external HyForm generator

An initial set of experiments was conducted after delivery and commissioning of the FC unit using prototype 1 (electrically heated) as reformate feed source. Fuel cell performance and stability were characterized for a direct HyForm reformate feed at different fuel cell work points. Figure 6 shows the stack voltage for a 6-hour test run at various output current settings. It can be seen that no cell voltage degradation was observed over the experiment’s time frame. It has to be noted, however, that a 5% air bleed flow was necessary to maintain cell performance.

The insert of Figure 6 shows the FC’s voltage-current characteristics extracted for the performance data. The extended linear region indicates that the cell is working in the Ohmic regime.

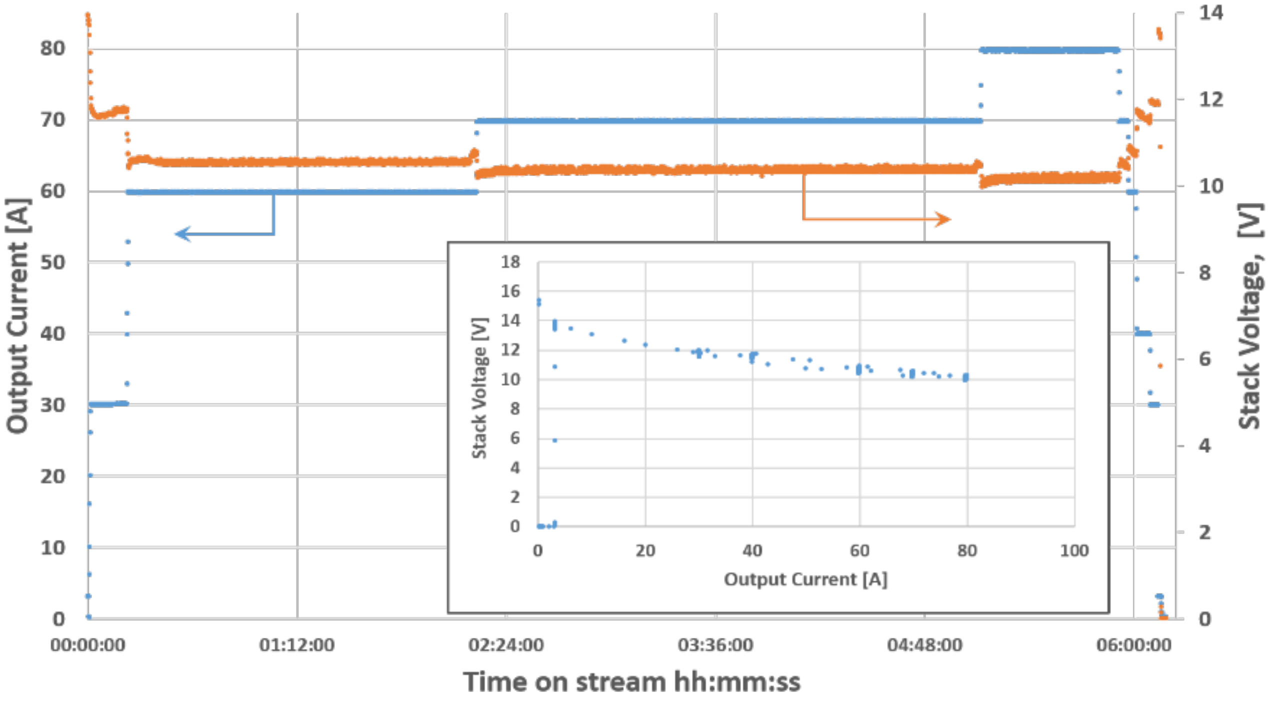

Figure 6: Fc output current and voltage during stability tests with external HyForm generator as hydrogen source

4.3 Reactor design

Using the results of pressure drop and combustion experiments, the reactor design could be finalized: The construction was based on standard tube and weld-on flange elements (PN40, DN 150) adapted to the special requirements of the HyForm process:

The main reaction volume to contain 3.5L of the formic acid decomposition catalyst solution is formed by two stainless steel disks welded to the inside of the inside of the tubular reactor. The disks hold the heat transfer/combustion tube bundle as the axial dip tubes, all welded in place from the outside. The anode off- gas mix enters the combustion system through an access tube (DN50) welded onto the inlet blind flange. It is then distributed between the 61 combustion tubes in the cylindrical volume formed between the inner reactor wall disk and the inlet blind flange. The hot combustion off-gas is collected in a similar volume at the tube bundle outlet and passed through the downstream blind flange.

