Friedrich-Alexander-Universität
Technische Fakultät

Design of a formic acid production plant

Executive Summary

CBI Project Course Fall 2021

Partner: BASF SE

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Partner and task

The industrial partner of the project planning course in autumn 2021 was *BASF SE*, an international acting chemistry company. The task for this project planning course provided by *BASF SE* is to develop a new plant to produce formic acid while gaining the substrates methanol and carbon monoxide environmentally friendly from biogas. The reaction sequence of the process can be seen below and consists of two steps. The first step (1) is the carbonylation of methanol with carbon monoxide to methyl formate. Methyl formate is then hydrolysed to formic acid and methanol (2).

$$CH_3OH + CO \longrightarrow CH_3OCOH \qquad (1)$$

$$CH_3OCOH + H_2O \rightleftharpoons HCOOH + CH_3OH \qquad (2)$$

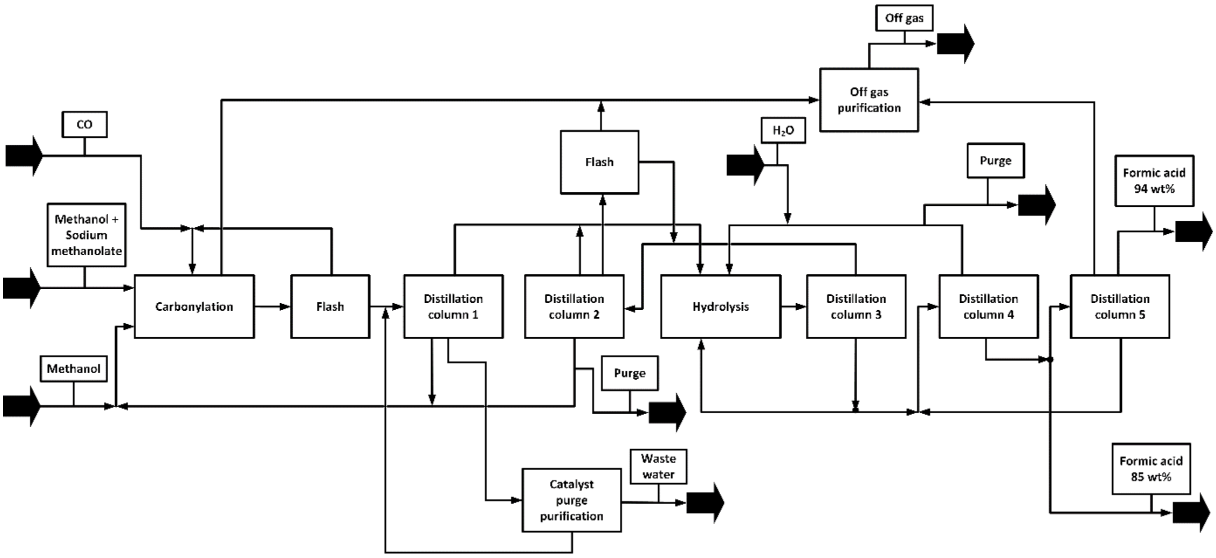
$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$CO + H_2O \rightleftharpoons HCOOH$$

The goal of the process is to yield 50,000 t a^{-1} of formic acid, consisting of 25,000 t a^{-1} 85 wt% formic acid and 25,000 t a^{-1} of 94 wt% formic acid.

Results

The groups of the project planning course solved the project task to design the process as shown in the **block flowchart**. The reactants carbon monoxide, methanol, and the catalyst sodium methanolate react in the carbonylation reactor. Afterwards, carbon monoxide is regained in the first flash and the reaction mixture is separated in distillation column 1. The methyl formate rich phase then reacts with water in the hydrolysis reactor. Through consecutive distillation steps, the mixture containing formic acid is separated and purified so that the product can be collected in the two concentrations 85 wt% and 94 wt%. All off-gas and wastewater are treated in respective purification units.



