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Innovative Membrane Separation as a Link Between Biotechnological and Chemical Processes

Unter der Leitung von

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Abstract

Methyl ethyl ketone, or MEK is an important organic solvent for the chemical industry that is usually made of petrochemicals (LIU et al. 2006). Due to the increasing costs of petroleum and the demand in energy, the research respective to alternative production methods is gaining attention (Shao and Kumar 2009). An alternative production method of MEK is the chemical catalysis of fermentative produced 2,3-butanediol to MEK (Tran and Chambers 1986). As a link between fermentation and chemical catalysis membrane separation via pervaporation is a promising energy saving separation technology which has been little studied in this field of application (Koros 2004) (Van Der Bruggen and Luis 2014).

The goal of this scientific work was to find pervaporation membranes suitable for the required separation steps between the fermentative 2,3-butanediol (BD) production and the subsequent chemical catalysis to MEK and to study the effect of the varied process parameters. Therefore, a design of experiment was set up with “Statgraphics” to show the effect of varying the concentration of feed components and the feed temperature on flux, selectivity and rejection coefficient. First two hypothetical process combinations were created: serial process combination and one pot integration. Four different separation steps were required to study these hypothetical process combinations, conducted with a pervaporation pilot plant and synthetic feed mixtures. To choose a suitable membrane for each separation step a membrane screening was undertaken. According to the results an Optimised Silica membrane was chosen to separate water from BD and from MEK. A PDMS membrane was chosen to separate MEK from BD and to separate a ternary mixture consisting of MEK, BD and H_2O.

All experiments showed, that the flux is increasing with higher feed temperature. The highest flux achieved was 13.25 kg/m²h when separating water from BD with the Optimised Silica membrane at 75°C and 1.51 wt.% BD in the feed. The Optimised Silica membrane showed no permeability for BD and mostly no permeability for MEK and therefore up to 100 wt.% H_2O in the permeate in the separation steps BD / H_2O and MEK / H_2O. According to the statistical evaluation, the temperature has no significant effect on rejection coefficient or selectivity when separating MEK and BD with the PDMS membrane. Still, the highest permeate purity of 99.33 wt.% MEK was achieved at the lowest temperatures. In the separation step MEK / BD / H_2O rising concentration of MEK and temperature conducted to higher flux but also to less favoured MEK in the permeate.

The hypothetical one pot integration is feasible as planned. The hypothetical continuous serial process must be split into two discontinuous steps, because none of the tested membranes prefers 2,3-butanediol as permeate. As all experiments were undertaken with synthetic feed mixtures, further research with fermentation broth is necessary.

Abstract

Methylethylketon oder MEK ist ein wichtiges organisches Lösungsmittel für die chemische Industrie, das üblicherweise aus Erdölchemikalien hergestellt wird (LIU et al. 2006). Aufgrund der steigenden Kosten für Erdöl und wachsender Nachfrage nach Energie, gewinnt die Forschung zu alternativen Produktionsmethoden zunehmend an Aufmerksamkeit (Shao und Kumar 2009). Eine alternative Produktionsmöglichkeit für MEK ist die chemische Katalyse von fermentativ hergestelltem 2,3-Butandiol (BD) zu MEK (Tran und Chambers 1986). Als Bindeglied zwischen Fermentation und chemischer Katalyse ist die Membranseparation mittels Pervaporation eine vielversprechende energiesparende Trenntechnologie, die in diesem Anwendungsgebiet wenig untersucht wurde (Koros 2004) (Van Der Bruggen und Luis 2014).

Ziel dieser wissenschaftlichen Arbeit war es, Pervaporationsmembranen zu finden, die für die erforderlichen Trennschritte zwischen der fermentativen BD-Produktion und der anschließenden chemischen Katalyse zu MEK geeignet sind und den Effekt der variierten Prozessparameter zu untersuchen. Dafür wurde ein statistischer Versuchsplan mit „Statgraphics“ erstellt und die Auswirkung von Änderung der Konzentration der Feedkomponenten und -temperatur auf Flux, Selektivität und Rückhaltevermögen untersucht. Davor wurden zwei hypothetische Prozesskombinationen erstellt: serielle Prozesskombination und Ein-Topf-Integration. Zur Untersuchung dieser Verfahrenskombinationen, die mit einer Pervaporation-Pilotanlage und synthetischen Feedmischungen durchgeführt wurden, waren vier verschiedene Trennschritte erforderlich. Um für jeden Trennschritt eine geeignete Membran auszuwählen, wurde ein Membranscreening durchgeführt. Anhand der Ergebnisse wurde eine Optimised Silica Membran gewählt, um BD von Wasser und MEK von Wasser zu trennen und eine PDMS-Membran um MEK von BD zu trennen und ein ternäres Gemisch, bestehend aus BD, MEK und Wasser, zu trennen.

Alle Experimente zeigten, dass der Flux mit höherer Feedtemperatur ansteigt. Der höchste erzielte Flux betrug 13,25 kg/m^{2}h bei der Trennung von BD und Wasser bei 75 ° C und 1,51 wt.% BD im Feed mit der Optimised Silica Membran. Diese zeigte für BD keine und MEK kaum Permeabilität und daher bis zu 100 wt.% H_2O im Permeat bei den Trennschritten BD / H_2O und MEK / H_2O. Laut der statistischen Auswertung hat die Temperatur keine signifikante Auswirkung auf das Rückhaltevermögen oder die Selektivität, wenn MEK und BD mit der PDMS-Membran getrennt werden. Dennoch wurde die höchste Permeatreinheit von 99,33 wt.% MEK bei den niedrigsten Temperaturen erreicht. Im Trennschritt MEK / BD / H_2O steigt der Flux mit höherer Konzentration von MEK und Temperatur, aber es ergibt sich dadurch auch weniger bevorzugtes MEK im Permeat.

Die hypothetische Ein-Topf-Integration ist wie geplant möglich. Das hypothetische kontinuierliche serielle Verfahren muss in zwei diskontinuierliche Schritte aufgeteilt werden, da keine der getesteten Membranen BD als Permeat bevorzugt. Da alle Experimente mit synthetischen Futtermischungen durchgeführt wurden, sind weitere Untersuchungen mit Fermentationsbrühe notwendig.

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1. Introduction

1.1 Problem Statement

Methyl ethyl ketone, also known as 2-butanone or MEK, is an important organic solvent for the chemical industry. Next to acetone it is the most important commercially produced ketone. The worldwide amount of MEK production was 1 x 10^6 t in 2005 and has shown an average annual increase of 5-10%, with the interest in it growing since the 1980s. In 2006, 92% of MEK production capacities worldwide produced MEK by dehydrogenation of 2-butanol from petrochemical raffinates. MEK is used as a solvent in dye, paint, pharmaceutical and refining industries. It is considered to be in competition to ethyl acetate, especially as a low-boiling solvent. Because of its low viscosity, high solids concentration and wide diluents tolerance it is favoured as a lacquer solvent. Other uses of MEK are as an activator for oxidative reactions, as a selective extractive agent, as a special solvent for dewaxing mineral oil fractions and as a chemical intermediate (LIU et al. 2006) (Hoell et al. 2012). Petroleum products were relatively affordable in past decades. Because of that, petroleum-based synthesis of chemicals dominated and the growth of technological alternative manufacturing was limited. Recently the costs of petroleum and the demand in energy are increasing. Therefore, there is an increasing demand of research respective to alternative production methods of fuels and chemicals (Shao and Kumar 2009).

As explained in more detail in the following chapters, the alternative production of MEK has been explored for decades. In this alternative methods 2,3-butanediol (BD) is fermentative produced and subsequently dehydrated to MEK via chemical catalysis (Tran and Chambers 1986). The combination of biotechnological processes with subsequent chemical-catalytic conversion of bioproducts into platform chemicals represents a field that has not yet been established. To make this combination possible, the downstream of the fermented product before catalysis and the recovery of the final product is required. The steps of fermentation and dehydration are known very well, but the recovery and purification of BD and MEK represent a technological challenge and need to be researched more (Xiu and Zeng 2008).

As a link between these biotechnological and chemical processes membrane technology can provide large savings in costs and energy. It is believed that separation and purification accounts for more than half the price of commercial products (Shao and Kumar 2009). Pervaporation is a reasonable separation technology (Koros 2004) and Van Der Bruggen and Luis (2014) mentioned the vast potential of combining pervaporation membranes with classical technologies in a hybrid approach and that these have hardly been explored. Distillation can also be used for separation processes, but it is neither suitable for thermally sensitive organic compounds nor economical. Pervaporation has several advantages over traditional distillation: simple equipment, lower capital costs, and reduced energy demand (Liu et al. 1996). There are many different membranes available on the market. Novel pervaporation membranes with promising superior characteristics from the company Pervatech B.V were used for this scientific research.

Due to a lack of standardized tests the technical specifications of membranes are difficult to compare. That is why membranes need to be tested in lab scale for their suitability in a special field of application (Melin, Rautenbach 2007). To keep the number of necessary experiments low, a well-defined and well-structured experimental design is important. Design of Experiment (DoE) is a method for the design and statistical analysis of experiments. The aim of DoE is to learn as much as possible about the correlation between influencing parameters and results with the least possible effort. Information gained with DoE is statistically verified and the effects of input variables and their interactions can be quantified.

This scientific work shall build a base for further research to combine biotechnological BD production and subsequent chemical catalysis to MEK via pervaporation membranes. It shall show suitable membranes for the required separation steps, tested on synthetic feed mixtures in a pilot plant. The effect of varied feed temperature and feed composition on flux, selectivity and rejection coefficient of the membranes was researched with Design of Experiment. The experiments were not conducted with fermentation broth and potential by-products were not respected. For these aspects further research is necessary.

1.2 State of the Art

1.2.1 Production of MEK

1.2.1.1 Conventional Production of MEK

Today 92% of all production capacities worldwide produce MEK by dehydrogenation of 2-butanol. 2-butanol is a *sec*-butyl alcohol (SBA) that can be easily produced in a two-step process by hydration of n-butenes from petrochemical raffinates where liquid sulfuric acid is used as catalyst. It can also be produced in a single step process by direct addition of water and acidic ion exchange resin used as a catalyst. The dehydrogenation from SBA to MEK can be performed via gas dehydrogenation and liquid dehydrogenation, whereas gas dehydrogenation is widely used. (Hoell et al. 2012). According to LIU et al. (2006) this two-step process is called “two-step n-butylene technique”:

Two-step n-butylene technique

1. From petrochemicals fractionated butylene is hydrated to 2-butanol
2. Dehydrogenation from 2-butanol to MEK (2-butanone)

(LIU et al. 2006)

Other methods to produce MEK are by fatal production via Fischer-Tropsch or by catalytically oxidizing liquid n-butane. The Fischer-Tropsch process was improved by South African’s SASOL Ltd. and is performed in a two-step process. First, mineral coal is gasified to produce the synthesis gas consisting of carbon monoxide and hydrogen. Next, the synthesis gas is extensively purified by absorption in scrubber systems and then catalytically converted into hydrocarbons.

In this reaction MEK is achieved in a large variety of by-products and afterwards purified via traditional separation technologies to a high value solvent product (Hoell et al. 2012).

1.2.1.2 Alternative Production of MEK by Fermentation of BD and Chemical Catalysis to MEK

An alternative production method of MEK is the fermentative production of BD and subsequent dehydration to MEK (see figure 1) via chemical catalysis. In this method the use of petrochemicals as base product is not necessary.

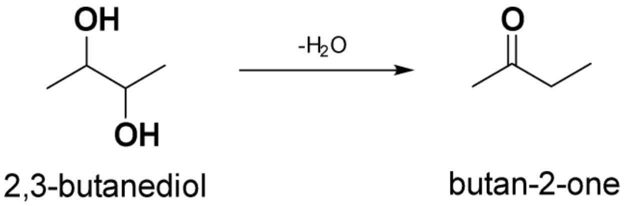

Figure 1: Dehydration of 2,3-Butanediol to Methyl Ethyl Ketone (Butan-2-one)

Several bacterial species are known to produce BD. Species with this ability are *Klebsiella pneumoniae, Klebsiella oxytoca, Paenibacillus polymyxa, Enterobacter areogenes, Enterobacter cloacae* and *Serratia marcescens*. These strains have been used to produce BD with high yields and productivities, but because of their potential pathogenicity they are unsuitable for industrial scale fermentation (Ji, Huang, and Ouyang 2011) . Thus, BD was produced with non-pathogenic *S. cerevisae*. The highest yield was 72.9 g/L BD(Kim and Hahn 2015). Another preferred candidate for the safe synthesis of BD is recombinant *E. coli*. In contrast to *S. cerevisiae*, *E. Coli* can consume xylose. Xylose is a very important sugar derived from lignocellulosic feedstock. A yield up to 73.8 g/L of BD was produced by using *E. Coli,* which is the highest achieved today (Xu et al. 2014).

