FRIEDRICH-ALEXANDER
UNIVERSITÄT
ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT

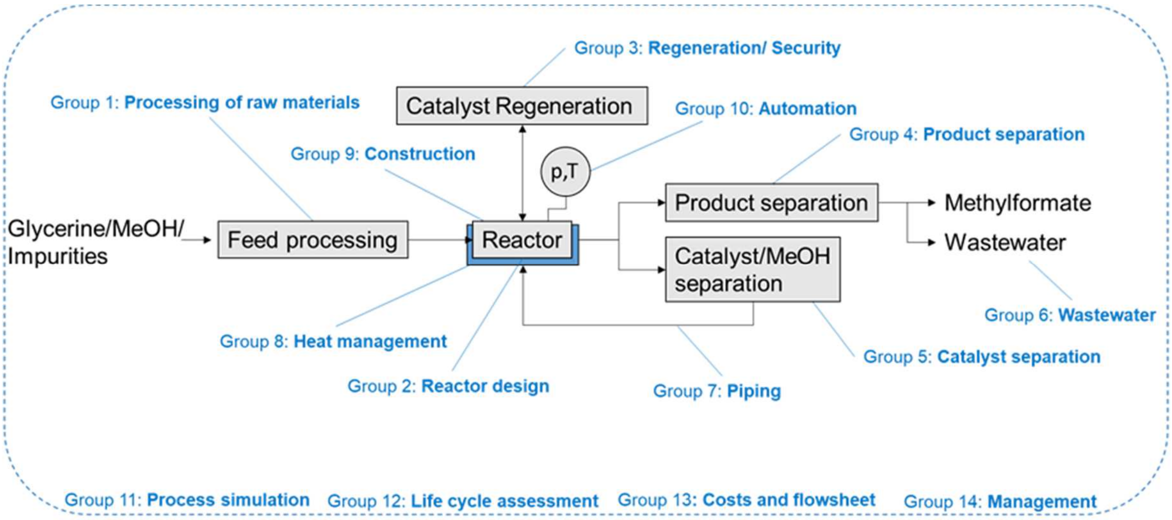
Production of methyl formate using renewable resources

CBI Project Course Spring 2021

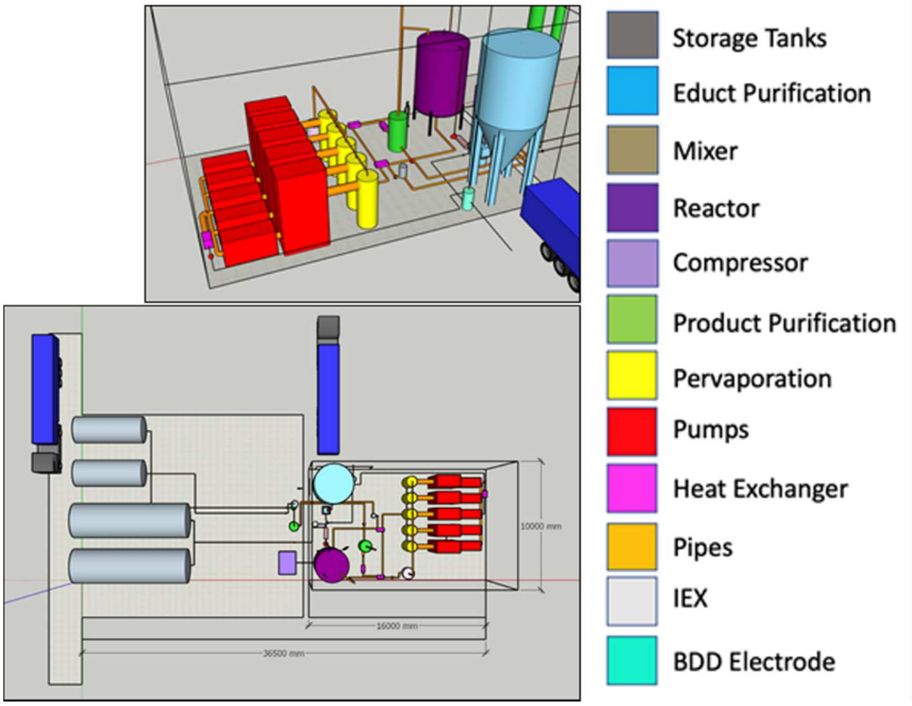
OxFA GmbH, Scheßlitz

www.crt.cbi.uni-erlangen.de

Currently, OxFA is the only company in the world that produces formic acid (HCOOH) sustainably and selectively from biomass. In the innovative OxFA process, renewable raw materials and biogenic residues can be converted into valuable, green chemicals. The central building block of the process and the OxFA technology is a homogeneous polyoxometalate (POM) catalyst, which allows the selective oxidation of biomass in aqueous media. The catalyst is regenerated by the addition of oxygen or air. In the established OxFA process, water was used as the solvent for the catalyst. In aqueous phase undesirable CO_2 is formed, reducing the carbon efficiency of the overall process. However, recent studies have shown that by using methanol (MeOH) as a solvent, the conversion of biomass is now complete to formic acid methyl ester (HCOOMe). This results in a significantly improved C-balance. However, the use of methanol poses a problem for a possible scaling up of the process. Explosive mixtures can form, especially during regeneration of the catalyst. Furthermore, the handling of larger quantities of methanol is much more critical from a safety point of view than with water. Hence, the aim of the project planning course was to design an appropriate process.