For methanol supply, methane obtained from a biogas plant is to be used as the starting material to **synthesize methanol enzymatically**. This can be done with the aid of soluble methane monooxygenase (sMMO), an enzyme found in methanotrophic bacteria. In addition to this enzymatic synthesis of methanol, the direct **fermentation of methane to formate** by methanotrophic bacteria was also investigated. In addition to methane, oxygen and NADH are consumed in stoichiometric ratios. Unlike in whole cells, NADH cannot be regenerated during the isolated enzymatic conversion. However, since NADH is a very valuable coenzyme, continuous addition is out of the question from an economic point of view. Therefore, it must be regenerated within the process itself. So far, the only industrial feasible method for this is a second enzymatic conversion, using secondary enzymes, e.g. glucose dehydrogenase (GDH) or formate dehydrogenase (FDH). These regenerate NAD+ to form NADH again. This can only be done by providing a secondary substrate. In addition to the investment costs for the process itself, the **NADH regeneration results in additional costs** that make an economically feasible application for the synthesis of methanol impossible. Furthermore, the bioconversion of methane to methanol has so far only been realized on a laboratory scale with low conversion rates and therefore must be optimized for industrial usage. The direct fermentation of methane to formate with **methanotrophic organisms** is also difficult to achieve, since these organisms generally **have a very slow growth rate** and a large portion of the supplied energy, in the form of methane, is required for the accumulation of cell mass. This results in a very low yield of formate in relation to the methane used. Due to these problems, it was decided not to include the enzymatic conversion of methane to methanol in the overall process. Instead, the **methanol will be obtained from an external source**.

For the second substrate, possible process for the **sustainable production of carbon monoxide** from biogas were evaluated, including steam reforming, partial oxidation, electrochemical carbon dioxide reduction and dry reforming. Based on the given conditions **dry reforming** presents a suitable way to obtain carbon monoxide from biogas. Considering dry reforming is an endothermic reaction, set reaction conditions are a temperature of 900 °C and a pressure of 20 bar. First, biogas is compressed, then pre-heated and fed into a tubular bundle reactor. Downstream processing of the obtained product mixture comprises cooling and subsequent hydrogen separation via membrane process. The collected hydrogen provides, combined with an external energy source, the heat required for the reaction. In addition to that the selected catalyst *BASF SynspireTM*, with nickel-oxide as an active component, is suited for catalyzing the dry reforming reaction. Further on, a Langmuir-Hinshelwood mechanism is proposed to model the reaction with regards to catalytic activity and deactivation as well as all occurring side reactions. The biogas stream made available is capable of **covering about 1.5 % of the carbon monoxide demand** of 3924 kg h^{-1} for formic acid production. Two more biogas volume flows have been analyzed more in detail. On the one hand the full usage of the adjoining biogas plant, producing about 22 % of the needed carbon monoxide. On the other hand, identifying the amount of biogas required to cover the complete carbon monoxide demand. For each instance a conceptual reactor design, based on tubular bundle reactors, was developed. Moreover, the variable costs consisting of reactants, different heating sources and catalyst, are compared to those with externally purchased carbon monoxide. Under the given conditions, **externally purchased carbon monoxide is significantly cheaper** (approximately 21 times) in comparison to carbon monoxide produced from biogas via dry reforming.