The combination of the fermentation of BD and the dehydration to MEK was already researched by Tran and Chambers (1986). BD was fermented by *Klebsiella pneumoniae* with xylose as a substrate. They developed a solid acid catalyst consistent of sulfonic groups covalently bound to an inorganic matrice, to dehydrate BD to MEK. This catalyst can convert BD in the fermentation broth directly, compared to normally used activated bentonite or sulfuric acid. Hence the energy-intensive step of recovery and purification of BD from the fermentation broth prior catalysis can be eliminated. Unexpectedly they experienced catalyst deactivation during the catalysis from BD to MEK, that they attributed to loss of sulfonic acid groups. Multer et. al. (2013) produced MEK out of Biomass when determining the reaction kinetics of BD dehydration. BD was produced by fermentation with *Klebsiella oxytoca* and glucose as a substrate. Afterwards aqueous BD broth was catalytically dehydrated to MEK over a solid acid catalyst, the proton form of ZSM-5. The fermentation broth was only centrifuged to separate the solid from the liquid phase prior to feeding the liquid phase over the solid acid catalyst. The concentration of BD in the broth used for catalysis was 2.63 g/L. The broth was sent through the reactor at 200°C at 130 mL/h. After one hour of operating a conversion of 13% and selectivity greater than 90% was noted. MEK was the major product from BD dehydration but 2-methylpropanal was detected as side product.

The long-term stability of the catalyst was not assessed. To this day no alternative MEK production method was tested for industrial application.

1.2.1.3 Innovative Production of MEK: Pervaporation as a Link Between Novel Methods

This scientific research is based on the development of a new innovative production process of MEK. The innovation lies in the combination of novel methods. The sustainable biomass lignocellulose is fermented to BD by genetic modified *E. Coli*. In the process *E. Coli* is genetically modified to fix CO_2. The combination of a waste material substrate and the utilization of industrially produced CO_2 stand out clearly from other approaches. Yields of 25 g/L BD should be achieved. With subsequent chemical-catalysis BD is converted to MEK. For the dehydration of BD ZSM-5 zeolites with different Si/Al-proportions and chemical modified zeolites with different acidity are researched. The combination of biotechnological processes with subsequent chemical-catalytic conversion of bioproducts into platform chemicals represents a relatively new field that has not yet been established. For this there is still little activity in this area. To combine the fermentation with the chemical catalysis a reasonable downstream of BD and recovery of MEK is necessary. Pervaporation is chosen for this application as a reasonable technology with great potential.

1.2.2 Downstream Processes

1.2.2.1 Membrane Separation: Pervaporation as a Promising Downstream Technology

It is believed that downstream processes account for more than half of the price of commercial products. Using membrane technology can provide large savings in costs and energy (Shao and Kumar 2009). In the last decades membrane separation technologies gained more and more attention compared to conventional separation technologies. They are important in chemical, environmental and medicinal industries. For example, for the purification of blood, the concentration of protein, beverage preparation and desalination of seawater membrane separation is nearly unrivalled. The reasons for this success are the fast growth of this technology, continuous development of new membrane materials, construction concepts and methods of operation.

Membranes can be classified due to their origin and material. Membranes are a selective barrier between two different phases. They are first classified in biological and synthetic membranes. Biological membranes exist in a lipid bilayer and are essential for any kind of terrestrial life. Biological membranes are unrivalled regarding to their selectivity and flux and are a benchmark for the development of synthetic membranes. Synthetic membranes are separated into liquid and solid membranes. The synthetic solid membranes are made from organic or inorganic materials. Organic membranes consist of polymers and inorganic membranes consist of metal or ceramic. The most common membranes are organic polymer membranes. The number of inorganic membranes on offer has increased in the last years and in the meantime, hybrid membranes have become available which combine the benefits of both organic and inorganic materials. Another possible classification of membranes is due of their morphology and structure. Membranes for pervaporation are mostly nonporous and asymmetric and depending on their raw material, hydrophilic or hydrophobic (Melin, Rautenbach 2007).

The membrane market provides a wide offer of selective and robust membranes from multiple specialised producers. Commercial membranes were optimised for their specific field of application regarding to selectivity and flux. Through selected membrane materials and manufacturing methods, chemical robustness and mechanical and thermal long-term stability were improved. (Melin, Rautenbach 2007). Such innovative materials are developed by the company Pervatech B.V. (The Netherlands). They offer novel hydrophilic membranes on ceramic substrate, hydrophilic Hybrid Silica membranes and organophilic membranes on a polymeric or ceramic substrate with superior characteristics for pervaporation membrane processes. Improved pervaporative membranes result in lower energy consumption, lower waste streams and higher product quality (http://pervaporation-membranes.com/products/membranes/ accessed June 13, 2018).

Pervaporation is a promising membrane separation technology that was already described in a publication in 1956 by Heisler et al. He defined it as the passage of a liquid through a semipermeable membrane and the subsequent evaporation of the liquid (Heisler, E.G., Hunter, A.S., Sicillano, J., Treadway 1956). The downstream side is usually kept under vacuum. Pervaporation has the advantages of high separation factors, low operating costs and ease of scale up in industrial use. Distillation can also be used for separation processes, but it is neither suitable for thermally sensitive organic compounds nor economical. Pervaporation has several advantages over traditional distillation: simple equipment, lower capital costs, and reduced energy demand (Liu et al. 1996). Pervaporation is utilized for separation processes where the conventional methods are ineffective in their use of energy, need high instrumental effort or fail completely. The most important application is for chemicals with nearby boiling points and azeotropic mixtures. Their separation usually requires special processes like double pressure or entrainer rectification (Melin, Rautenbach 2007). Van Der Bruggen and Luis (2014) said that pervaporation has a great potential in applications beyond the classical areas. They also mentioned the vast potential of combining pervaporation membranes with classical technologies in a hybrid approach and that these have hardly been explored.

Dehydration of organic liquids using hydrophilic membranes remains the main application of pervaporation in the industry today. In recent years pervaporation for the separation of organic-organic mixtures has been gaining attention. One of the reasons is that separation of organic-organic mixtures with classic technologies is tough, due to their generally similar physical and chemical properties (Smitha et al. 2004). According to Van Der Bruggen and Luis (2014) there are only modest attempts that demonstrate the feasibility of organophilic membrane separations. This leads back to the selectivity of currently available membranes. The best selectivity that can be obtained for such separations with any membrane can never be high. Scientists spend many efforts in developing more selective membranes. The results with the most advanced materials indicate that selectivities below 10 are to be expected. Typical values of 3-4 are common.

1.2.2.2 Conventional and Alternative Downstream of BD after Fermentation

Several studies for the recovery of BD from water and fermentation broth are present. The main method for the recovery of high boiling organics, such as BD, is still the distillation. Due to the low concentration in which fermentative products are produced, distillation is an energy intensive process limiting its cost effectiveness. Fermentative products have to be separated from complex broth mixtures containing of metabolites, proteins, salts, sugars and other nutrients (John et al. 2016). According to Xiu and Zeng (2008) the main methods studied for the separation of BD from fermentation broth are steam stripping, pervaporation, reverse osmosis and solvent extraction but no method has proven to be simple and efficient. Improvements regarding to yield, purity and energy consumption are needed. They also said that pervaporation, aqueous two-phase extraction, reverse osmosis and in situ extractive or pervaporative fermentations deserve more attention in the future. Other researched methods for the recovery of BD from fermentation broth are salting-out (Xie et al. 2016) and sugaring-out extraction (Dai, Liu, and Xiu 2015). With salting out 100% BD was recovered, whereas with sugaring-out only 76.3% BD distributed into the top phase. Wheat et al. (1948) developed a countercurrent steam stripping for the recovery of BD. This method is not used today because of large energy consumption. For single distillation a large amount of energy is also required. Integrated processes of reverse osmosis and distillation can slightly decrease processing costs (Xiu and Zeng 2008). Qureshi and Meagher (1994) studied the recovery of BD from fermentation broth with vacuum membrane distillation. With vacuum membrane distillation, using a polytetrafluoroethylene membrane, a concentration of BD from 40 g/L to 430 g/L was achieved. Liquid-liquid extraction has been attracting much attention. Birajdar et al. (2015) for example used continuous countercurrent liquid-liquid extraction to separate BD from fermentation broth using n-butanol and phosphate salt. They figured out, that six theoretical stages and a minimum solvent to feed ratio of approximately 1:1.5 is required to achieve 99% 2,3-butanediol extraction. Shao and Kumar (2009) researched an integrated separation scheme based on solvent extraction and pervaporation to recover BD from a synthetic fermentation broth. Based on their preliminary work they thought that pervaporation alone is not promising for recovering BD from fermentation broth. Their reasons for that were the extreme hydrophilic characteristic of BD and consequently the difficulty in finding a material which can show adequate affinity preference for BD over water. They also experienced an unfavourable diffusion of BD in the membrane. All their tested materials tended to be water-selective although they are hydrophobic. For the integrated separation scheme, a polydimethylsiloxane (PDMS) membrane was used to further enrich the BD in the organic phase. The selected extraction solvent was 1-butanol. They reached purity of BD up to 98.3 wt.% which is higher than the purity of the commercial 2,3-butanediol product (98.0 wt.%). Water was found to be the most permeable in the membrane, followed by 1-butanol. According to the solution-diffusion theory the PDMS membrane displays a much higher permeability for water than for BD. Neither the hydrophilic nature nor the big molecular size favours its permeation in the membrane.

Therefore, for the recovery of BD from aqueous solutions it is better to treat it as the retentate of the PDMS membrane, implying that the purification of BD could be achieved by using the PDMS membrane alone (Shao and Kumar 2009).

1.2.2.3 Conventional and Alternative Downstream of MEK after Chemical Catalysis

There is only little research for the recovery of MEK. In conventional production, MEK is purified in three consecutive distillation steps, which operate under normal atmospheric pressure. After catalysis the stream contains by-products like unconverted SBA, 5-methyl-3-heptanone, higher ketones and water. In the last distillation step MEK with a typical purity over 99% is achieved (Hoell et al. 2012). Liu et al. (1996) researched the separation of organics from water with a silicalite membrane and mentioned it as an effective technique over a wide range of concentrations. They obtained higher separation factors and higher fluxes when a stainless-steel support was used instead of alumina when separating methanol from water. Separation factor was decreasing and mass flux increasing at raising acetone concentration. At 43 wt.% acetone concentration the flux was as high as 0.95 kg/m²h. Smetana, Falconer, and Noble (1996) separated MEK from water by pervaporation using a silicalite membrane. MEK was treated as permeate. Feed concentrations between 0.8 and 15.4 wt.% MEK were used and the MEK fluxes increased from 0.06 to 0.36 kg/m²h over this range and the separation factors were between 70 and 146. The highest flux was obtained at the highest MEK concentration. The highest amount of MEK achieved was 95.4 wt.% at 15.4 wt.% MEK in the feed. Unlike distillation, the membrane separated beyond the azeotrope of 87.5 wt.% MEK. Chen et al. (2008) achieved a flux of 0.25 kg/m²h and a separation factor of 32 000 when separating MEK from water at 30°C and 5 wt.% MEK. They used silicalite membranes prepared by in situ crystallization on the outer surface of porous tubular mullite supports with tetraethoxysilane (TEOS) and tetrapropylammonium hydroxide (TPAOH) as a silica source and organic structure directing agent, respectively. Thiyagarajan, Ravi, and Bhattacharya (2011) studied the separation of MEK from water with pervaporation through a polydimethylsiloxane-membrane. The experiments were carried out from 10-15 wt.% MEK concentration in the feed and 40-60°C. The permeate pressure was 4-10 mbar at 40°C and 4 mbar permeate pressure with 10 wt.% MEK they observed a selectivity around 100 and a flux of 0.06 kg/m²h. No study was found for the separation of MEK and water where MEK is treated as retentate.

1.3 Goal and Scientific Hypothesis

The goal of this scientific work is to find pervaporation membranes that are suitable as a link between fermentative 2,3-butanediol production and subsequent chemical catalysis to methyl ethyl ketone. The effect of varying feed composition and temperature on flux, selectivity and rejection coefficient is studied. Only novel pervaporation membranes developed by Pervatech Netherlands are tested. The desired final product is MEK with 99.5% purity. For the experiments, synthetic feed mixtures are separated via membrane separation in a pervaporation pilot plant.