The **raw material processing** is crucial to ensure the accurate supply of the reactor feed regarding the required amount and composition. The raw materials used in this process are crude glycerol from biodiesel production and methanol. The crude glycerol consists of 66.8 wt% glycerol, 22.6 wt% water, 5.5 wt% ash (potassium sulfate) and 5.1 wt% MONG (Matter organic non glycerol). The MONG with a composition of fatty acids, di- and monoglycerides, methanol, glycols, glycerol ethers (with methanol) was assumed to be stearic acid for the calculations. Every 12 days 30,000 kg crude glycerol is delivered and stored in a tank with a capacity of 45,000 kg. Using the solubility of the constituents, it was calculated that more than half of the potassium sulfate must be present as a precipitated solid in the glycerol-water mixture. Therefore, the storage tank was designed in the form of a cone with a settling area in order to partly remove precipitated potassium sulfate prior to any purification step. To remove any solid potassium sulfate that has not settled in the storage tank, a microfiltration step was implemented. This microfiltration is carried out using ceramic membranes in the crossflow process scheme. Since the water content has a negative effect on the following catalyzed reaction, it must be reduced to less than 2.5 wt%. Accordingly, it was decided to use a vacuum distillation after the filtration step. The polymerization temperature of glycerol of 200 °C sets the temperature limit of the distillation. The column was designed with three trays, an applied pressure of 0.4 bar, 171 °C at the sump and 74 °C at the head. A mixture of water and methanol is drawn off at the head. The glycerol and MONG remain in the sump with a residual water content of 2.3 wt%. The bottom product is then pumped to a mixer where the purified glycerol is mixed with fresh methanol and 98 % sulfuric acid to adjust the pH to 1-2. This mixture is then compressed to 40 bar and fed into the subsequent reactor.



For the **reactor design**, a mechanism for the reaction of glycerol to methyl formate was postulated, assuming that glycerol is converted to formaldehyde, then to formic acid and finally to methyl formate. These assumptions are based on the reaction pathway from glucose to formic acid. Most likely, the rate-determining step is the conversion of formaldehyde to formic acid. As a side reaction, only the conversion of methanol to dimethoxymethane (DMM) and dimethyl ether (DME) takes place. In this process it is assumed, that 5 mol% of the methanol in the reactor is converted to DMM and DME. The fraction is subsequently composed of 56.8 % DMM and 43.2 % DME based on a typical product distribution. Based on the postulated reaction path, a kinetic model for the conversion of sucrose in aqueous solvent was adapted to the conversion of glycerol in methanol by two coefficients. The first coefficient is the substrate factor, which includes the change from glucose to glycerol. On the other hand, the solvent factor, which describes the change from the solvent water to the solvent methanol, is added to the kinetics equation.

The **reaction conditions** were chosen equivalent to the best conditions reported in literature (*dissertations of D. Voß and C. Kumpidet, both FAU*). In the previously conducted experiments of glucose in water and glucose in methanol, it was shown that 90 °C, 8 bar oxygen partial pressure and a pH of 2 are the optimal reaction conditions. Due to safety-related conditions, the 8 bar oxygen partial pressure is realized via a 40 bar air flow. This results in a total air flow of 13 m^3/h. Based on the quantity of methyl formate to be produced per year, a reaction volume can now be determined in conjunction with the kinetics. The residence time is set to 1 hour. A liquid-phase volume of 13.06 m^3 is calculated. However, since some gaseous oxygen is necessary for catalyst regeneration, the reactor is a biphasic system. To determine the total **reaction volume** based on the liquid-phase volume, a liquid hold up must be calculated. The liquid holdup is 0.82 and therefore the total reactor volume is 15.88 m^3. Based on DIN 28136-1, a reactor with a total volume of 17.5 m^3 was designed. Next, the enthalpy is determined using the standard enthalpies at 20°C and adjusted to the temperature of 90°C. This gives a reaction enthalpy of -951.87 kJ/mol, which equals 204 kW reaction heat. Noteworthy, this amount can be removed by a combined convective (recycling) flow and a tailored cooling jacket to ensure safe reactor operation.