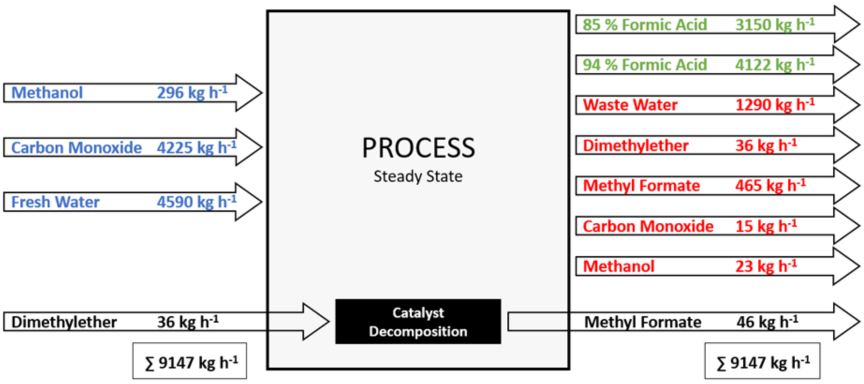
The main task of the **reactor design** is to choose suitable reactors, in which the overall reaction of carbon monoxide (CO) and water to formic acid (FA) can take place. The **carbonylation reactor is a continuous stirred tank reactor** (CSTR) with a height-diameter ratio (h:d) of at least 2.2:1. The purpose of the chosen h:d ratio is to enable the carbon monoxide bubbles a longer path in the reactor, thus maximizing the matter transport. As reaction conditions, $p = 45$ bar and $T = 90$ °C are chosen. Sodium methoxide as catalyst (0.4 mol l^{-1}) and suitable reaction kinetics were found in literature. For the **hydrolysis step, a plug flow tubular reactor** (PFTR) is used. The reason for that is to prevent the back mixing of FA, which can trigger an unfavorable equilibrium state. The kinetic data used was taken from literature as well. The catalyst ratio compared to MF is set to 1:10 (FA:MF) at the reactor inlet. Temperature and pressure are set to be 90 °C and 20 bar. These reactors were simulated with help of ASPEN plus in order to **solve the mass and energy balances**. The results obtained from the simulations showed conversion rates of 70 % relative to CO per single pass for the carbonylation reaction and 42 % relative to methyl formate (MF) per single pass for the hydrolysis reaction, which corresponds to the values found in the literature. The simulations had to be adjusted several times, to fit the substrate streams and the product streams with the values provided by the thermal separation group. The modelled CSTR has a reaction volume of 17.4 m^3 and the PFTR reactor has a length of 10 m and a diameter of 0.5 m. The **energy balances** were also solved via simulation, the carbonylation reaction will set free 1044 kW, which can be consumed in the hydrolysis reaction, which will take up 605 kW.

The **separations for the whole process** can be categorized into two parts. The first separation takes place right after the carbonylation reactor. The **CO is separated in a flash unit**, where the pressure is lowered from 45 bars to 4 bars. This leads to vaporization of the CO. **Separation of methyl formate (MF) and methanol (MeOH)** requires a distillation column. This column (D-1) runs at a pressure of 2 bars since the vapor-liquid-equilibrium allows an easier separation at this pressure level. The achieved head concentration of methyl formate after D-1 is 92.6 wt%, the bottom concentration of methanol is 99 wt%. **Separation of the outlet of reactor 2** happens in column D-3. Here, MF and MeOH serve as head products and water and formic acid are the bottom products. The separation of the bottom product of D-3 is more complex as water and FA form an azeotrope. Concerning the ratio of water to FA in the mixture, extraction was discarded. Therefore, a pressure swing distillation is the process of choice. In the first column, running at 3 bars, the bottom purity of FA is 85 wt% which already corresponds to one of the two desired products. The head product (99 wt% water) of D-4 can be **recycled into reactor 2**. The remaining bottom stream is transferred into column D-5. This column is operated at a pressure of 0.27 bars and reaches a head purity of 94 wt% of FA, which corresponds to the second desired product quality. With the use of two columns running at different pressures the problems associated with the azeotrope can be overcome.

In the carbonylation reactor, the **catalyst sodium methanolate** reacts in small amounts to sodium formate. Sodium formate is catalytically inactive regarding the carbonylation reaction. To prevent accumulation of the formate salt in the methanol recycle, a **liquid purge stream** is subtracted from the methanol recycle and sent to steam distillation. As soon as sodium methanolate gets in contact with water, it reacts to methanol and sodium hydroxide. All sodium components exit the column in the aqueous bottom stream. The top stream consists of methanol with only 300 ppm water.

Without sulphur, chlorine or other hazardous elements in the process, only the **emissions** of carbon monoxide, total organic carbon and total particle amount need to be controlled according to the *TA Luft*. Due to the relatively small off-gas stream, **complete thermal oxidation** was selected. It is possible to reach a 99.5% conversion of CO to CO_2 and provide heat for further processes. To inhibit particle and NO_x formation, excessive air is fed into the combustion chamber. A cyclone is used to separate out small particles. After off-gas treatment all legal thresholds are achieved.