There are two potential options of process combination:

- **Serial Process Combination:** In a bioreactor BD is produced via the fermentation from *E. Coli*. The first connected membrane separation step should separate BD from the fermentation broth, so that BD can be directly used for chemical catalysis. Then MEK is produced via catalytical dehydration of BD. Afterwards, a second membrane should separate MEK from the remaining BD.

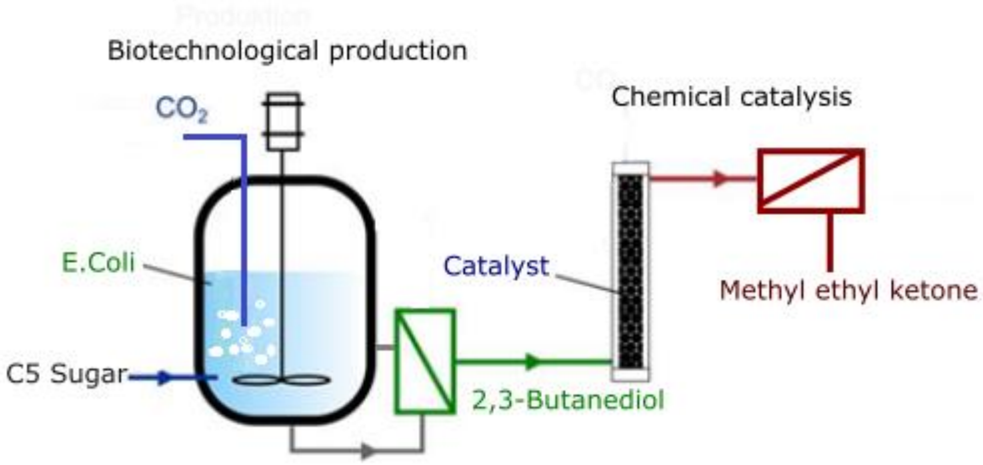

Figure 2: Hypothesis of Serial Process Combination

- **One Pot Integration:** The bioreactor where BD is produced through fermentation already contains the catalyst for MEK production via catalytical dehydration of BD. A membrane separation step should separate MEK from fermentation broth and remaining BD directly afterwards. A second subsequent membrane could be necessary if the ternary mixture cannot be separated in one step.

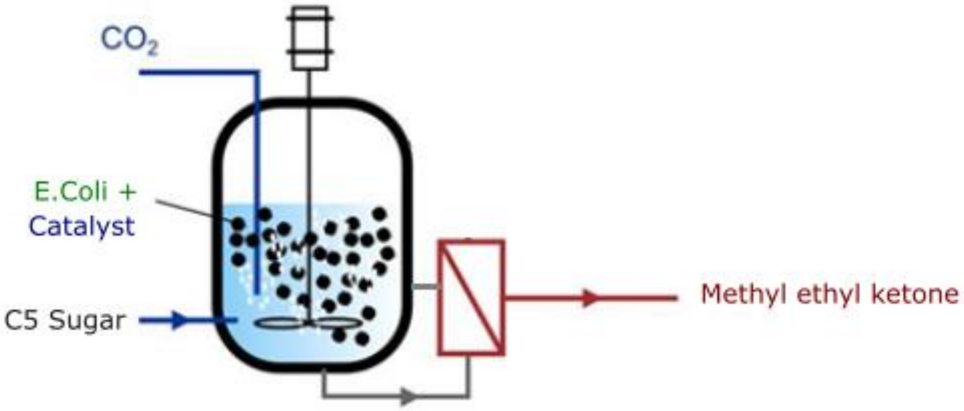

Figure 3: Hypothesis of One Pot Integration

There are four different separation steps required to test:

- **Separation Step 1: BD / H_2O:** to separate BD from the fermentation broth in the serial process combination
- **Separation Step 2: MEK / BD:** to separate remaining BD from MEK after chemical catalysis
- **Separation Step 3: MEK / BD / H_2O:** to separate MEK from the ternary mixture in the one pot integration process
- **Separation Step 4: MEK / H_2O:** to separate possibly remaining water from MEK after separation step 3

1.4 Workflow

At first a membrane screening was undertaken to find suitable membranes for the experimental design. Following membranes from Pervatech B.V. were screened:

- HybSi Open
- HybSi Standard
- HybSi Dense
- PDMS
- Optimised Silica

The membrane screening for selection was carried out with “trial and error” tests. The Experiments were undertaken and data was collected with the VapoMem pervaporation construction. Permeate compositions were analysed with a refractometer and gas-phase chromatograph. The collected raw data was analysed in Excel. Flux and permeate purity were calculated. With the help of these results a membrane was chosen for each separation step. The membranes with the highest flux and permeate purity were preferred.

To show the effect of varying temperature and feed composition on flux, selectivity and rejection coefficient a design of experiment (DoE) was created for each separation step. The program “Statgraphics” was used to create experimental design. Experimental performance and analysis of permeate compositions were operated as in the membrane screening. After execution of the DoE experiments, the raw data was analysed. Flux, selectivity and rejection coefficient were calculated. The statistical evaluation of the results was designed with “Statgraphics”.

2. Material and Methods

2.1 Materials

2.1.1 Equipment

Table 1 shows the used equipment for the experiments. The used VapoMem Pervaporation Construction with the required attachments is shown in figure 4. The detailed experimental setup is shown in chapter 2.2.1. Experimental Setup and Performance

Table 1: List of Used Equipment

Nr.	**Equipment**	**Producer/Type**
1	Pervaporation Construction	PS Prozesstechnik GmbH, VapoMem Membrane Separation
2	Control Cabinet	Endress + Hauser RSG30
3	Cooling Trap	GlasKeller Basel AG
4	Cooling System for Cooling Trap	Lauda, Eco Silver RE 630
5	Vacuum Pump	KNF Lab, Laboport
6	Heating System	Julabo, CF41
	Scales	Sartorius, BP 3100 S
	Refractometer	A.Krüss, Optronic Abbe-Refraktometer AR4
	Gase-phase Chromatograph	Agilent, 5890 Serie II
	Disposable Pipettes	BRAND

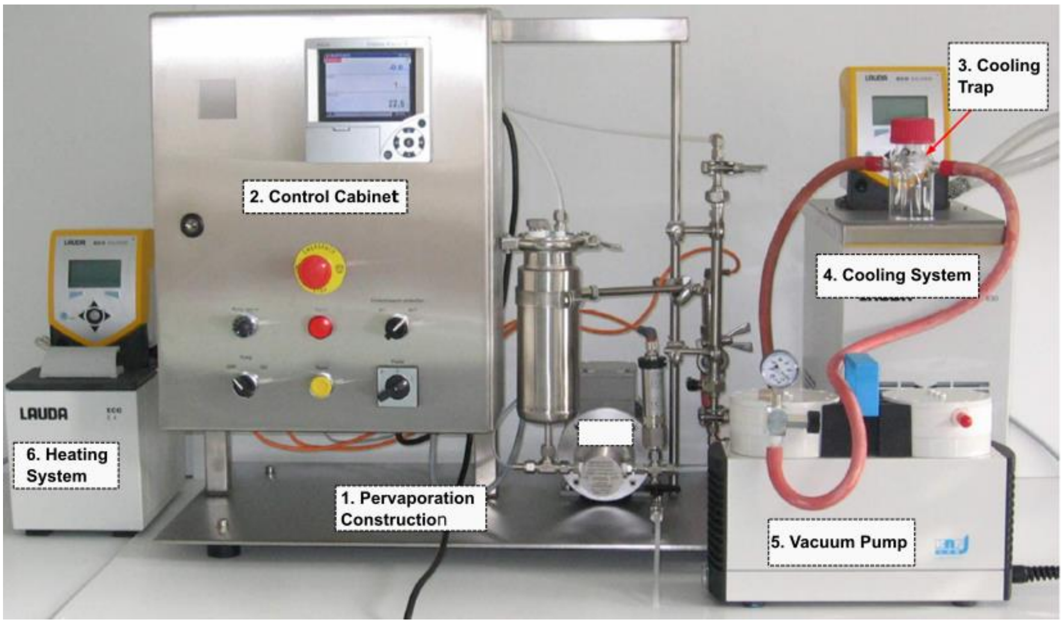

Figure 4: VapoMem Pervaporation Construction with Required Attachments

2.1.2 Chemicals

Table 2 shows the list of used chemicals for the experiments. The physical and chemical properties of MEK and BD are described in more detail in table 3 and table 4.

Table 2: List of Used Chemicals

Chemical	**Producer/Type**
2,3-Butanediol	Acros organics 98% mixture of racemic and meso forms
Methyl ethyl ketone	Alfa Aesar, HPLC Grade 99.5+%
Distilled water	-

Table 3: Physical and Chemical Properties of Methyl Ethyl Ketone (Hoell et al. 2012)

Chemical Names	2-Butanone, Methyl Ethyl Ketone, MEK
Characteristics	Colourless, low-viscosity, flammable, acetone-like smell
Boiling Point	79.6 °C
Solubility at 20°C	27.5 wt. % MEK in water 12.5 wt. % water in MEK
Refractive Index at 25°C	1.3764 nD25
Standard Specification Purity	min. 99.5 wt%
Azeotropic Mixture with Water	88.7 wt.% MEK
Boiling Point Azeotrope with Water	73.4°C

Table 4: Physical and Chemical Properties of 2,3-Butanediol (https://pubchem.ncbi.nlm.nih.gov/compound/262; accessed Nov. 3, 2017)

Chemical Names	2,3-Butanediol, Butane-2,3-diol,
Characteristics	Odourless, nearly colourless, crystalline solid or liquid
Boiling Point	182°C
Solubility at 20°C	Easily soluble in low molecular mass alcohols and ketones, miscible in water
Refractive Index at 25°C	1.4366

2.1.3 Membranes

All tested membranes are novel pervaporation membranes developed by Pervatech B.V. Pervatech B.V. offers hydrophilic membranes on ceramic substrate, hydrophilic Hybrid Silica membranes and organophilic membranes on a polymeric or ceramic substrate. The company's core activities are the development and production of ceramic membranes for both hydrophilic and organophilic separation processes. Through scientific co-operations with leading universities and institutions they develop today's and tomorrow's pervaporative membranes with superior characteristics. Improved membranes result in lower energy consumption, lower waste streams and higher product quality. Pervatech says their membranes are stable in dehydration of organic solvents with relative high water concentrations at high temperatures, in (a)protic solvents and in the presence of acids and can be used both in stand-alone solutions and in add-on hybrid systems. The following chapters will discuss the properties of the specific membranes. The datasheets of the membranes are attached in the appendix chapter 7.3. Membrane Datasheets, p.77.

2.1.3.1 HybSi Standard, HybSi Dense, HybSi Open

Table 5 shows the characteristics of the HybSi Membranes. Hybrid Silica AR Membranes have hydrophilic characteristics, meaning that the water content of the feed passes preferentially through the membrane. According to manufacturer specification the main advantages of the Pervatech hydrophilic Hybrid Silica membranes are energy saving, perfect azeotrope separation, decrease usage if cooling water, enhanced product quality through milder conditions, reduced formation of side products, higher plant availability, chemical resistance and stability up to high temperatures. The HybSi membranes differ in their distribution of the pore sizes. They all have pores from 0.3-0.5 nm, in which the HybSi dense membrane has more small pores, the HybSi Standard membrane is midway and the HybSi open membrane has more big pores.

Table 5: Characteristics of HybSi Membranes

Membrane Construction	
Pore Size	0.3- 0.5 nm
Size	1-channel tube 250 x 10 x 7 mm, effective area 0.005 m²
Substrate material	α-Al_2O_3
Top layer	Hybrid Silica AR
Coating position	Inside of the tube
Limits of Operation	
Temperature	150°C
Pressure	max. 10 bar
pH	0.5-8.5

2.1.3.2 Optimised Silica

Table 6 shows the characteristics of the Optimised Silica membranes. Optimised Silica membranes have hydrophilic characteristics. They have an Optimised Silica coating the inside of the support tube. Possible applications for the Optimised Silica membrane are breaking of azeotrope, removal of water from organics, in situ dehydration of condensation reactions, dehydration of essential oils and separation of low molecular weight from higher molecular weight solvents.