For **safe operation** of the total chemical plant, several safety considerations have to be taken into account to protect health, the environment and the financial investments. In addition to this, a multitude of legal guidelines must be followed in order to get an official permission to operate this plant. First suggestions can be taken out of safety data sheets regarding the species of methanol, formic acid, methyl formate and dimethoxymethane. Especially methanol and methyl format are important due to the significant amounts present in the process. The safety guidelines concern in particular the explosion limit, explosion pressure and ignition temperature in addition to health and safety measures. The reactant stream itself is not dangerous. The **regeneration of the catalyst** takes place in situ with compressed air with a gas inlet stirrer at 40 bar pressure. Due to the high solubility of oxygen in methanol and the high dilution of the catalyst, the catalyst can be re-oxidized at all times during the reaction, especially since lab-size experiments have shown that oxygen transfer through the surface is sufficient. To avoid an explosive atmosphere, during start-up and shut-down the reactor has to be inertized with nitrogen. Inertization is redundant during the running process, as the catalyst is depleting the oxygen fraction of the incoming airstream, which prevents the formation of an explosive atmosphere. The term explosion protection refers to protection against explosion hazards caused by explosive atmospheres. Effective explosion protection prevents damage to people, machinery, and equipment. For explosion protection, there are the *ATEX* guidelines and these only apply to atmospheric conditions. *The Technical Rules for Industrial Safety* (TRBS) concretize the Industrial Safety Regulation. In addition, the *Technical Rules for Hazardous Substances* (TRGS) and the German statutory accident insurance VBG and DGUV guidelines must be observed. The process is monitored by temperature, pressure, filling level control and EX-sensors outside the reactor. In addition, all devices, pumps, and pipelines must be grounded. In case of an emergency, the reactor is shut down by cooling and inerting. As a chemical is produced in large quantities and exceeds a certain amount of product per year, the products must be registered under *REACH*. For the **storage of methanol and methyl formate** double walled tanks with leak indicators could be used. The tanks can be grouped together, when the minimum distance between them is 0.3 times the diameter but at least 1 m. The closest proximity to nearby buildings must be at least 10 m, respectively five meters to filling stations. If less space is available, there may be deviations possible regarding TRGS 509. All tanks with flammable contents must be protected against lightning and need a level indicator for minimum and maximum level. Furthermore, ventilation during filling is necessary. Sulfuric acid and nitric acid can be stored together in a vented lockable hazardous materials cabinet, as they are in compatible storage classes according to TRGS 510. Since the educt is no hazardous substance, it can be stored in a simple silo. Another aspect is the personal protective equipment (PPE), which has to be provided by the employer. Before use, it is important for the employees to undergo an instruction. When working in a potentially explosive area, the floor should be static dissipative. The essential gear for workers consists of static dissipative shoes, protective coat, conductive gloves, and safety glasses and, if needed, an industrial helmet protection. The PPE must be CE-certified and should be maintained and checked on a regular base. In case of an emergency, the evacuation plan comes in handy. It defines on how to act in the event of imminent danger so that people can leave in a safe and structured manner without anyone being harmed. It contains elements such as the building layout, assembly points, possible escape routes, location of first aid facilities and fire protection facilities.

Product separation is the key step to isolate a desired product at a certain purity from a composition. Thereby it is important to reduce the losses of the desired product in the separation steps as much as possible. Beside the desired product, further potentially valuable byproducts can be isolated and sold to improve the economic potential of a process. In this process, the starting feed stream for the product separation was a liquid phase from the reactor with a temperature of 90 °C and a pressure of 40 bar. The liquid phase consists of methanol, methyl formate, water, dimethyl ether, dimethoxymethane, nitrogen, formaldehyde and oxygen. Thereby, methanol is present in a significant surplus. The liquid is throttled to 1 bar and cooled to 30°C before being pumped in a phase separator. Under the acquired conditions methyl formate primarily remains in the liquid phase while nitrogen and dimethyl ether volatilize predominantly into the vapor phase. Although this vapor phase contains 5% of methyl formate, it was treated as waste gas. Possible techniques to recover methyl formate from the vapor phase as absorption and membrane separation were investigated. Both could be applied to separate nitrogen from the organic compounds. However, the separation of methyl formate and dimethyl ether would require further separation processes, which would make this recovery economically not feasible. The next separation step for the liquid phase is a distillation unit. The feed is induced with 30°C and 1 bar into a column with a temperature of 39°C on top and 65°C on bottom. Under the column temperature, methyl formate is present in gaseous form and can be recovered together with dimethoxymethane and remaining gaseous methanol at the head of the distillation column. The bottom product of this step consists mainly of methanol, water and reduced catalyst. This liquid phase will be further processed to separate this ternary system and enable the recycling of methanol and catalyst. The gaseous phase of the first column is processed again in a second distillation. This stream mainly consists of methyl formate and dimethoxymethane and a considerable amount of gaseous methanol. The second distillation column has a top temperature of 32°C and a bottom temperature of 43°C. With these operational conditions, the emerging gas phase on the top of the column consists of 97% methyl formate and a small amount of dimethoxymethane. The liquid bottom phase consists of dimethoxymethane and methanol in a 2:1 ratio and a small amount of methyl formate. Since dimethoxymethane is a valuable product, and the contained methanol can be recycled, it should be further considered to process the bottom phase to improve the economic potential of the whole process. Along all separation steps, the total loss of methyl formate is around of 10%. The phase separation accounts for 5% of the loss. It is estimated that the recovery of the product from the gaseous phase is not economic, since the costs for acquisition and operation of the additional separation stages wouldn't be economically reasonable. Another 3% methyl formate is lost in the bottom stream of the second distillation. Since a further processing of that phase should be considered (to remove dimethoxymethane from methanol), an additional recovery of the desired product might be possible and thereby an increase on the economic potential of the process. The separation of methyl formate from the second column bottom product can reduce the loss to a total of 7%.