The suggested production route of formic acid was simulated in AspenPlus. Here, the primary goals are to achieve a simulation of the core process with its desired product streams as well as the closure of recycle loops and further **optimization of the process**. The feed is represented by pure carbon monoxide and pure methanol. In the final **AspenPlus steady-state simulation**, rigorous models for the reactors (utilizing the RPLUG and RCSTR models), as well as the distillation columns (utilizing the RadFrac model), were implemented. Additionally, six out of seven recycle streams were closed completely. Although the methanol recycle stream was not closed, a theoretical value for the methanol make-up stream (based on the difference between the recycle stream and the feed stream) was determined. To close the **overall mass balance**, the group iteratively adjusted the

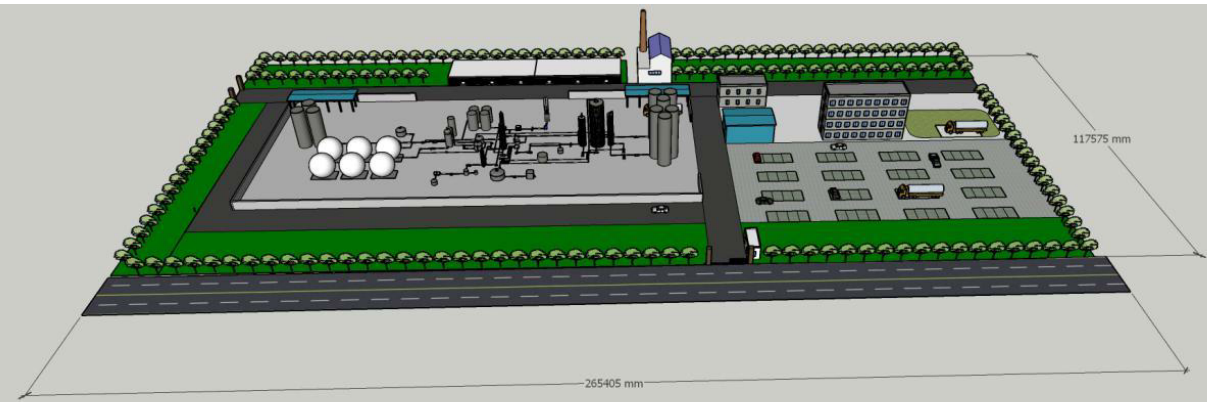


make-up stream so that the combined recycle and make-up reflected the desired value given by the feed stream, while adjusting distillation columns as deemed necessary.

The **heat management** analyzed the behavior of the heat flows and predicted the demand of the heat and cold duties. To achieve these results, the Pinch method has been used and a heat exchanger network was created to minimize the energy consumption for heating and cooling of the system. Due to the adiabatic behavior of the columns two different heat exchanger networks have been constructed, one for the columns and one considering the rest of the heat flows. As a result, the **separation columns were identified as the most significant energy consumers**, especially column D-4, which needs 22.6 MW, as both, heating and cooling duty. By connecting all possible streams, energy savings of 37.7 MW or 44.9 % have been achieved. In order to provide the heat power of 23.2 MW for the plant, it was suggested to use two heating pumps (3 MW) and two steam boilers (21 MW). During the summer heating can be powered by 5 % via photovoltaics. Additionally, the steam boilers are powered by biogas combustion during the whole year. To provide the cold utility of 24.6 MW two different cooling cycles were used, one water-cooled (0.8 MW) and one refrigerating machine (23.8 MW) cycle. Unfortunately, the high current consumption of 8.3 MW of the refrigerating machines is a major disadvantage.