Table 6: Characteristics of Optimised Silica Membrane

Membrane Construction	
Pore Size	0.3-0.5 nm
Size	1-channel tube: 250 x 10 x 7 mm, effective area 0.005 m²
Substrate material	α-Al_2O_3
Intermediate layer	Gamma alumina
Top layer	Optimised Silica coating the inside of the support tube
Limits of Operation	
Temperature	95°C
Pressure	max. 10 bar
pH	2-8

2.1.3.3 PDMS

Table 7 shows the characteristics of the PDMS (Poly Di Methyl Siloxane) membrane. PDMS membranes have hydrophobic/organophilic characteristics, in which the organic constituent of the feed passes preferentially through the membrane. The main advantages of the Pervatech organophilic membranes are that they are selective for high value products like aromas, flavours and fragrances, they increase the efficiency of fermentation processes and are stable up to high temperatures and broad pH range. Pervatech also mentions the possible combination of the PDMS membrane with bioreactors in production of alcohols. The PDMS membrane must be stored in a solution of water and 10-5% isopropyl alcohol, or water with 2500 ppm sodium meta bisulphite after use.

Table 7: Characteristics of PDMS Membrane

PDMS Membrane	
Size	1-channel tube 250 x 10 x 7 mm, effective area 0.005 m²
Substrate material	α-Al_2O_3
Top layer	Poly Di Methyl Siloxane
Coating position	Inside of the tube
Limits of Operation	
Temperature	70°C (short-term 80°C)
Pressure	max. 10 bar
pH	1-12

(http://pervaporation-membranes.com/products/membranes/ accessed June 13, 2018).

2.2 Methods

2.2.1 Experimental Setup and Performance

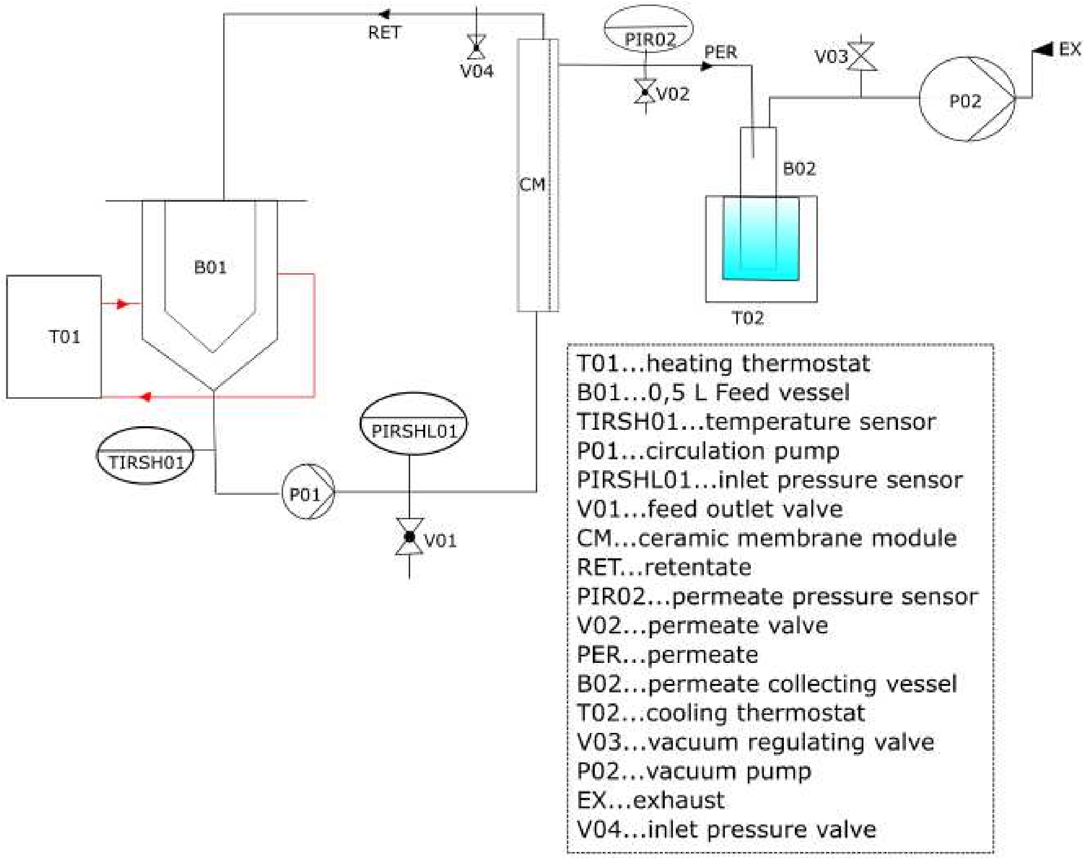

Figure 5: Experimental Setup of VapoMem Pervaporation Construction

The experimental setup of the VapoMem pervaporation construction is shown in figure 5. To start-up the experiment the membrane is fixed into the membrane module. The cooling system for the cooling trap is switched on and checked for the right adjustment of -20°C. The cooling trap is scaled with caps and the weight is noted as TARA. Once these preparations are completed, the cooling trap is put into the cooling system and connected to the vacuum pump and the permeate tube.

After that, the feed solution needs to be mixed. With a scale and a pipette, the chemicals are weighed to the desired concentration. When the mixture is filled into the feed vessel, the feed-heating system is switched on to the desired temperature. At this step, temperature differences between the heating system adjustment and the real feed temperature can occur. This is because the circulation pump is heating up during the experiment. To hold the desired feed temperature, the temperature of the feed-heating system must be adapted during the experiment. The VapoMem can also be switched on. It takes a few minutes for the cooling trap system to cool down and the feed to heat up, so the temperatures are constant when the experiment starts. Then the vacuum pump is switched on and the permeate valve is opened. At this stage the circulation pump is slowly turned up until it reaches the maximum. Now the inlet pressure is adjusted to 3bar and the permeate pressure to 20mbar. When all adjustments are constant, the experiment has started. It is important to note the time of the start and the end of the experiment. To stop the experiment, the permeate valve is closed and the circulation pump turned off. The cooling trap is disconnected from the vacuum pump and closed with some caps. Any silicone oil or moisture must be removed from the cooling trap before scaling. The weight is written down to determine the permeate mass. Finally, the permeate composition can be analysed.

2.2.2 Determination of Flux

The flux describes the mass of permeate [kg], permeating the membrane surface [m²] in a specific time [h]. It is determined to predict which factors influence how fast the separation process can pass off.

$$J = \frac{m}{A \cdot t}$$

J…flux [kg/m²h]

m…permeate mass [kg]

The permeate mass was determined by subtracting the weight of the empty cooling trap from the weight of the cooling trap containing the permeate.

A…membrane surface [m²]

The membrane surface value was taken from manufacturer information. For each membrane, the membrane surface is 0.005 m².

t…test duration [h]

The approximate test duration is recorded manually. The exact test duration is determined by the period of the constant inlet and permeate pressure during one experiment. Time, inlet pressure and permeate pressure are recorded by the VapoMem pervaporation construction at an interval of 30 seconds.

2.2.3 Determination of Permeate Composition

The permeate composition was determined with the refractive index and gas chromatography. The refractometer was calibrated with mixtures of MEK / H_2O, MEK / BD and BD / H_2O in different concentrations (see table 8). The formulas of the calibration graphs are shown in table 9. Some permeates could not be analysed with the refractive index because they showed phase separation due to the miscibility gap of MEK. The permeates of the ternary mixture with MEK / BD / H_2O were also not analysed with refractive index, because the refractometer could not be calibrated for this mixture. The composition of the feed mixture before and after the experiment was analysed with gas chromatography instead. The difference between the concentrations in the feed mixtures before and after the experiment showed how much of each chemical has permeated into the cooling trap. The gas chromatography samples were submitted for analysis to an internal subdivision.

Table 8: Composition of Mixtures for Calibration of Refractometer

BD in H_2O [wt.%]	nD [20°C]	MEK in H_2O [wt.%]	nD [20°C]	BD in MEK [wt.%]	nD [20°C]
0	1.3315	0	1.3320	10	1.3825
20	1.3560	5	1.3355	30	1.3935
40	1.3810	10	1.3395	50	1.4050
60	1.4035	15	1.3430	70	1.4170
80	1.4215	20	1.3460	90	1.4295
100	1.4350	-	-	100	1.4345

Table 9: Calibration of Refractometer

Mixture	Formula Calibration Graph	R^2 Calibration Graph
BD in H_2O	y = 0.0011x + 1.3355	0.9888
MEK in H_2O	y = 0.0007x + 1.3321	0.9968
BD in MEK	y = 0.0006x + 1.3771	0.9986

2.2.4 Determination of Selectivity

The selectivity is unitless and shows the ratio of preferential and discriminated component in feed and permeate. It shows the ability of the membrane to differ from the components of a mixture.

$$S_{ij}\big|_W = \frac{w_{iP} \,/\, w_{jP}}{w_{iF} \,/\, w_{jF}}$$

$S_{ij}|_W$…selectivity

w_{iP}…weight percent of preferential component in permeate

w_{jP}…weight percent of discriminated component in permeate

w_{iF}…weight percent of preferential component in feed

w_{jF}…weight percent of discriminated component in feed

2.2.5 Determination of Rejection Coefficient

The rejection coefficient is another unitless measure for the separation effect of the membrane. It shows how good a component is retained from a membrane. The membrane is completely impermeable when **R_i**= 1.

$$R_i = \frac{w_{iF} - w_{iP}}{w_{iF}} = 1 - \frac{w_{iP}}{w_{iF}}$$

R_i…rejection coefficient

2.2.6 Membrane Screening for Membrane Selection

To create an experimental design, some suitable membranes need to be chosen. To facilitate the selection of one suitable membrane for each separation step, some “trial and error” tests with different membranes were undertaken. The membrane screening was conducted to get an appreciation for the flux and selectivity of the membranes. For all membrane screening tests, the constant process parameters in table 10 were used. The tests were undertaken with feed compositions of 10% MEK / 90% H2O, 100% MEK and 50% MEK / 50% BD. The tested membranes are shown in table 11.

Table 10: Constant Process Parameters for Membrane Screening

Constant Process Parameters	
Inlet pressure	3bar
Permeate pressure	20mbar
Pump speed	3 L/min
Temperature of cooling trap	-20°C
Feed Temperature	50°C

Table 11: Membrane Screening Tests

Feed Composition	Tested Membranes
10% MEK / 90% H_2O	• HybSi standard • HybSi open • HybSi dense • Optimised Silica • PDMS
100% MEK	• HybSi standard • HybSi open • PDMS
50% MEK / 50% BD	• HybSi standard • HybSi open • PDMS • Optimised Silica

2.2.7 Design of Experiments

Design of Experiment (DoE) is a method for the design and statistical analysis of experiments. The aim of DoE is to learn as much as possible about the correlation between influencing parameters and results with the least possible effort. Information gained with DoE is statistically verified and the effects of input variables and their interactions can be quantified. The experiments were designed with the statistic program “Statgraphics”. The response surface design was chosen and three-level factorial designs were created: 3^2 designs which will study the effects of two factors in eleven runs. These design settings were chosen for all the separation steps.

Each design of experiment is to be run in a single block. The order of the experiments has been fully randomized. This provides protection against the effects of lurking variables. The variable adjustments or factors are feed composition and feed temperature. The responses are flux, selectivity and rejection coefficient. For each experiment the constant adjustments shown in table 12 were chosen. To show the standardized effect of the factors on the responses flux, selectivity and rejection coefficient, a standardized pareto chart was created for each response. The statistical significance of the effects was tested with ANOVA (see appendix, chapter 7.2. Analysis of variance (ANOVA) for Design of Experiment, p.61.)

Table 12: Constant Process Parameters for Design of Experiment

Inlet pressure	3bar
Permeate pressure	20mbar
Pump speed	3 L/min
Temperature of cooling trap	-20°C
Test duration	~ 2 h

2.2.7.1 Design of Experiment for Separation Step 1: BD / H_2O

The experimental design for separation step 1: BD / H_2O is shown in figure 6. The experiments are undertaken with the Optimised Silica membrane. The variable process parameters (see table 13) are the concentration of BD in the feed, with amounts between 0.5 wt.% and 2.5 wt.%, and the feed temperature from 25°C to 75°C. For the innovative production of MEK, a BD concentration of 25 g/L in the fermentation broth is pursued. That's why a maximum BD concentration of 2.5 wt.% in the feed was chosen for the experiments.