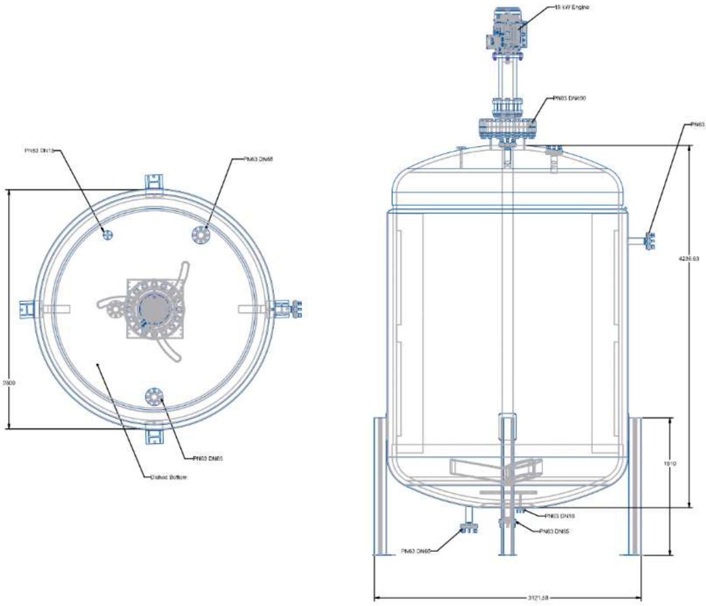
The aim was to **separate methanol and catalyst** from water and unreacted accompanying substances. This goal, however, changed as the course progressed. The new objective became the separation of water from the mass flow coming from the product separation. This is usually an organic solution that contains water. The high-mass component is described by the methanol it contains. Some by-products should also be mentioned here, but they play a minor role in terms of their mass fraction. The separation of a liquid mixture of several substances is industrially preferably carried out via a distillation or rectification column since the thermodynamics can usually be determined based on outdated vapor-liquid equilibria. For the present plant, a distillation process was simulated using the *AspenPlus* platform. Based on this, an initial evaluation discusses whether distillation appears to be useful for this separation process. Due to the significant methanol surplus in the mixture, the required energy for the separation by distillation would exceed the economic scope of the overall process. Therefore, a novel advanced membrane separation process of organic solutions, which is called pervaporation, was chosen. Pervaporation generally describes a membrane process. It is preferably used for the separation of liquid mixtures that would exhibit an azeotrope during distillation. Pervaporation following a distillation stage is a common practice in industry. It is also used in the dehydrogenation of organic solutions. The operating principle of pervaporation is essentially based on two driving forces: First, the membrane works selectively towards a polar component (hydrophilic membranes work selectively towards water). Second, the component to be permeated is evaporated via an applied vacuum, creating a partial pressure gradient from the retentate side to the back of the membrane. For this separation, pervaporation is preferred over distillation for energy efficiency reasons and will be highlighted for further procedure and to fulfil the separation task. The mass flow of the feed, which contains approx. 96 % methanol, 4 % water and a small amount of catalyst, is heated up to 70 °C and pressurized to 3 bar. Using this separation technique, it is possible to achieve almost complete water separation. In addition, in cooperation with the pumps and piping group, a vacuum pump is selected that is suitable for this application. From the calculations of the membrane fluxes, the membrane area required to carry out the pervaporation is determined. All these assumptions and calculations are based on a publication by E. Haaz and A.J. Toth. In collaboration with DeltaMem AG, it is decided that the DeltaMem PERVAP™4510 is found to be suitable.