Radial access points for sensors, process flows and safety switches are welded onto the cylindrical reactor wall, while the formic acid feed tube as well as radial dip tubes for two electrical heating cartridges and a redundant temperature sensor are passed through the blind flanges with radial compression seals ensuring tightness of the combustion system. Figure 7 shows a 3D representation of the resulting reactor design. All instruments/components mounted on the reactor vessel are listed in Tableau.

Table 2: Process components - Reactor

Component ID	**Description**
R48-S	Vibrating fork level switch
R60-SCH	Safety Pressure switch, overpressure
R61-SCH	Safety Temperature switch, overtemperature
R43-S	Reaction pressure sensor
R41-S, R42-S	Redundant temperature sensors, Pt1000
R34-E, R35-E	Electrical heating cartridges, 2 x 250W
R54-S, R59-S	Internal temperature sensors R34/35-E
R02-V	Pressure relief valve

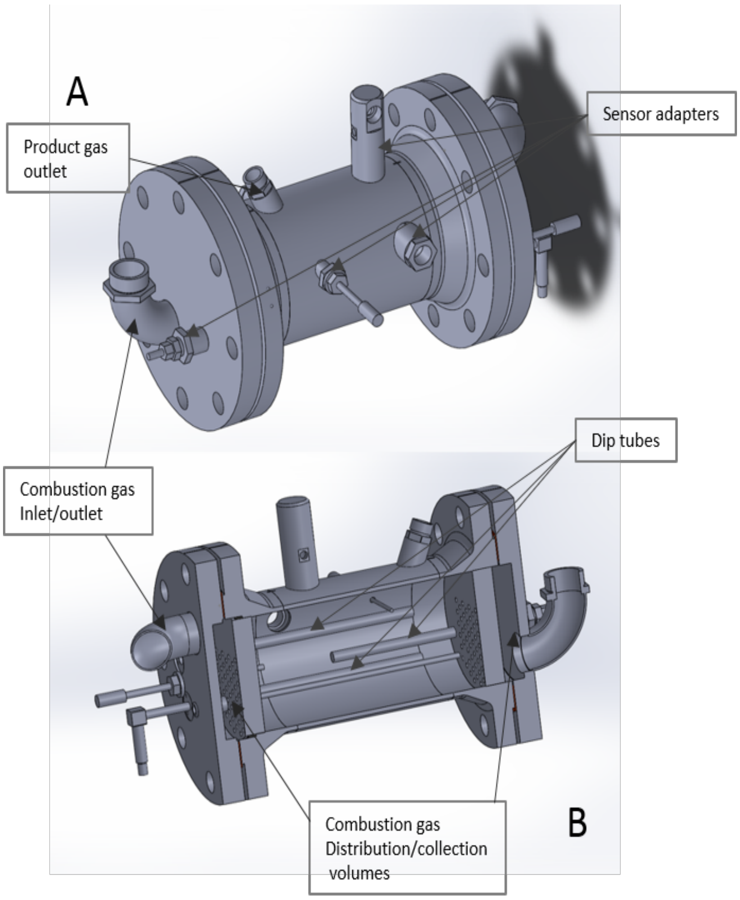

Figure 7: Graphical representation of the HyForm reactor design. For better visibility, the heat transfer tube bundle was omitted from this view.

4.4 Process control & safety concept

4.5 Process safety

Due to the dangers associated with corrosive substances and hydrogen production (especially at elevated pressures), the HyForm FC process requires a careful and comprehensive risk assessment strategy as well as its implementation in constructive measures. Measures were designed to qualify the system as a Zone 2 environment according to ATEX directives 2014/34/EU and 99/92/EC.

4.5.1 Reactor safety monitoring

All reaction parameters are monitored using redundant sensors. In case of control system failure, the reactor is fitted with both a temperature and a pressure safety switch with SIL level 2, set to switch at critical over-pressure and –temperature. Both are hardwired into the general process safety chain designed to safely shut down the process.
The reactor is secured against under temperature (85°C) by a safety temperature switch acting on the two electrical heating cartridges installed in the main reaction volume.

4.5.2 Process isolation

Due to the nature and the requirements of the HyForm process, there will always be an inherent risk of major hydrogen gas leaks, e.g. due to structural integrity failure of pressure lines or vessels. Therefore, the reformer module is divided into two sections, containing the high-pressure reformate system and the low-pressure periphery, respectively.