Table 13: Variable Process Parameters for Design of Experiment of Separation Step 1: BD / H_2O

Membrane	Optimised Silica
Experimental Design	Response Surface
Feed composition	0.5 – 2.5 wt.% BD in H_2O
Feed Temperature	25-75°C

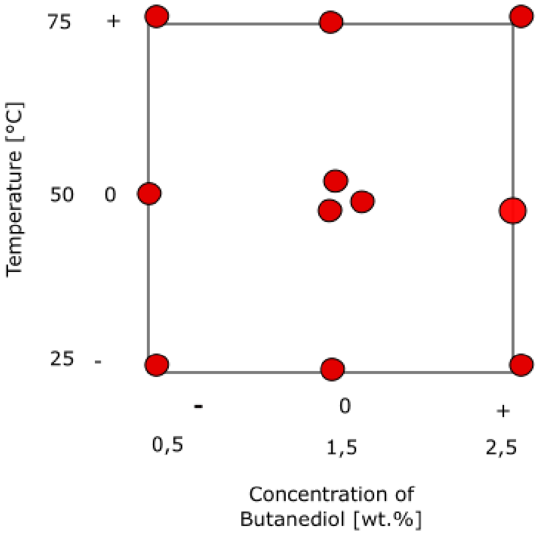

Figure 6: Experimental Design for Separation Step 1: BD / H_2O – the red dots show the testing points, a 3^2 response surface design with eleven testing points, including three central points

2.2.7.2 Design of Experiment for Separation Step 2: MEK / BD

The experimental design for separation step 2: MEK / BD is shown in figure 7. The experiments are undertaken with the PDMS membrane. The variable process parameters (see table 14) are the concentration of MEK in the feed, with amounts between 25 wt.% and 75 wt.%, and the feed temperature from 25°C to 55°C. The maximum temperature for the PDMS membrane is lower, because earlier tests showed decreasing selectivity at temperatures above 55°C.

Table 14: Variable Process Parameters for Design of Experiment of Separation Step 2: MEK / BD

Membrane	PDMS
Experimental Design	Response Surface
Feed composition	25-75% MEK in BD
Temperature	25-55°C

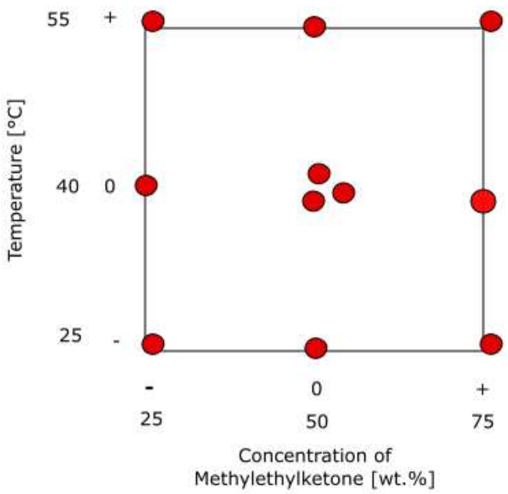

Figure 7: Experimental Design for Separation Step 2: MEK / BD – the red dots show the testing points, a 3^2 response surface design with eleven testing points, including three central points

2.2.7.3 Design of Experiment for Separation Step 3: MEK / BD / H_2O

The experimental design for separation step 3: MEK / BD / H_2O is shown in figure 8. The experiments are undertaken with the PDMS membrane. The variable process parameters (see table 15) are the concentration of MEK in the feed, with amounts between 1 wt.% and 5 wt.%, and a feed temperature from 25°C to 55°C. In this experiment, the concentration of BD was held constant because a previous experiment (see appendix chapter 7.1 Design of Experiment for Separation Step 3: MEK / BD / H_2O – BD variable, p.55) showed that varying the concentration of BD has no effect on the examined parameters.

Table 15: Variable Process Parameters for Design of Experiment of Separation Step 3: MEK / BD / H_2O

Membrane	PDMS
Experimental Design	Response Surface
Feed composition	1-5% MEK and 1.5 % BD in H_2O
Temperature	25-55°C

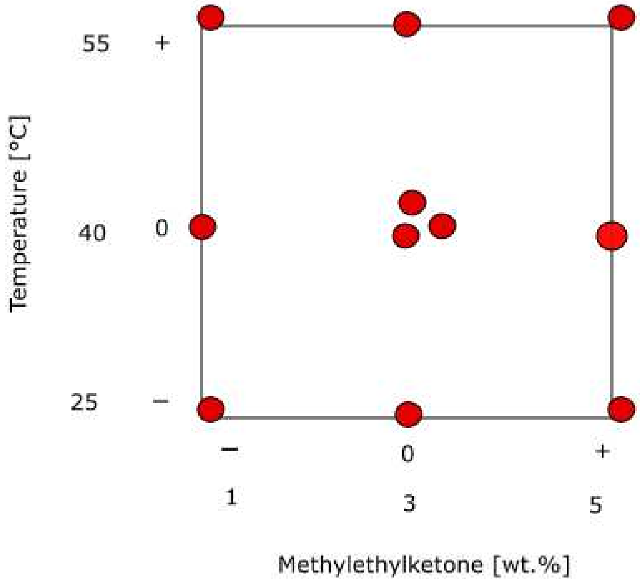

Figure 8: Experimental Design for Separation Step 3: MEK / BD / H_2O – the red dots show the testing points, a 3^2 response surface design with eleven testing points, including three central points

2.2.7.4 Design of Experiment for Separation Step 4: MEK / H_2O

The experimental design for separation step 4: MEK and water is shown in figure 9. The experiments are undertaken with the Optimised Silica membrane. This separation step is supposed to separate remaining water from MEK after the separation of the ternary mixture. The variable process parameters (see table 16) are the concentration of MEK in the feed, with amounts between 5 wt.% and 15 wt.%, and a feed temperature from 25°C to 75°C. Although higher amounts of MEK are expected after the separation from the ternary mixture, concentrations higher than 15 wt.% MEK were not used because of the limited solubility of MEK in water.

Table 16: Variable Process Parameters for Design of Experiment of Separation Step 4: MEK / H_2O

Membrane	Optimised Silica
Experimental Design	Response Surface
Feed composition	5-15% MEK in H_2O
Temperature	25-75°C

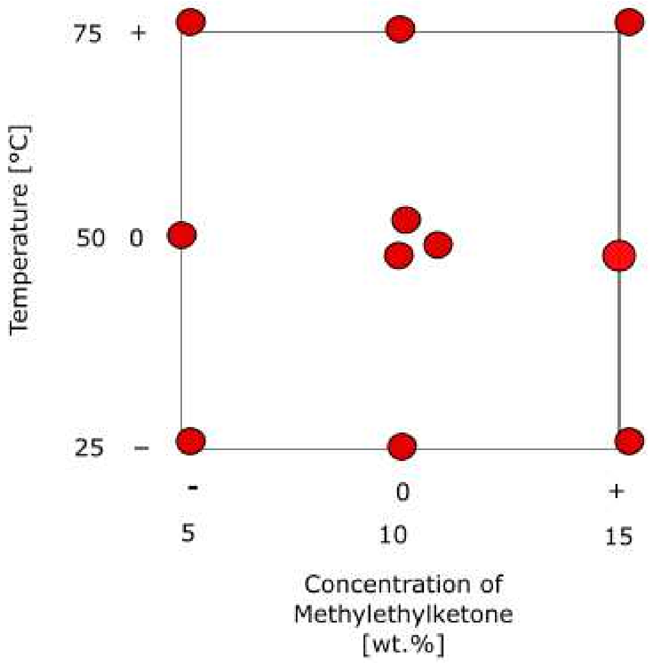

Figure 9: Experimental Design for Separation Step 4: MEK / H_2O – the red dots show the testing points, a 3^2 response surface design with eleven testing points, including three central points

3. Results

3.1 Results of Membrane Screening

To find a suitable membrane for the experimental design of each separation step, a membrane screening was undertaken. The membranes HybSi Standard, HybSi Open, HybSi Dense, Optimised Silica and PDMS were screened with compositions of 10% MEK / 90% H20, 100% MEK and 50% MEK / 50% BD. The screening was operated with the constant adjustments shown in Table 10, page 19. Table 17 shows which membranes were chosen for the design of experiment after the membrane screening.

Table 17: Chosen Membranes for Design of Experiment

Separation Step	Chosen Membranes
1: BD / H_2O	Optimised Silica Membrane
2: MEK / BD	PDMS Membrane
3: MEK / BD / H_2O	PDMS Membrane
4: MEK / H_2O	Optimised Silica Membrane

3.1.1 Results of Membrane Screening: Separation Step 1 – BD / H_2O

The results of membrane screening for separation step 2 – MEK / BD show, that none of the membranes is permeable for BD. This means, that BD must be treated as retentate. As BD was meant to be treated as permeate, the hypothetical serial process is not possible as planned. The results of membrane screening for separation step 4 – MEK / H_2O show, that the Optimised Silica membrane has the highest flux for water. Therefore, the Optimised Silica membrane is chosen to separate water from BD. As the results of the other membrane screening tests already showed that the Optimised Silica membrane is suitable for the separation of BD / H_2O, there was no extra screening conducted for separation step 1 – BD / H_2O.

3.1.2 Results of Membrane Screening: Separation Step 2 – MEK / BD

Table 18 and figure 10 show the results of membrane screening for the separation 2 – MEK / BD. The PDMS membrane is suitable for further tests for this separation step. It reached a flux of 3.71 kg/m²h and a permeate purity of 96.28 wt.% MEK. Selectivity should be improvable with adaption of temperature. The other membranes are not suitable because of much lower flux rates, due to hydrophilic characteristics.

Table 18: Results of Membrane Screening for the Separation of MEK / BD

Membrane	Flux [kg/m²h]	Permeate Purity [wt. % MEK]	Temperature [°C]
HybSi Standard	0.46	97 %	50.97
HybSi Open	0.08	100%	51.10
PDMS	3.71	96%	52.90
Optimised Silica	0.42	100%	51.90

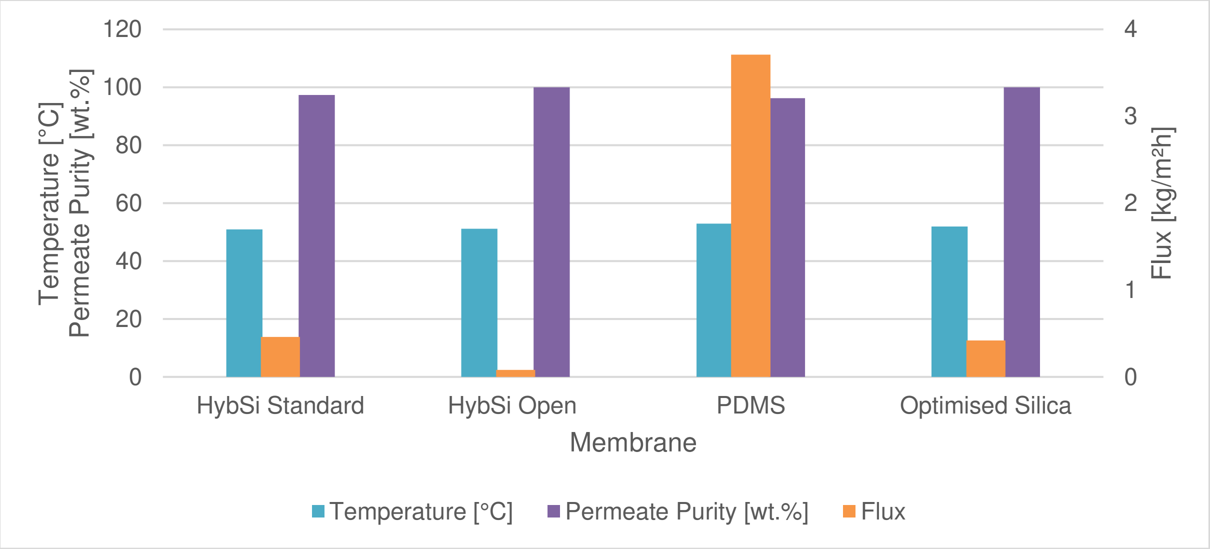

Figure 10: Results of membrane screening for the separation of MEK / BD – The PDMS membrane shows the best result with a flux of 3.71 kg/m²h and 96.28 wt.% permeate purity

3.1.3 Results of Membrane Screening: Separation Step 3 – MEK / BD / H_2O

As the results of separation step 2 – MEK / BD show, the PDMS membrane has the highest flux when separating MEK from BD. The results of membrane screening for separation step 4 – MEK / H_2O show, that the PDMS membrane is permeable for water. Therefore, two separation steps are required for separation step 3 – MEK / BD / H_2O. First, MEK and H_2O can be separated from BD with the PDMS membrane. In the second step, MEK can be purified by separating remaining water with the Optimised Silica Membrane. As shown in the results of membrane screening for separation step 4: MEK / H_2O, with a flux of 3.83 kg/m²h and 100% permeate purity, the Optimised Silica Membrane turned out to fit the separation of MEK and water. There was no extra membrane screening conducted for the separation step 3 – MEK / BD / H_2O because the other membrane screening tests showed, that the PDMS membrane and the Optimised Silica membrane are suitable for separation step 3 -– MEK / BD / H_2O.