The **treatment of the wastewater streams**, which are contaminated mainly with methanol and glycerol, is mandatory. The calculation of the BOD value, which indicates the amount of oxygen consumed to aerobically degrade organic materials, resulted in a value of approximately 43 g/l, which is above the limit of 20 mg/l specified in the Wastewater Discharge Act §3. This means that direct discharge into surface water is prohibited and indirect discharge into the local sewage treatment plant or in-house treatment is mandatory. In the first step, the possibilities of purification at the selected site, the *Industry Center Obernburg / Mainsite*, were examined. The consulted Mainsite Wastewater Department, assured a favorable industrial fee of less than 0.25 €/h, assuming the estimated wastewater volume flow. This option is the simplest and cheapest approach. The wastewater generated during pervaporation and rectification can be discharged via the industrial park to the local wastewater treatment plants without any further intermediate steps. The second option is direct discharge to a local wastewater treatment plant. In this case, somewhat more expensive discharge fees (about 8 €/h) are incurred (compared to disposal through the Industry Center Mainsite). In this case, no intermediate steps and thus further purification are necessary. The most complex case is the complete in-house purification of the wastewater, which enables direct discharge into surface water. A suitable option for the purification of organic materials is the Boron doped diamond electrode. In this technique, methanol and glycerol, as well as other organic materials, are electrochemically oxidized. An electrode membrane of size 0.5 m^2 is needed for the wastewater flow. In addition, a voltage of 1.2 V is applied. The pure investment costs are about 8,200 – 10,900 €. Additionally, there are running electricity costs of approx. 11.80 €/h. In the event of leakage or membrane fracture and the associated occurrence of catalyst residues in the wastewater, it is important to carry out regular sampling tests, e.g., by means of photometric detection or atomic adsorption spectrometry (e.g., GF-AAS) to detect traces of metal ions. This step is important because the metal ions show high fish toxicity even in very low concentrations. In case of heavy metals in wastewater, it is recommended to connect a precipitation reactor upstream of the electrode. In this process, poorly soluble metal sulfates are formed, which can be easily removed from the wastewater.

For the **pipe constructions** several calculations were done using *Excel*. Based on these calculations, for example, pressure shocks, highest flow velocities and pipe vibrations were considered. Pipe materials were selected in cooperation with the other groups, to assure optimal material pairing. For example, corrosivity, composition and aggregate state of the fluid were important for material selection or possible coatings and therefore for the material values. In cooperation with the simulation group, the required volume flows were discussed and considered as constant values. For uncommitted volume flows a back-of-the-envelope calculation was done using the ideal gas law. These initial calculations made it possible to select first DIN pipes. In cooperation with the construction and finances groups an agreement was made to use DIN pipes whenever possible, to on the one hand facilitate the connection of the different plant components and on the other hand to avoid extra costs for custom designs. Furthermore, a **3D-visualization of the plant** was done using SketchUp Pro 2021. This feature required an implementation of gathered process information, which was obtained by constant correspondence with the other groups. This information pool included for example different tank dimensions which were designed by the construction group, safety regularities such as escape routes which were determined by the security group or potential component arrangements, established by the flowsheet group. The 3D-visualization also included a specific color-code to facilitate the determination of specific process steps and components. For the **pump selection**, data collecting with other groups was required. Depending on different parameters such as volume flows and required pressures, possible pumps and compressors were selected. A data collection with possible pump and compressor solutions was created. In here, key data for the machinery such as required volume flow, required pressure, pressure loss and manufacturer data were summarized. All possible machinery was forwarded to the finance group to discuss prices and possibilities. In cooperation with the heat integration group, used heat exchangers were designed integrated into the 3D simulation. Most of the practical adjustment of the different plant components in combination with the pipe constructions was planned using SketchUp as well. Possible pipe lengths were established. Pipe vibrations and necessary fixpoints were calculated to avoid structural vibrations inside the whole plant. First price calculations for the use of compressed air were done using several sources.

The desired outcome of optimal **heat integration** is a decreased dependence on external heat and energy sources and thus lowered project costs and an increased sustainability. Heat integration means heating up the cold flows using the hot ones inside the process. The goal was achieved with help of the PinchAnalysis. In general, a higher degree of heat integration comes along with higher capital costs due to additional heat exchangers, yet smaller energy costs. For a tradeoff between energy- and capital costs, we considered three different cases. In case 1 no heat is integrated into the process, i.e., all energy demand is provided externally. That results in remarkably high energy costs, but low capital costs. In the second case all possible heat is integrated, which leads to a decrease of the energy costs, but to an increase of the invest costs for additional heat exchangers. Case 3 will find an optimum between case 1 and 2. In total an amount of 1601 kW heat needs to be supplied and 1735 kW of heat needs to be removed. Additionally, the reaction of the process provides 203,5 kW energy. One part of this heat will be utilized to warm up the feed stream from 40°C to 90°C (reaction temperature) and to reheat the recycle flow from 80°C to 90°C. The remaining amount of 68 kW of the reaction enthalpy is removed via the reactor cooling jacket. The maximum amount of heat that can be integrated into the process is 500 kW. To achieve this, several additional heat exchangers are needed at the bottom of a distillation column, which is technically hard to realize. Therefore, evaporation in distillation columns were neglected. Furthermore, the heat of the condensers of the columns cannot be integrated due to their low condensation temperatures. This scenario (case 2) results in a possible heat integration of 340 kW. This heat, coming from the liquid reactor product stream, can be used to heat up the feed for the pervaporation and the recycle stream. Which results in four additional heat exchangers and the liquid reactor product stream needs to be split into two streams. For case 3, the complete heat integration was optimized by combining the four additional heat exchangers from case 2 to only one apparatus and by not splitting the product stream. This leads to smaller temperature difference between hot and cold streams compared to case 2, but in zero additional heat exchangers and in the same integrated heat amount of 340 kW. At the location, it is possible to cool with river water from the Main or with artificial cooling offered by the industry park. As heating utilities, low pressure steam (3 bar) and middle pressure steam (21 bar) are available. The capital costs of the heat exchangers are based on offers by Apparate- und Anlagentechnik-Nürnberg GmbH. When the process is operated without heat integration, the annual energy costs will sum up to 451,600 €/a, followed by 58,500 € for the heat exchangers. For the complete heat integration, the annual energy costs will reduce to 366,700 €/a, but the investment costs will rise to 80,600 €. Considering the optimized heat integration, the energy costs will stay the same as for the complete heat integration. With reducing the number of needed heat exchanger, the invest costs will drop to 70,400 €. With the optimized heat integration, the energy costs will significantly drop, but higher capital costs have to be taken into account compared to the case when no heat is integrated. With recuring saves for the energy costs, the higher invest will be paid off by 0.14 years.