All instruments, valves and accessories in the former section are certified for ATEX Zone 2 environments. It is hermetically sealed from the rest of the system apart from localized ventilation holes guarded by a dedicated hydrogen detector (see 4.5.4)
The latter contains low pressure AOG lines, the bypass combustion system and all non-critical peripheral systems. Here, explosion protection is realized by multiple leak detection sensors and sufficient ventilation (see. 4.5.4)

4.5.3 H_2 combustion safety

Both the main and bypass AOG combustion systems are equipped with flame arrestors and multiple temperature sensors to detect over-temperature or ignition events. Combustion air is supplied to both systems separately using two MFCs. Their measurements are used to monitor the air flow rate. In case of ignition the air supply is shut off, all combustion lines are flooded with nitrogen and the whole system is immediately shut down.
Multiple temperature switches are mounted at critical locations of the main and bypass combustion system and wired into the systems main safety chain. In case an ignition is not detected directly, increasing surface temperature will switch one or more of these safeguard switches and the system will shut down.

4.5.4 H2 leak detection and system ventilation

Hydrogen leak detectors are installed at three critical positions inside the unit housing:

- Inside the high-pressure section, close to the top ventilation access. This sensor acts on minor and major leaks from reformate lines in the HP section
- Inside the low-pressure section, above the FC stack. This sensor acts on leaks from lines and components anywhere in the low-pressure section
- Inside the low-pressure section, above the ventilation holes leading to the high-pressure section. This sensor is placed specifically to act on major leaks in the high-pressure section where hydrogen leak flow is sufficient to cause back-flow into the low pressure section.

Both the high and low pressure section are equipped with ventilation systems dimensioned to avoid explosive hydrogen atmospheres. While the LP system is ventilated to the surroundings, the HP system is vented to the main off-gas line that needs to be connected either to the outside or to a separate ventilation system.

4.5.5 Corrosion safety / material selection

Formic acid is a corrosive liquid with a flash point of 69°C. All low-pressure components in contact with pure FA are therefore made from appropriate plastic material (PTFE, PP, PVDF), all components exposed to pure or dilute FA at elevated pressures and/or temperatures are made from high grade austenitic stainless steel (316L, 316Ti, 904L).

4.6 Process control

4.6.1 Reaction temperature

Reaction temperature is controlled by adjusting the reaction pressure, thus adjusting the amount of solvent evaporation and shifting the heat balance to the required equilibrium temperature. This indirect solution became necessary as, the amount of combustion heat available is directly linked to the product gas flow through the fuel cell's fixed hydrogen stoichiometry factor.
To set the equilibrium pressure to the desired range, a defined amount of AOG is sent to the bypass combustion line. The split ratio can be set by manual needle valve installed in the AOG distribution line

4.6.2 Reformate flow and reaction pressure

The reformate flow is controlled indirectly thorough the formic acid flow fed to the reactor and the main reaction pressure control valve installed in the reformate outlet line. This indirect approach is necessary, as due to the elevated reformate temperature and high relative humidity involved in the reformate lines condensation of solvent cannot be excluded, making the use of standard MFCs as direct gas flow control elements impractical.

Under steady state conditions reformate flow and formic acid feed flow are equivalent, whereas under non-steady state conditions (start-up, shut down, reactor pressure change) feed flow rates are adapted to ensure a constant reformate flow to the fuel cell.

4.6.3 Reactor solvent holdup/liquid level

Maintaining a defined and constant level of solvent inside the reactor is crucial for both the functionality of the FA decomposition process and the catalytic combustion. A vibrating fork level switch (R48-S), installed on the reaction vessel coupled to a membrane pump (R43-E) is used to top up the reactor with DI water whenever the catalyst solution drops below critical levels.

4.7 HyForm reformer / FC Process structure

The HyForm-FC process flow diagram can be found in Appendix 1. It consists of six main subsystems:

1. **Hydrogen production in the main reactor volume and high pressure reformate make-up**

   The formic acid injected into the HyForm catalyst solution is almost instantaneously split into H_2 and CO_2. This product gas mixture is generated as small bubbles throughout the reaction volume, rises to the surface and forms a quickly collapsing foam. This bubble formation also ensures mixing/distribution of the freshly injected formic acid.