3.1.4 Results of Membrane Screening: Separation Step 4 – MEK / H_2O

Table 19 and figure 11 show the results of membrane screening for the separation step 4 – MEK / H_2O. The results show that the Optimised Silica Membrane achieved the second highest flux with 3.83 kg/m²h and 100 wt.% permeate purity. As the Optimised Silica membrane is a hydrophilic membrane, the permeate is water. The organophilic PDMS membrane showed the highest flux with 4.79 kg/m²h, but only 65 wt.% permeate purity. That is why the Optimised Silica membrane is chosen for further tests for the separation of water from MEK despite MEK being preferred as a permeate.

Table 19: Results of Membrane Screening for the Separation of 10% MEK / 90% H_2O

Membrane	Flux [kg/m²h]	Permeate Purity [wt. %]	Temperature [°C]
HybSi Standard	1.33	99% H_2O	52.23
HybSi Open	3.55	100% H_2O	51.43
PDMS	4.79	65% MEK	50.10
Optimised Silica	3.83	100% H_2O	52.23
HybSi Dense	1.20	100% H_2O	52.80

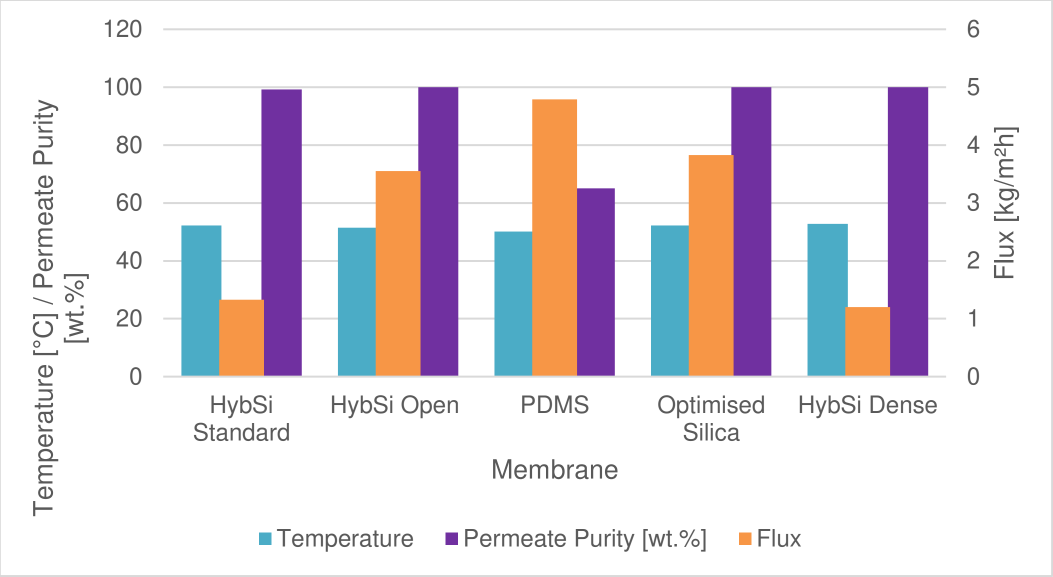

Figure 11: Results of Membrane Screening for the Separation of MEK / H_2O – The Optimised Silica Membrane shows a flux of 3.83 kg/m²h at 100% permeate purity.

3.1.5 Results of Membrane Screening: Permeability of MEK

Table 20 and figure 12 show the results of membrane screening for the permeability of MEK. The membrane screening showed that the PDMS membrane has the best permeability for MEK from all membranes. The PDMS membrane showed a flux of 26.45 kg/m²h and 100 wt.% permeate purity at 50°C. The flux is more than 5 times higher than the flux of the PDMS membrane in the separation step 4 - MEK / H_2O. This result indicates, that the flux is rising with higher concentration of MEK in the feed. Because the HybSi membranes have hydrophilic characteristics, they show a very low flux (0.6 and 0.25 kg/m²h) with MEK as feed components. The permeate of the HybSi Open membrane contains water, which is lead back to remaining humidity in the membrane. In the future, the membrane should be washed with the feed component beforehand. The HybSi dense and Optimised Silica membrane were not tested in this separation step, because separation step 4 - MEK / H_2O showed that these two membranes are not permeable for MEK.

Table 20: Results of Membrane Screening for the Permeability of MEK

Membrane	Flux [kg/m²h]	Permeate Purity [wt. %]	Temperature [°C]
HybSi Standard	0.60	100% MEK	51.70
HybSi Open	0.25	23% MEK	51.17
PDMS	26.45	100% MEK	50.78

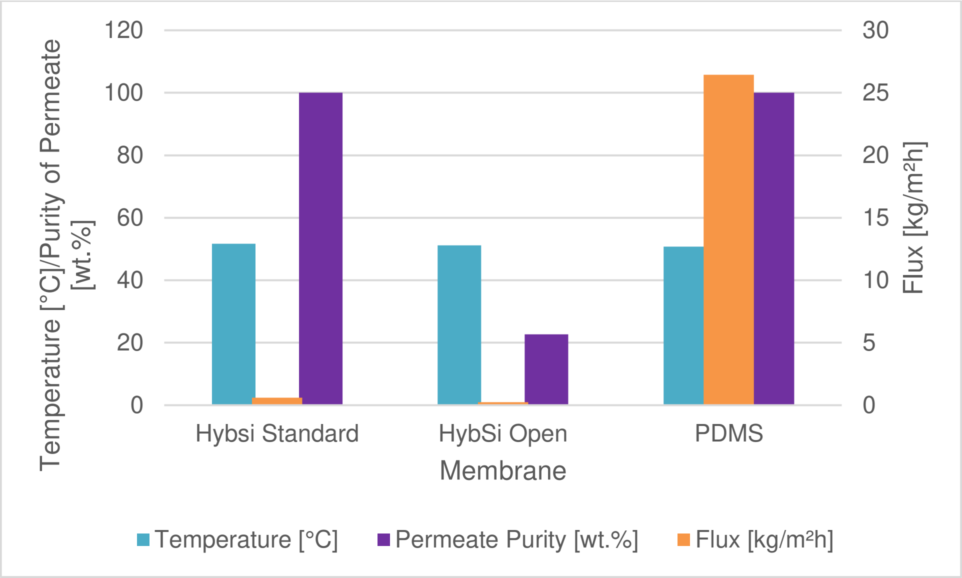

Figure 12: Results of Membrane Screening for the Permeability of MEK – With a flux of 26,45 kg/m²h and 100 wt.% MEK permeate purity, the PDMS membrane has the best permeability for MEK.

3.2 Results of Design of Experiment (DoE)

An experimental design for each separation step was created as shown in chapter 2.2.7, p. 22-25 Design of Experiment. The constant adjustments for the experiments are shown in table 12, p. 21. The analysis of permeate composition and calculation of flux, selectivity and rejection coefficient were conducted as shown in chapter 2.2 methods. To show the standardized effect of the factors on the responses flux, selectivity and rejection coefficient, a standardized pareto chart was created for each response. The statistical significance of the effects was tested with ANOVA (see appendix chapter 7.2. Analysis of Variance (ANOVA) for Design of Experiment, p.61).

3.2.1 Results for Design of Experiment: Separation Step 1 – BD / H_2O

The experimental design for the separation step of BD and water was undertaken with the Optimised Silica membrane. The variable factors are the concentration of BD in the feed, with amounts between 0.5 wt.% and 2.5 wt.%, and the feed temperature from 25°C to 75°C. Table 21 shows the data for statistical analysis in statgraphics for the separation step 1 – BD / H_2O. As the results show, the membrane was not permeable for BD and water was not rejected. That’s why the values for selectivity and rejection coefficient are all equal and therefore couldn’t be used for statistical analysis.

Table 21: Data for Statistical Analysis of Separation Step 1 – BD / H_2O

Experiment	**Concentration of BD in Feed**	**Temperature**	**Flux**	**H_2O in Permeate**	**Selectivity**	**Rejection Coefficient BD**	**Rejection Coefficient H_2O**
	[wt.%]	**[°C]**	**[kg/m²h]**	**[wt.%]**			
1	0.50	24.8	0.32	100%	∞	1.00	0.00
2	0.50	51.1	3.75	100%	∞	1.00	0.00
3	2.66	24.7	0.32	100%	∞	1.00	0.00
4	2.56	74.2	11.42	100%	∞	1.00	0.00
5	1.51	51.4	2.79	100%	∞	1.00	0.00
6	1.51	50.8	4.05	100%	∞	1.00	0.00
7	0.50	75.0	12.59	100%	∞	1.00	0.00
8	1.50	50.2	4.13	100%	∞	1.00	0.00
9	1.50	24.8	0.41	100%	∞	1.00	0.00
10	1.51	75.1	13.25	100%	∞	1.00	0.00
11	2.51	50.6	4.36	100%	∞	1.00	0.00

3.2.1.1 Results for Design of Experiment: Separation Step 1 – BD / H_2O – Flux

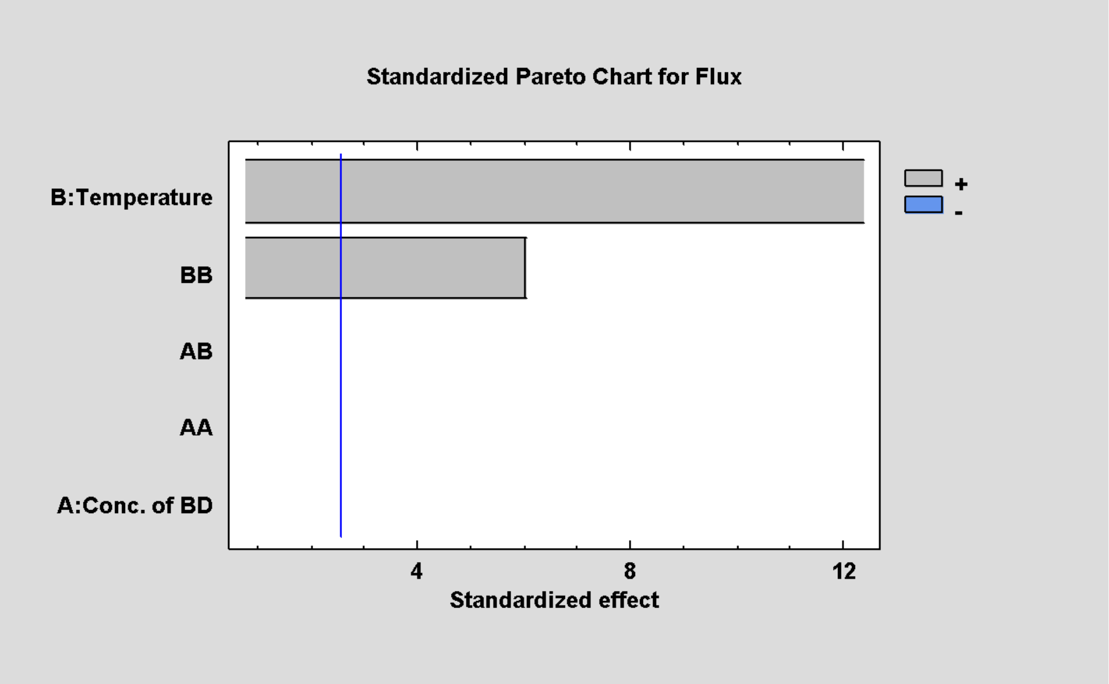

Figure 13: Standardized Pareto Chart for Flux – the figure shows the standardized effect of factor B: Temperature and factor A: Concentration of BD on the response flux for the separation step 1 – BD / H_2O.