For the **construction of apparatus**es, it was important to comply with regulations such as DIN standards. Since pressure vessels are sometimes required for the process, the guidelines of the AD 2000 regulations also had to be considered. The design and technical drawings were carried out using the program *Creo Parametric*. After the process flowsheet and the material flows were determined, a continuous stirred tank reactor (CSTR), storage vessels, a pervaporation module, and two vacuum distillation columns need to be designed. However, since some important information were missing for the construction of the pervaporation module as well as the columns, these could only be roughly presented. The first task was to find a suitable material for the construction of the reactor, with reaction parameters, properties such as weldability and yield strength, but also economic aspects playing a major role. In consultation with the piping department, the choice finally fell on the austenitic stainless steel 1.4571. This steel is frequently used in process engineering and exhibits high resistance both at moderate pressures and temperatures and at low pH values.

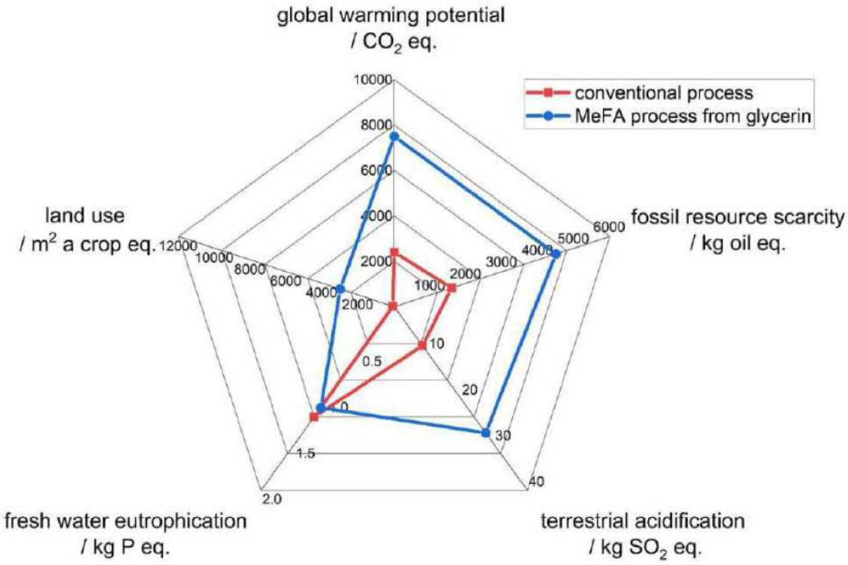


One of the most important pieces of equipment in the process is the **stirred tank reactor**. Since it is a pressurized vessel, the wall thicknesses is a crucial parameter. In addition to the two dished ends, which serve as the bottom and lid of the reactor, the cylinder jacket, cooling jacket, nozzles, connecting flanges and the stirring unit with an impeller stirrer were designed in detail. Connections for measuring and control systems were left out. Due to the applied operating pressure of 40 bar, it is not possible to fit a manhole. In order to simplify the installation of the stirrer and to enable possible inspections from the inside, there is an oversized stirrer flange on the roof of the reactor as an alternative to the manhole. In addition to the reactor, the storage tanks for the raw materials methanol and glycerol and the product methyl formate had to be designed. Since these pure substances do not require tank materials with high requirements, a low-grade steel such as 1.4401 can be used here. Due to the fact that methanol and methyl formate are substances with relatively high vapor pressures, pressure vessels should also be used here. Because of the high flammability of Methanol and methyl formate the storage tanks have to be double walled. Two distillation columns with 36 stages each are required for product separation. However, since neither the column diameter nor the stage height were determined, these sizes could only be estimated roughly for a design. The same applies to the design of the pervaporation unit for the separation of the catalyst. Here, there was only the information that flat membrane modules with a total area of about 580 square meters are necessary. At the end a BOMs for every apparatus is generated and handed over to the cost department.