   The raw reformate gas exits the reactor saturated with catalyst solvent (water) and is cooled down to optimum FC feed temperature (60-65°C) in a high-pressure plate heat exchanger before passing through a condensate separator and the reactor pressure control valve. All components are listed in Table 3:

Table **3**: Process components – reformate production

Component ID	**description**
R24_E	Main reactor vessel
R31-E	Reformate cooler
R22-E	Condensate separator /recycling
R01-V	Reaction pressure control valve
R08-V	Reformate shut-off valve

2. **Power generation in the FC stack**

   The low-pressure reformate coming from the reactor pressure control valve is sent to the fuel cell. Due to the pressure reduction from reaction to fuel cell inlet pressure the relative humidity of the reformate drops to values insufficient for direct FC injection. A membrane humidifier fed by ID water had to be installed at the anode inlet to increase reformate humidity. The humid and filtered reformate is then fed to the fuel cell; the hydrogen depleted AOG is directly sent back to the AOG combustion system situated in the reformer module.

   During start-up and shut-down of the system reformate can be sent back to the reformer combustion via a bypass valve. All components are listed in Table 4

Table **4**: Process components – Power generation

Component ID	**Description**
B13_V	FC Stack bypass valve
B14_V, B15_V	FC Stack shut off valve
BW4	Reformate humidifier
BF2	Reformate filter

3. **Main AOG combustion inside the reactor combustion tube bundle & post combustion**

At the standard stoichiometry settings during normal operation (λ_{H2} of 1.4) the off gas from the FC anode still contains ~20vol% of hydrogen. The majority of this combustion gas is mixed with combustion air and sent to the catalytic combustion tube bundle inside the reactor. The Pt catalyst pellets lodged in these tubes burn the gas mixture, the released heat is transferred to the FA decomposition catalyst solution. In case of incomplete H_2 conversion in the tube bundle a catalytic post combustion step (metallic corrugated monolith, SüdChemie) is installed between tube bundle outlet and off-gas stack. Combustion temperatures are monitored at critical positions in the system to ensure functionality of the system. All components are listed in Table 5.

Table **5**: Process components – Main AOG combustion

Component ID	**Description**
R09_V	Main combustion shut-off valve, NC
R06_V, R10_V	Bypass combustion shut-off valve, NO
R50_S	Combustion air MFC
R100_V	Bypass combustion split adaptation needle valve
R26_E	Combustion gas static mixer
R25_E	Flame arrestor
R42_E	Catalytic post-combustion reactor

4. **Bypass AOG combustion**
10-20% of the overall AOG flow is split off from the main combustion line at the AOG outlet. The split ratio is fixed manually by a needle valve. This is necessary to fine tune the reactor's energy balance to push the equilibrium reactor pressure to the correct range. The split flow is mixed with air and sent to a catalytic bypass combustion unit (metallic corrugated monolith, SüdChemie). Combustion temperatures are monitored inside the catalytic bed (one monolith channel) and at the bed outlet. All components are listed in Table 6:

Table **6**: Process components – Bypass AOG combustion

Component ID	**Description**
R65_S, R14_V	Combustion Air MFM & proportional valve
R37_E	Bypass combustion gas static mixer
R38_E	Bypass flame arrestor
R40_E	Bypass Catalytic combustion reactor

5. **Formic acid feed**
The formic acid feed system comprises a formic acid reservoir with low and high level switch, manual and automatic shut off valves, a high-pressure membrane pump with a corrosion resistant turbine flow meter installed on the pump's suction side. A corrosion resistant check valve is installed between feed pump and FA dispersion tube to avoid catalyst back flow into the FA reservoir. All components are listed in Table 7:

Table **7**: Process components – Formic acid feed

Component ID	**Description**
R21_E	FA reservoir
R05_V	Manual FA feed shut-off valve
R13_V	Automatic FA shut-off valve
R64_E	Turbine FA flow meter
R23_E	FA feed pump
R67_S	FA feed over-pressure sensor
R03_V	FA feed check valve

6. **Cooling system**
Fuel cell and reformer share a common cooling system, supplying both the FC stack and the reformate cooler. Cooling water flow to both systems is maintained by two separate pumps, a

finned tube radiator with ventilation to the outside of the unit is used as common heat sink. All components are listed in

Table **8**: Process components – Cooling system

Component ID	**Description**
B51_M, B53_M	Cooling water pumps FC/reformer unit
BW3	Heat sink; forced convection finned tube radiator

4.8 Unit commissioning / initial characterization & testing

Following assembly of the combined HyForm-FC unit, the installation of the process control electronics built by Inhouse Engineering and the wiring of all valves and instruments, commissioning of the system started with tests of all subsystems and electrical components, to be followed by full system tests.