To show the standardized effect of the factors on the response flux in the separation step BD / H_2O, a Standardized Pareto Chart was created (see figure 13). It shows the effect of the factors feed temperature and concentration of BD in the feed. The significant standardized effects on flux are as follows:

- Effect B, temperature: 19.75
- Effect BB, the quadratic effect of temperature: 6.02

That means, that the flux is rising with increasing feed temperature. The highest flux achieved is 13.25 kg/m²h at 75.1 °C and 1.51 wt.% BD. Effect A, concentration of BD, has no significant effect on flux. There is also no significant interaction between factor A and B. The statistical significance of the effects was tested with ANOVA (see appendix chapter 7.2. Analysis of Variance (ANOVA) for Design of Experiment, p.61). In this case the effect of temperature and the quadratic effect of temperature have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

3.2.2 Results for Design of Experiment: Separation Step 2 – MEK / BD

The experimental design for the separation step of MEK and BD was undertaken with the PDMS membrane. The variable factors are the concentration of MEK in the feed, with amounts between 25 wt.% and 75 wt.%, and the feed temperature from 25°C to 55°C. Table 22 shows the data for statistical analysis in statgraphics for the separation step 2 – MEK / BD. As the results show, BD was not completely rejected from the PDMS membrane. The negative rejection coefficient MEK means, that the concentration of MEK in the permeate is higher than in the feed. The results of selectivity suggest that a rising concentration of MEK has a negative effect on the selectivity, because the highest selectivity was achieved at the lowest MEK concentration.

Table 22: Data for Statistical Analysis of Separation Step 2 – MEK / BD

Experiment	**Concentration of MEK in Feed**	**Temperature**	**Flux**	**MEK in Permeate**	**Selectivity**	**Rejection Coefficient MEK**	**Rejection Coefficient BD**
	[wt.%]	**[°C]**	**[kg/m²h]**	**[wt.%]**			
1	75.01	55.8	7.84	96.83	10.2	-0.29	0.87
2	49.96	41.4	1.29	95.17	19.7	-0.90	0.90
3	50.13	25.2	0.14	96.83	30.4	-0.93	0.94
4	50.02	57.7	3.15	96.83	30.6	-0.94	0.94
5	50.07	40.6	1.80	96.83	30.5	-0.93	0.94
6	74.93	25.4	1.35	96.83	10.2	-0.29	0.87
7	24.91	25.5	0.15	99.33	449.3	-2.99	0.99
8	24.85	41.5	0.40	99.33	450.7	-3.00	0.99
9	50.08	40.0	1.71	96.83	30.5	-0.93	0.94
10	25.18	57.0	0.82	99.33	442.7	-2.94	0.99
11	75.07	40.6	4.52	98.50	21.8	-0.31	0.94

3.2.2.1 Results for Design of Experiment: Separation Step 2 – MEK / BD – Flux

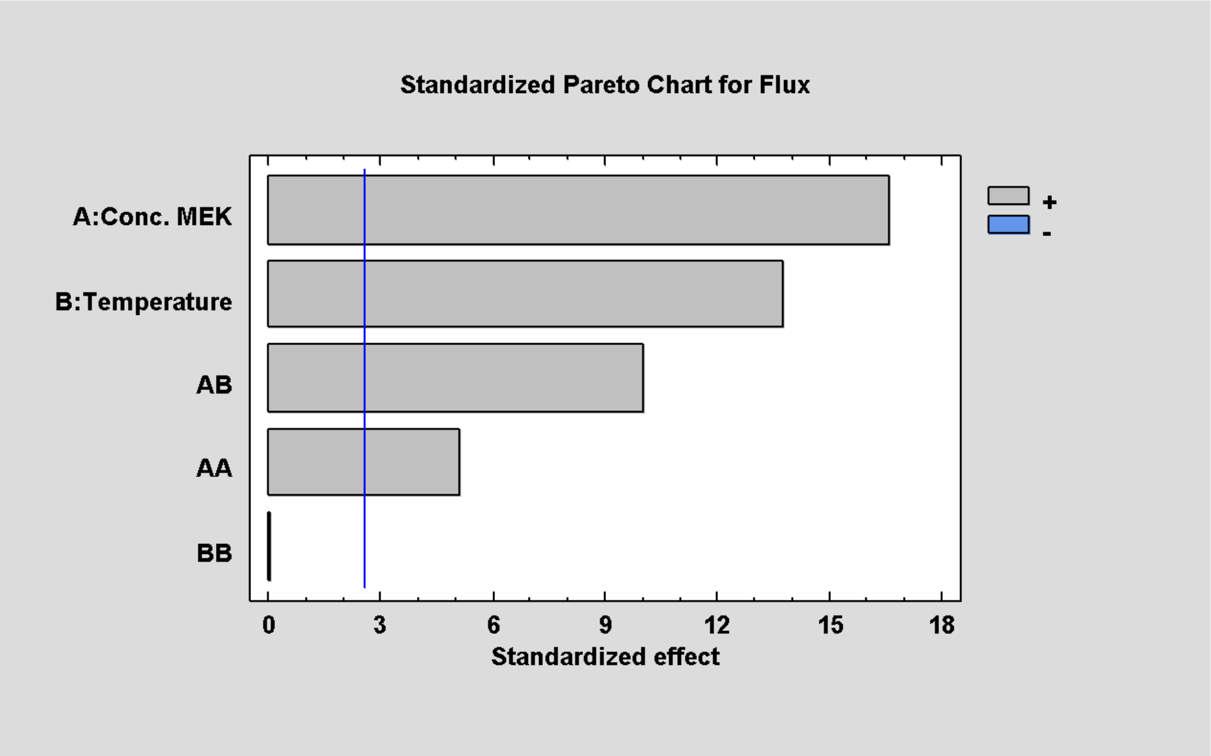

Figure 14: Standardized Pareto Chart for Flux - the figure shows the standardized effect of factor A: Concentration of MEK and factor B: Temperature on the response flux in the separation step 2 – MEK / BD

Figure 14 shows the effect of the factors feed temperature and concentration of MEK in the feed on the response flux. The significant standardized effects on flux are:

- effect A, Concentration of MEK: 16.61
- effect AA, the quadratic effect of concentration of MEK: 5.08
- effect B, temperature: 13.76
- effect AB, interaction between concentration of MEK and temperature: 10.02

The factor BB: quadratic effect of temperature has no significant effect on flux. This means that the flux is rising with higher temperature and concentration of MEK in the feed. The highest achieved flux is 7.84 kg/m²h at 55.8°C and 75.01 wt.% MEK. There is also a significant positive interaction between temperature and concentration of MEK. The effects A, AA, B and AB have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

3.2.2.2 Results for Design of Experiment: Separation Step 2 – MEK / BD – Selectivity

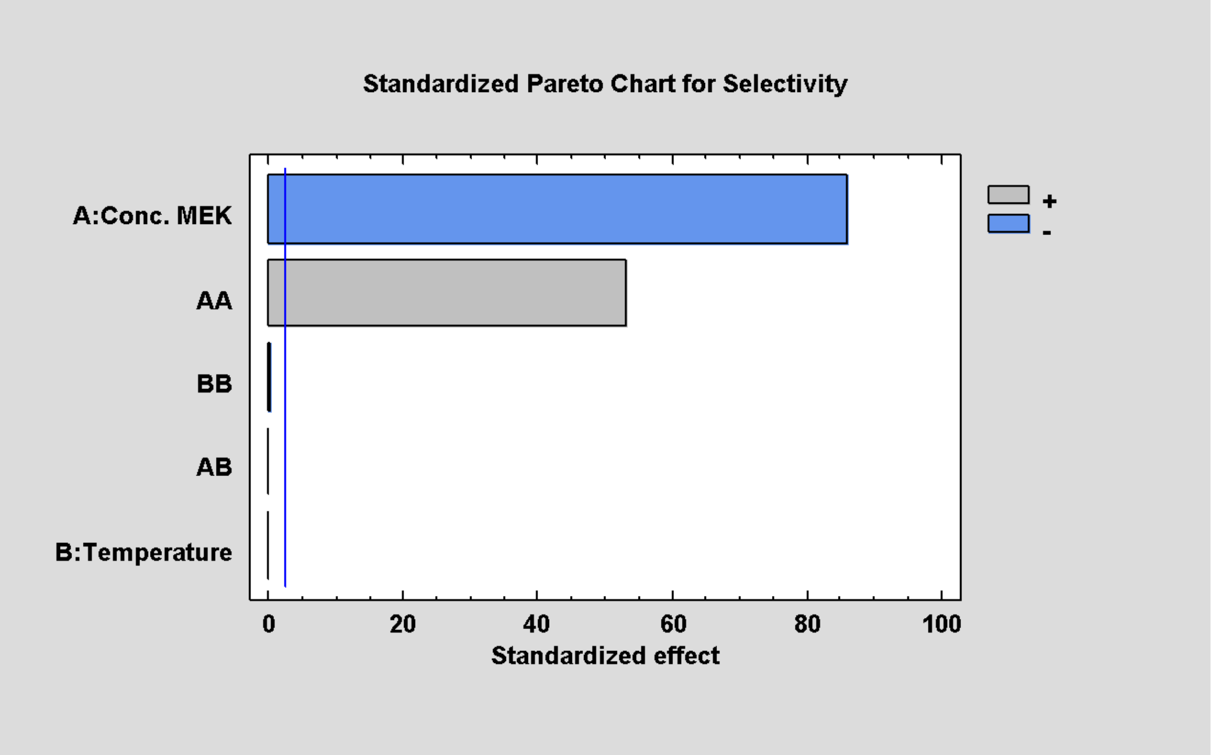

Figure 15: Standardized Pareto Chart for Selectivity - the figure shows the standardized effect of factor A: Concentration of methyl ethyl ketone and factor B: Temperature, on the response selectivity in the separation step 2: MEK/BD

To show the standardized effect of the factors on the response selectivity in the separation step MEK/ BD a Standardized Pareto Chart was created (see figure 15). It shows the effect of the factors feed temperature and concentration of MEK in the feed. The significant standardized effects on selectivity are:

- A, concentration of MEK: -86.08
- AA, quadratic effect of concentration of MEK: 53.11

That means that the selectivity significantly decreases with rising MEK concentration. The concentration of MEK in the permeate varied from 95.15 - 99.33 wt.%. The standard specification purity of min. 99.5 wt.% MEK was not achieved. B: temperature, BB: quadratic effect of temperature and AB: interaction between temperature and concentration of MEK show no significant effect on the selectivity. MEK concentration shows a positive quadratic effect on the selectivity. The temperature shows no significant effect on the selectivity. The statistical significance of the effects was tested with ANOVA (see appendix chapter 7.2. Analysis of Variance (ANOVA) for Design of Experiment, p.61). In this case the effect A, and AA have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

3.2.2.3 Results for Design of Experiment: Separation Step 2 – MEK / BD – Rejection Coefficient MEK

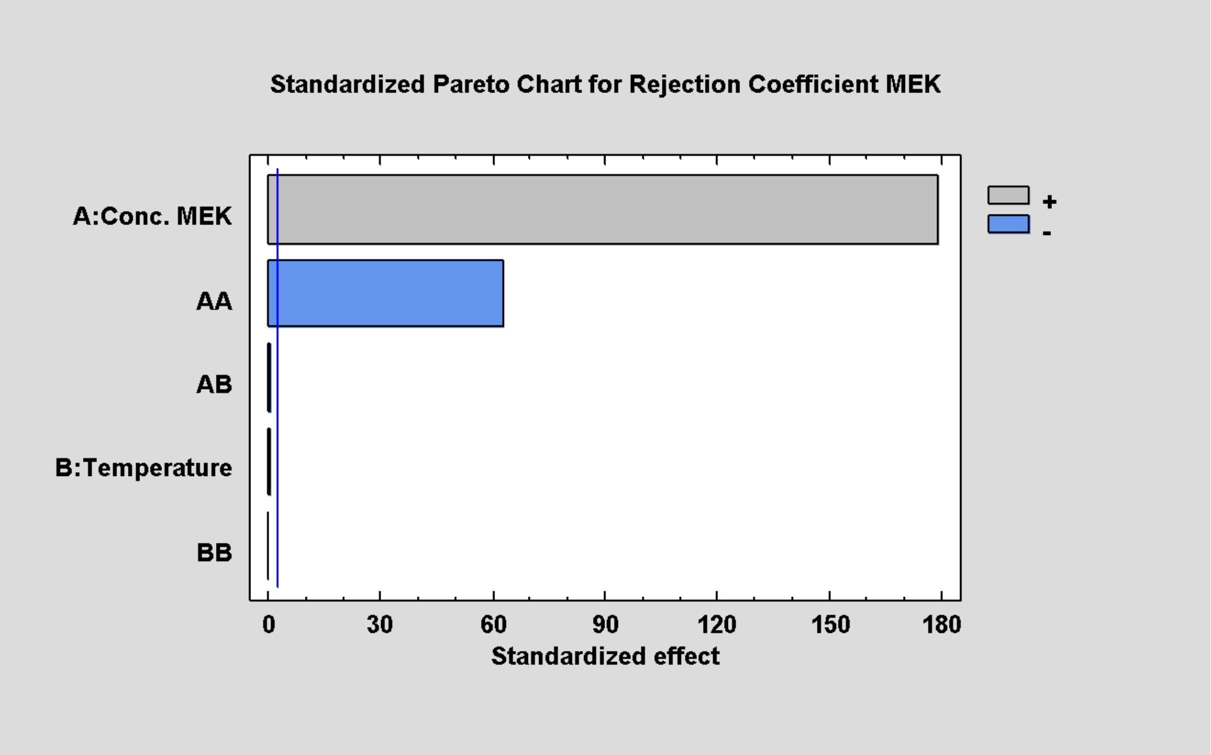

Figure 16: Standardized Pareto Chart for Rejection Coefficient MEK - the figure shows the standardized effect of factor A: Concentration of MEK and factor B: Temperature, on the response rejection coefficient MEK in the separation step MEK / BD