The most essential task of the **automation** is to ensure safe and desired running of the different system components. Therefore, different measurement, regulation and control strategies for the plant are designed. Besides the design aspects, the automation is responsible for the startup and shutdown of the plant and for creating a strategy for possible emergency scenarios. In general, two principles are used in the automation of the process. First, a technique called feedback control, in which the controller and the plant form a closed loop system. By tracking the measured signal and comparing it with the desired behavior, the controller dynamically applies correction on the system input. Second, the feedforward control, where the control sends its control signal in a predefined way without responding to how the load reacts. Those methods are used to control the biobased methylformate process, which can be divided into four main sections. The first section is feed preparation. This section further consists of a microfiltration, a vacuum distillation, and a mixer. For the operation of the microfiltration, the main prerequisite is maintaining the correct pressure, which is accomplished by a pressure-maintaining valve. After the microfiltration, a buffer tank is installed to ensure a constant volume flow towards the vacuum distillation column. The separated glycerol flows to the mixer. Sulfuric acid and methanol are dosed in a ratio depending on the glycerol flow via controlling the pumps. The feed preparation is followed by the reaction: The main requirement for the reaction is to provide oxygen at a partial pressure of 8bar. Therefore, air is compressed at a pressure of 40bar and fed through the reactor. A pressure-maintaining valve is controlling if the right pressure is set. Additionally, the reaction should take place at 90°C. Since the reaction is exothermic, heat needs to be removed. The flow of the cooling medium is controlled via a pump. Furthermore, the pH-value needs to keep between one and two. H_2SO_4 can be dosed in the upstream mixer to adjust to possible fluctuations. Afterwards product separation takes place: Two distillation columns are utilized in this section. In the first column formic acid methyl formate (main product) and dimethoxymethane (DMM) are extracted from water and methanol/catalyst. In the second column the product is divided from the remaining DMM. In both columns it is important to set a constant feed flow. Therefore, a buffer tank is built before the columns, so that the flow can be controlled continuously via a pump. Besides, the pressure, temperature, and level of the columns are controlled.

The **simulation of the complete process** from biomass feedstock to purified products and residues was carried out in *Aspen Plus V10*, to provide an overview of all process streams and required units. This software was also used to determine thermodynamic properties as well as stream compositions. The global property method of choice was the *Non-Random-Two-Liquid* model (NRTL). The reaction conditions of a temperature of 90 °C and an oxygen partial pressure of 8 bar were taken directly from literature. Byproducts due to the oxidation of methanol like dimethoxymethane (DMM) and dimethyl ether (DME) were also considered. The molar conversion was implemented with the help of the reactor design group. The purification steps required for the biomass feedstock to achieve optimal reaction conditions were determined and planned out. The implementation of the up-streaming process was done in collaboration with the respective group. Solid separation was implemented with microfiltration to remove salts, followed by a vacuum distillation to remove any water content. This was done to prevent the shift of reaction equilibrium towards formic acid in the presence of water. The pH level in the reactor was maintained between 1 and 3 with a stream of sulfuric acid. Next, the reactor was simulated using a stochiometric reactor model, RStoic, where the reaction of glycerol to methyl formate with total conversion of glycerol was implemented. For the final simulation, the stochiometric reactor model *REquil* was chosen as it is capable of carrying out chemical and phase equilibrium calculations simultaneously. It was not possible to reflect the actual choice of a continuous stirred-tank reactor (CSTR) in the simulation, as this kinetic reactor model in Aspen requires an accurate description of reaction kinetics. This was not studied in depth within the framework of this course. The down-streaming process began with the removal of the gas phase after expansion of the reaction mixture from a pressure of 40 bar to 1 bar. The byproduct DME is separated with the gas phase. Then, two distillation columns, each at 1 bar, were used to separate the solvent methanol and byproduct DMM from methyl formate to achieve the required purity of 97 wt.-%. These columns were first simulated with a shortcut method (*DSTWU*), then with a rigorous model (*RadFrac*). Finally, a recycle stream of methanol and formaldehyde, carrying the catalyst, was implemented. The main contribution of the simulation to the process development was the determination of stream compositions and states, as well as thermodynamic and material properties for the design of the up- and down-streaming processes as well as pipes, pumps and compressors. Lastly, the utilities of the units were determined for the calculation of energy costs.