The **reactors and columns** required for the carbonylation and hydrolysis reactions as well as the downstream processing of the product were individually **designed and modelled in CAD**. During the initial phase, the main components of pressure vessels such as bottoms, nozzles, various types of flanges, cylinders and several types of internals were modelled using CREO Parametric. Accurate **construction of the apparatuses** was carried out using AD-2000 and various DIN (EN) standards. For this, an overview of the subsequent calculations and relations was created in Excel. In the meantime, online and literature research had been conducted in order to find **suitable materials for construction** of the different components. This was done in close cooperation with the group pipes and pumps. Formic acid is a highly corrosive substance, whereas the severity of corrosion increases at higher temperatures. Considering this, four different types of materials were shortlisted: stainless steels, enamel coatings, PTFE and nickel alloys. However, the last two materials were excluded due to high costs and weaknesses in workability and pressure sensitivity, as well as limiting corrosion resistance at higher temperatures. Since enamel coatings can only be used to a limited extent at elevated pressures, the stainless steel 1.4462 with its high mechanical stability was chosen for both reactors, since they are operating at pressures of 45 bar and 20 bar. Furthermore, this steel shows very good corrosion resistance at the specific reaction conditions. Due to the relatively low price and the widespread use of this stainless steel in the chemical industry, it was also chosen for columns D-1 and D-2, where formic acid may be present at very small concentrations only. Columns D-3, D-4 and D-5 separate and concentrate the formed product, thus operating at a wide range of temperatures and formic acid concentrations. The base material for these columns is the less expensive common steel P265, which is being coated with an enamel layer, giving it excellent corrosion resistance over the entire range of operating conditions. Once the reactor and separation column designs had been determined, the apparatuses were modelled in more detail using the excel sheets and parametrized components, also considering limiting factors such as the mass transfer between gaseous carbon monoxide and liquid methanol in the carbonylation reactor. Based on this, an **estimation of steel masses** was conducted, and the **power input for the agitator** was calculated. Finally, assemblies of the two reactors and the three different types of columns (tunnel trays, random packings and enamel coated column with structured packings) were created in CREO Parametric.

The **installation plan** was visualized using the drawing software SketchUp Pro 2020, taking real size of the equipment and minimum **safety distances** between apparatuses into account. The overall plan of the site is based on the location and the flow chart of the entire process, only excluding the possible connections of heat exchangers using the pinch method of the heat management. The **piping** arrangements are effectively established and the calculation of pipe lengths and potential pipe geometries is made possible.



The most critical component for **piping material selection** was formic acid, since it is highly corrosive, even more so if it is boiling. The selected materials were PE-100 for pipes with fresh and waste water, PTFE for seals and pumps, carbon steel P235TR2 for CO pipes, stainless steel 1.4462 for piping with low formic acid concentrations and 1.4539 for higher concentrations. **Pumps and compressors** as well as one vacuum pump were selected with the criteria of pressure difference, volume flow, viscosity, and operating conditions as specified above. Most pumps are self-priming centrifugal pumps, which enable an easier starting procedure. Only in front of the reactors, where high pressures are required, eccentric screw pumps were selected, because these are able to fulfill the tasks of high-volume flow and high pressure difference.

The **development of an automation concept** for all plant components included the consideration of temporal dependencies at interfaces between different individual components and applications and the formulation of a first **concept for the start-up and shut-down** of the plant. Furthermore, an outlook on early fault detection via sensors and changes in manipulated variables is given. When considering automation, it is important to set stable operating points safely and quickly by means of correct regulation and control equipment. For this purpose, the most important control variables to be set as well as the associated manipulated variables and measuring points are identified and control loops or controllers for setting the required variables such as pressure, temperature, concentration, or flow rate are defined. The associated information is then entered into a Piping and Instrumentation Diagram (P&ID). This procedure allows plant operation to approach the respective variables to be set and to set up stable operation.