Full commissioning of the combined unit ran into unexpected technical problems that prevented the system from being tested and optimized. A number of issues were identified that need to be addressed before the full functionality of the system can be tested/achieved:

1. **Formic acid feed flow control**
   First tests of the FA feed flow assembly showed that the installed turbine flow meter does not generate stable output signals even at constant pump speeds against ambient pressure. On a signal curve recorded during a calibration run at 20% pump speed using water as calibration fluid, we observed that the signal fluctuates more that ±25% around the average value, making the measurement system unsuitable for the precise measurement need for reformate flow control.
2. **Reaction pressure control (control valve R01_V)**
   The central control valve R01_V electronics were damaged. Repairs were organized immediately. With this component missing, tests of the reformer/reactor could not be effected; tests of the overall functionality and process control concept were not possible.
3. **Main AOG combustion**
   The main AOG combustion system was tested using artificial combustion gas mix. As expected, a temperature increase inside the main reactor volume was observed, indicating combustion and heat production inside the main AOG combustion tubes. However, important amounts of hydrogen were detected in the off-gas vent, a clear indication for incomplete combustion.
   Contrary to expectations, the temperature inside the post-combustion catalyst during these tests did not show the increase normally associated with incomplete combustion in the main combustion system, i.e. gas feeds containing hydrogen/air mixtures.
4. **Bypass combustion**
   The bypass combustion system was tested using a synthetic AOG mix containing 10vol% H_2. Even at a high air to fuel ratio of 2.2 the mixture ignited. The ignition event is especially interesting as the theoretical adiabatic temperature rise of the tested combustion mixture was estimated at 280K – not enough to cause ignition of even stoichiometric hydrogen/air mixtures. This indicates insufficient mixing of the combustion gas, causing local hydrogen concentration peaks reaching ignition temperatures inside the combustion monolith.

Despite these issues, a number of subsystem tests were carried out successfully, all control functions not affected by the technical issues were characterized and optimized.

5 Discussion / appraisal of the results / findings

The successful initial tests combining the fuel cell with an external HyForm reformer (see 4.2) confirmed that the basic concept tested in this project is sound: The HyForm reformate is a suitable feed for direct use in a PEM fuel cell and does not cause fuel cell deterioration over the tested time on stream.

The comparatively low hydrogen concentration of the reformate gas makes it necessary to operate the fuel cell at considerable hydrogen excess (minimum λ_{H2} of 1.4 recommended by the FC manufacturer).

Experimental results from preliminary single tube tests show that the FC anode off gas can successfully be burned over a commercial combustion catalyst to supply heat to the reformer/reactor. The optimized catalyst concentration profile avoids overheating and ignition over a wide range of hydrogen concentrations, making AOG combustion a viable and highly efficient replacement for electrical heating.

Tests with the fully assembled system did not run satisfactorily or were prevented by technical issues: The approach to formic acid feed control needs to be modified, either by replacing the flow measurement with a more accurate system or by changing the reformate flow control system.

The issues identified during the combustion tests that could be performed could partly be explained, but clearly need some more dedicated experimental work to fully understand the observed behavior.

6 Conclusions, outlook, next steps after closure of the project

As the prototype activity ended in the laboratory, GRT Group SA is setting up a project and related financing to finalize properly the startup and test phase.

If confirmed by successful tests, the project opens the route to a product development for 5-10 kWe range stationary units, for off-grid and back-up power applications.