In the feasibility study regarding the production of methyl formate from renewable raw materials, the task is to implement a **life cycle assessment** of the selected process scheme. This enables to consider the ecological dimension in addition to the technical, economic, and legal framework conditions. The core parameter of the considerations should be the specific greenhouse gas emissions. This life cycle assessment is done according to *DIN EN ISO 14040* for the process of the production of methyl formate out of biomass and the sustainability assessment of the plant. The goal of the study was to assess the sustainability of the production system and assessment of the ecological impacts of the process. For this production process, the "Cradle-to-Grave" approach was selected as the scope for the size of the life cycle assessment. "Cradle-to-Gate" was chosen, as the OxFA GmbH is not responsible for further processing of the product. The functional unit of the process is one-ton methyl formate. This means, that the influence of the procurement of raw materials, construction, and mining up to the recycling of the materials in relation to one ton of methyl formate is considered. The functional unit helps to compare different processes. In the Life Cycle Inventory (LCI), all inputs are considered, which can then be implemented into the "OpenLCA" program. The program itself is connected to the "EcoInvent" database, which automatically provided the values for the chosen impact indicators, which are "global warming potential", "land use", "fossil resource scarcity", "terrestrial acidification", and "freshwater eutrophication". As a comparison, the conventional process for the production of methyl formate is used. The methanol required for the process is taken from conventional sources, as the availability of methanol from sustainable sources is still under development. After both processes have been implemented in OpenLCA, it becomes clear how the large amounts of conventional methanol have an impact on the process.



The **global warming potential** for the conventional process is approximately 2,400 CO_2 equivalents and for the new methanol/glycerol process, it is 7,500 CO_2 equivalents. The consumption of fossil resources also increases from 1,200 kg oil equivalents to 3,800 kg oil equivalents. This is due to the use of enormous amounts of methanol, which must also be separated in the distillation column, for which natural gas is needed for steam production. Therefore, both the feed methanol directly and the cyclic carrying of the methanol is responsible for the high global warming potential. The "land use" rises from about 0 m^2 equivalents for the conventional process to about 4,000 m^2 equivalents for this novel biomass based process. This is due to the fact that the production of glycerin out of biomass relies on agricultural cultivation. This cultivation also contributes negatively to the "freshwater eutrophication", as the fields are fertilized and the fertilizer then seeps into the groundwater. The cultivation of biomass also increases "terrestrial acidification". In order to increase the sustainability and to reduce the ecological impact, the amount of methanol used must be drastically reduced. With a consumption of only 10% of the initially used amount of methanol, the "fossil resource scarcity" and the "global warming potential" would be at 900 kg oil equivalents or 3,000 kg CO_2 equivalents. This would result in a fewer "fossil resource scarcity" than for the conventional process. Further improvement can be achieved by obtaining the methanol and the electricity from sustainable and renewable sources. While this would further increase "land use" and "freshwater eutrophication" because more biomass is needed, "global warming potential" and "fossil resource scarcity" would decrease, so this could ensure a green and sustainable process.

The **overall costs** were summarized in four subcategories namely investment, material, operating and payroll costs. All the necessary equipment to build the plant, such as the reactor, piping material, instruments et cetera, are covered under investment costs. To determine the reliability of the investment costs and thus the total costs of the plant, the total costs will be multiplied with a so-called *Lang-factor* of 3.86. The investment costs add up to 14.3 Mio. € in total. Material costs contain not only raw material like methanol or biomass but also auxiliary material like the catalyst, sulfuric and nitric acid. They also cover operating materials like lubricants or detergents. In total, the feed input in the reactor sums up to 1,750 € per ton of product. Operating costs encompass prices for electricity (0.18 €/kWh), wastewater (<1 €/m^3), CO_2-emissions and -tax, maintenance, quality control, low pressure steam (20 €/t), medium pressure steam (26 €/t), cooling water (50.15 €/t), and transport (1.81 €/km). The amount and costs for the heat management were summed up over the different evaporators, coolers, and condensers. The drinking water fee (0.5 €/m^3) was determined based on the price at the Industry Center Mainsite with an approximated consumption of 104.58 m^3/a. For the transport costs, a truck load of 30,000 kg was assumed. The costs for insurance (1 %), maintenance (6 %), and taxes (3 %) were calculated from the total investment costs. In total, the operating costs sum up to 4,650 € per ton of product with the largest contribution from the vacuum pumps for the pervaporation. The overall annual energy costs with optimal heat integration sum up to 367,000 €, initial investment costs of 70,000 € and annual investment costs of 9,000 €. Payroll costs cover all salaries according to the chemical tariff fee, considering that start-up salaries are 30% lower in average. Also, holiday and sick pay, as well as benefits that the employees have a legal entitlement to, are included in the calculation. This results in a factor of 1.4 of the total payroll costs. With a three-shift system and additional night shift bonus of 25 % the payroll costs then consist of 560,000 € per year. One administrator and one chemical engineer work a normal shift from 8 am to 4 pm. Each of the three production shifts contain one shift supervisor and three production workers. As the reaction does not emit CO_2 anymore, the saving of the CO_2 tax compared to the original OxFA process in aqueous phase was calculated. Over the next five years it amounts to 43,000 €. For the product methyl formate with a purity of over 97 %, a price of 1400 €/t is realistic. With this price, the net present value is negative and pay-out time is approximately 12.5 years, so an investment in this process would not be recommended. However, further cost analysis and **optimization approaches** have shown that the pervaporation could work as well with 30 mbar instead of former 3 mbar. This leads to extremely reduced investment- but also operating-costs. With the same expected selling price the pay-out time is already reached after 4.5 years.