A local sewage plant and a biogas plant are located in the immediate vicinity of the planned production site. According to 4. BImSchG (*Bundes-Immissionsschutzgesetz*) the **plant is classified** as a plant for the production of oxygenated hydrocarbons. While the **approval procedure** of such a plant generally takes two to four years the costs depend on the total building costs of the plant. Important documents to be submitted in advance include a baseline condition report (AZB) and an environmental impact assessment (UVP). Additional reports have to be confirmed with the local authorities. To store the reactants and the product formic acid (85 wt% and 94 wt%) **safety measures** regarding the storage tanks have to be fulfilled. Methanol and formic acid are hazardous substances that must be handled according to the GefStoffV. Delivery and collection respectively are to be organized on a weekly schedule. Both substances are considered water polluting and must be stored according to the technical rule for stationary containers of hazardous substances, TRGS 509. Carbon monoxide (CO) must be delivered daily by train (GGVSEB, ADR/RID) to cover the consumption by the process plant. It is to be transported in tank wagons at 25 bars. To allow for CO availability during the change of trains, the necessary amount for 12 hours is stored in additional storage tanks (TRGS 746 for stationary compressed gas tanks). Long-time storage concepts proofed as disadvantageous due to CO still being gaseous at pressures up to 200 bar, complicating storage for larger volumes as required here. To prevent danger for life, health, and environment according to 12. BImSchV the **possible malfunctions** in the process plant had to be accounted for. In the scope of this course, only the most fatal malfunctions are highlighted, e.g. rising pressure inside a reactor or a defect heat supply of the columns. To guarantee the safety of the process plant a **safety concept** must be developed. The priority in this concept has to be occupational safety e.g. comply with AGW. Further aspects to be considered are periodic maintenance, checking of safety-relevant parts and training of personnel (12. BImSchV § 6). Fire protection e.g. fire extinguishing equipment, structural fire protection (12.

BImSchV § 4) and alarm and emergency plans (12. BImSchV §§ 6, 10, Anhang IV) are also part of the concept. The **wastewater treatment concept** features neutralization of the process wastewater with sulfuric acid and subsequent biological treatment. The neutralized wastewater stream is fed into a single biological treatment step together with the concentrated saltwater stream of the freshwater desalination. The resulting drain water is then discharged into the public sewage system while the emerging biological slurry can be delivered as a value product to the local biogas plant or other consumers.

The **total plant costs** are derived by summarizing the investments and the total operating costs. The investments are split into **direct and indirect investments**, with the indirect investments depending on the direct investments. The operating costs are divided into **variable and fixed operating costs**, the former depending on the production volume and the latter on the direct investments. Direct investments are estimated using the Hand-factor method, in which the equipment costs are multiplied by various factors depending on the equipment class. Both the indirect investments and the fixed operating costs were determined using cost factors that were multiplied by the direct investments. The **total investments** amount to a total of **168.2 million Euros** and the **total operating costs** to a total of **51.2 million Euros per year**. Presuming the selling price regarding 85% and 94% formic acid of 550 Euros and 1526 Euros, respectively, these **annual revenues** sum up to a total of **64.2 million Euros**. With these sales figures, the resulting **amortization period is 11.5 years**.

Direct investment costs			
Type of main cost unit	Heat management	Storage tanks	Thermal separation
Main cost unit / %	32.6	30.0	27.2
Variable operating costs			
Type of main cost unit	Energy costs	Fire department	Raw material
Main cost unit / %	40.1	9.3	5.2

To optimize the amortization period, the main cost units should be considered. One possibility would be changing the location of the plant construction. At a location with suitable infrastructure, this could have the investments decline to 132.6 million Euros and the operating costs decline to 39.9 million Euros due to the decrease in storage tank costs as well as the elimination of both the plant fire department and the train transport costs of carbon monoxide. Therefore, changing the location to a more suitable one could lead to a **shortened amortization period of 5.5 years**.

Conclusion

From an economic and technical point of view, the green production of carbon monoxide and methanol is not feasible nor target-oriented. Therefore, these two processes were excluded from the rest of the project and the necessary amount of carbon monoxide and methanol has to be purchased from external sources. An additional obstacle following the decision of purchasing carbon monoxide and methanol is the procurement and storage of the large quantities of carbon monoxide necessary to produce the given amounts of formic acid. This problem was overcome for the anticipated location with the help of daily deliveries via train. However, it could also be circumvented by relocating the plant near a facility that produces large quantities of carbon monoxide, which could then be fed directly into the process plant. To design an even more economical process, further improvements would be necessary regarding the integration and coupling of heat streams in the heat management sector, which is the biggest cost sector at the moment.

Literature

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