7 References (if applicable)

[1] "*A Viable Hydrogen-Storage System Based On Selective Formic Acid Decomposition with a Ruthenium Catalyst",* C. Fellay, P. J. Dyson, G. Laurenczy*, *Angew. Chem. Int. Ed*., **2008**, *47*, 3966.
[2] "*Efficient Dehydrogenation of Formic Acid Using an Iron Catalyst"* A. Boddien, D. Mellmann, F. Gaertner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy*, R. Ludwig*, M. Beller*, *Science,* **2011**, 333, 1733.
[3] "*Formic acid as hydrogen source – recent developments and future trends*", M. Grasemann, G. Laurenczy*, *Energy Environ. Sci.,* **2012**, 5, 8171.
[4] *"Hydrogen storage: beyond conventional methods",* A. Dalebrook, W. Gan, M. Grasemann, S. Moret, G. Laurenczy*, *Chem. Comm*., **2013,** *49*, 8735.
[5] *"A Well-Defined Iron Catalyst for the Reduction of Bicarbonates and Carbon Dioxide to Formates, Alkyl Formates, and Formamides",* C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy*, M. Beller*; *Angew. Chem. Int. Ed.,* **2010**, *49*, 9777.
[6] *"Direct Synthesis of Formic Acid from Carbon Dioxide by Hydrogenation in Acidic Media"*, S. Moret, P. J. Dyson, G. Laurenczy*, *Nature Communications,* **2014,** *5,* 4017; *doi: 10.1038/ncomms5017.*

8 Appendix: Flow diagram of the combined HyForm –FC unit

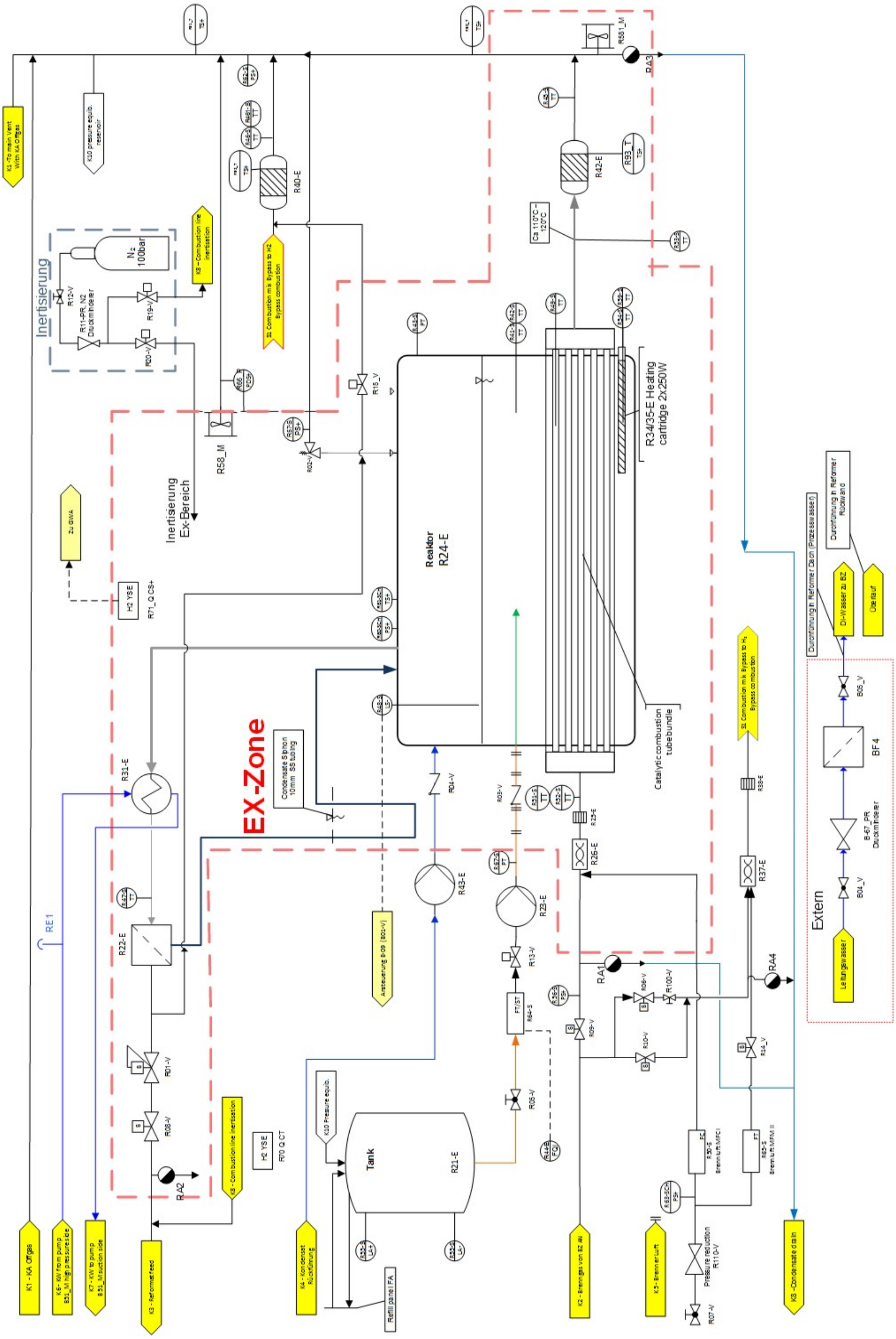

Figure A 1 Flow diagram of the HyForm reformer unit

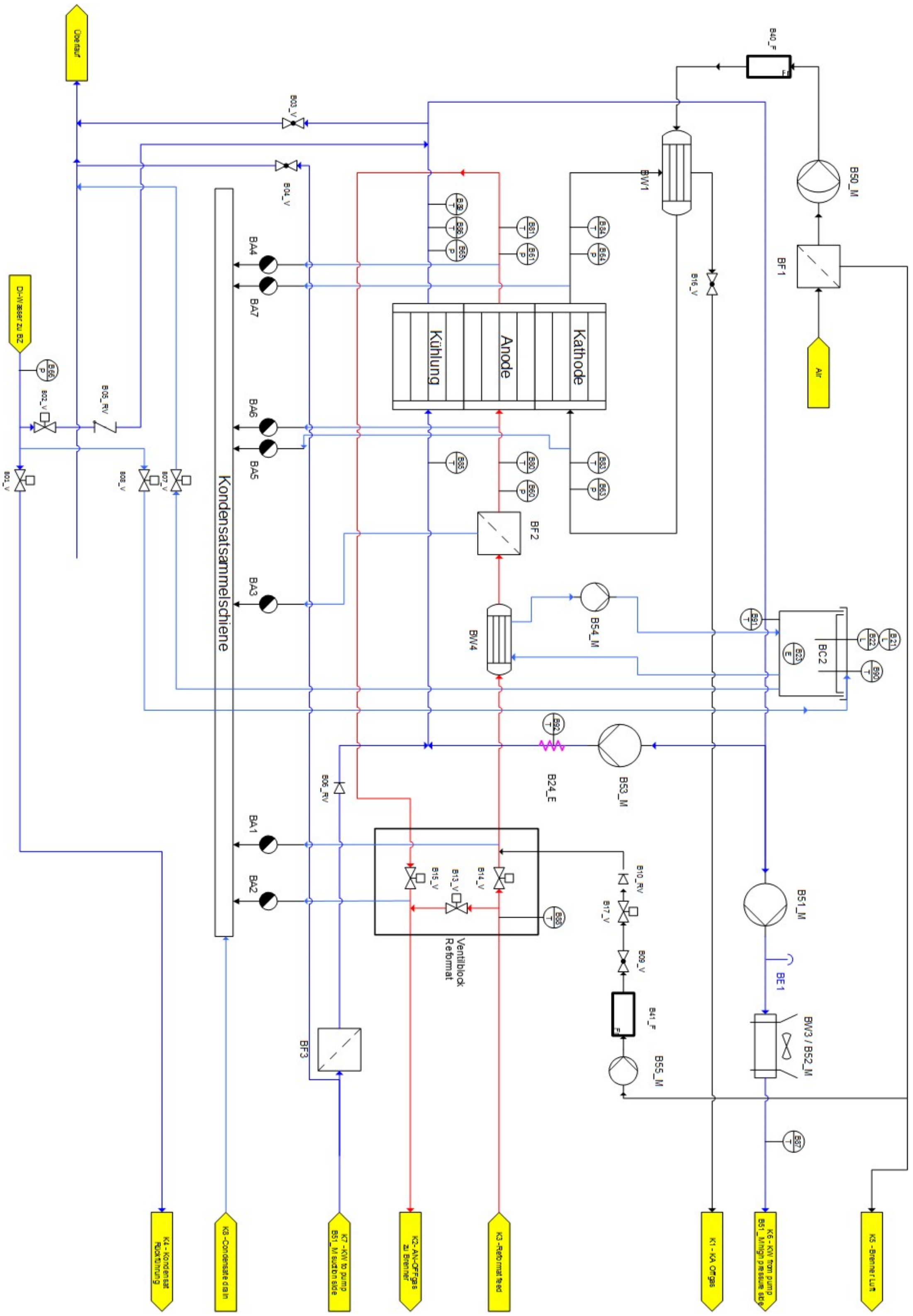

Figure A 2 Flow diagram of the FC unit