To show the standardized effect of the factors on the response rejection coefficient MEK in the separation step MEK/ BD a Standardized Pareto Chart was created (see figure 16). It shows the effect of the factors feed temperature and concentration of MEK in the feed. The significant standardized effects on rejection coefficient MEK are:

- A, concentration of MEK: 178.99
- AA, quadratic effect of concentration of methyl ethyl ketone: -62.51

That means that rejection coefficient MEK significantly rises with rising MEK concentration. Factor B: temperature, factor BB: quadratic effect of temperature and factor AB: interaction between temperature and concentration of MEK show no significant effect on the rejection coefficient MEK. MEK concentration shows a negative quadratic effect on the rejection coefficient MEK. The temperature shows no significant effect on the rejection coefficient MEK. The statistical significance of the effects was tested with ANOVA (see appendix chapter 7.2. Analysis of Variance (ANOVA) for Design of Experiment, p.61). In this case the effect A, and AA have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

3.2.2.4 Results for Design of Experiment: Separation Step 2 – MEK / BD – Rejection Coefficient BD

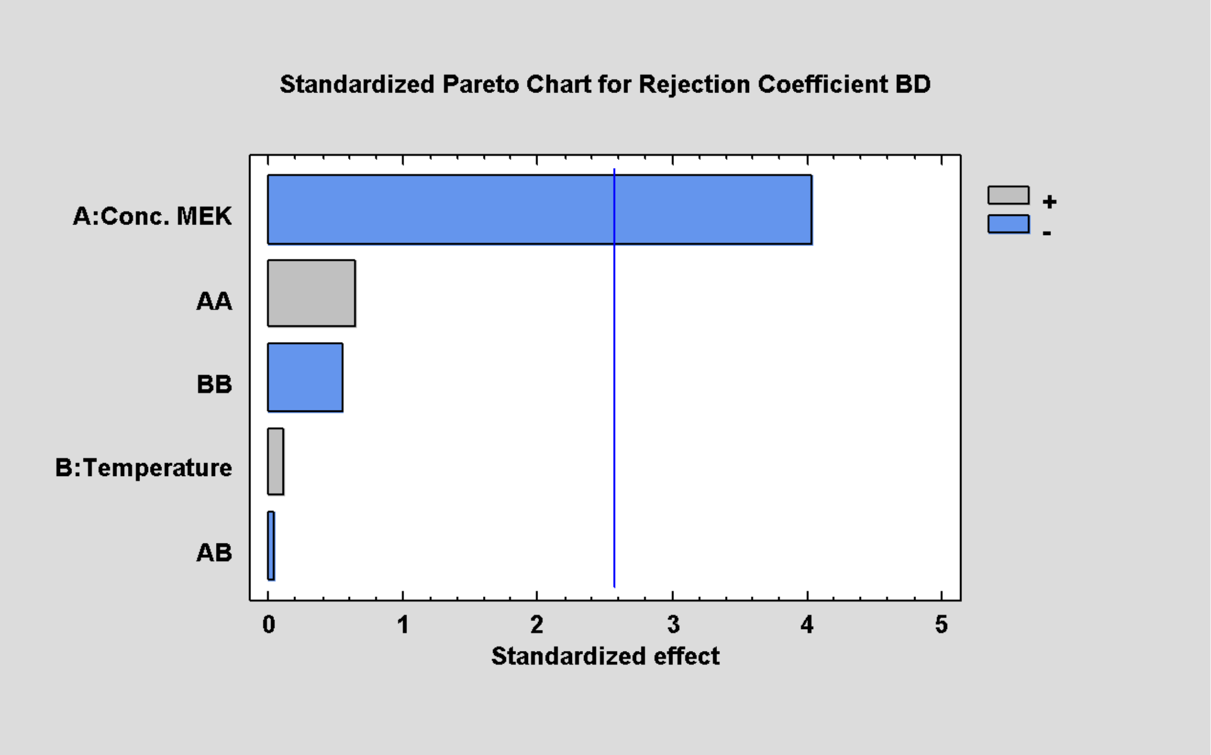

Figure 17: - Standardized Pareto Chart for Rejection Coefficient BD - the figure shows the standardized effect of factor A: Concentration of methyl ethyl ketone and factor B: Temperature, on the response rejection coefficient BD in the separation step MEK/BD

To show the standardized effect of the factors on the response rejection coefficient BD in the separation step MEK/ BD a Standardized Pareto Chart was created (see figure 17). It shows the effect of the factors feed temperature and concentration of MEK in the feed. The significant standardized effect on rejection coefficient BD is:

- A, concentration of MEK: -4.03

That means that rejection coefficient BD significantly decreases with rising MEK concentration. As already shown in the results for selectivity, a rising MEK concentration seems to promote the permeability of BD. Hence, the standard specification purity of 99.5 wt.% MEK was not achieved. According to the statistical evaluation of our results the temperature has no effect on selectivity or rejection coefficient. Still, the highest permeate purity of 99.33 wt.% MEK was achieved at 25.18, 24.91 and 24.85°C. Thus, the effect of temperature on selectivity and rejection coefficient should be studied further, to possibly enable higher purity of MEK.

Factor AA: quadratic effect of concentration of MEK, Factor B: temperature, factor BB: quadratic effect of temperature and factor AB: interaction between temperature and concentration of MEK show no significant effect on the rejection coefficient BD. The temperature shows no significant effect on the rejection coefficient MEK. There is no significant interaction between the effects. The statistical significance of the effects was tested with ANOVA (see appendix chapter 7.2. Analysis of Variance (ANOVA) for Design of Experiment, p.61). In this case the effect A has a P-value less than 0.05, indicating that it is significant. The other effects show no significance.

3.2.3 Results for Design of Experiment: Separation Step 3 – MEK / BD / H_2O

The experimental design for the separation step of MEK / BD / H_2O was undertaken with the PDMS membrane. The variable factors are the concentration of MEK in the feed and the feed temperature from 25°C to 55°C. Earlier tests showed that the concentration of BD has no effect on the examined parameters in this experiment (see appendix, chapter 7.1. Design of Experiment for Separation Step 3: MEK / BD / H_2O – BD variable, p.57), hence why the concentration of BD was held constant in this case. Table 23 shows the data for statistical analysis of separation step 3 – MEK / BD / H_2O. The negative rejection coefficient MEK means, that the concentration of MEK in the permeate is higher than in the feed. The rejection coefficient BD of experiment two and six is also negative, what means that the concentration of BD in the permeate is higher than in the feed. As experiment two and six have a concentration of 5 wt.% MEK in the feed, the results of rejection coefficient BD imply that a rising concentration of MEK has a negative effect on rejection coefficient BD.

Table 23: Data for Statistical Analysis of Separation Step 3 – MEK / BD / H_2O

Experiment	Concentration of MEK in Feed	Temperature	Flux	MEK Permeate	BD Permeate	Rejection Coefficient MEK	Rejection Coefficient BD	Selectivity MEK	Selectivity BD
	[wt.%]	[°C]	[kg/m²h]	[wt.%]	[wt.%]				
1	3.00	41.0	1.55	66.21	0.79	-16.31	0.25	49.27	0.75
2	5.20	24.9	1.05	98.28	2.48	-13.29	-1.29	772.20	2.36
3	1.10	25.5	0.21	40.74	0.11	-27.97	0.90	48.21	0.10
4	1.03	40.5	0.95	36.64	0.00	-26.03	1.00	42.08	0.00
5	3.10	40.3	1.29	84.40	0.42	-19.70	0.59	127.30	0.41
6	5.10	40.2	2.01	80.68	1.62	-12.04	-0.43	63.35	1.45
7	3.22	24.8	0.49	86.81	0.11	-21.57	0.89	164.52	0.11
8	3.14	40.4	1.46	69.83	0.23	-17.45	0.78	58.83	0.22
9	3.17	55.5	2.19	57.49	0.00	-14.65	1.00	35.46	0.00
10	1.05	55.0	1.67	25.79	0.00	-19.06	1.00	26.69	0.00
11	4.99	54.7	2.74	76.55	0.09	-11.56	0.91	50.30	0.09

3.2.3.1 Results for Design of Experiment: Separation Step 3 – MEK / BD / H_2O – Flux

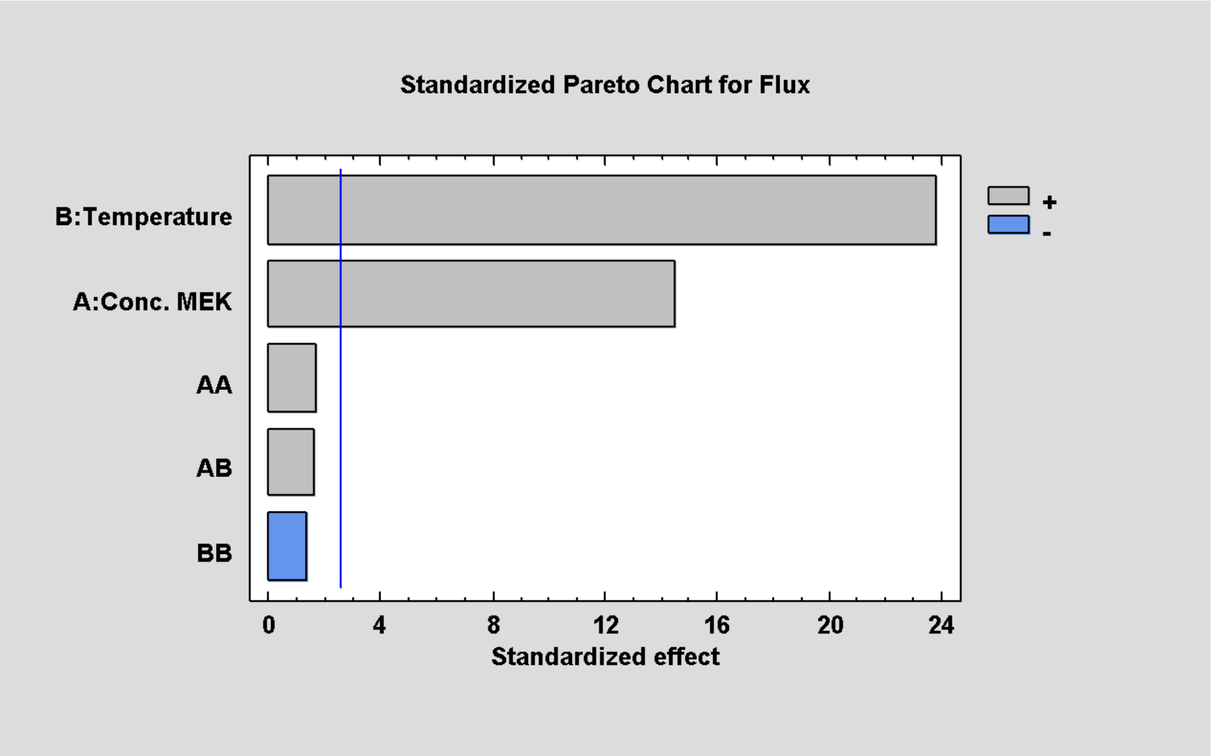

Figure 18: Standardized Pareto Chart for Flux - the figure shows the standardized effect of factor A: Concentration of MEK and factor B: Temperature, on the response Flux in the separation step 3 – MEK / BD / H_2O

Figure 18 shows the effect of the factors feed temperature and concentration of MEK in the feed on the response flux for the separation step MEK / BD / H_2O. The significant standardized effects on flux are:

- A, concentration of MEK: 14.49
- B, temperature: 23.83

That means, that the flux is increasing with rising concentration of MEK and temperature. The highest achieved flux is 2.74 kg/m²h at 54.7 °C and 4.99 wt.% MEK in the feed. There is no significant positive interaction between factor A and B. The factors AA and BB show no significant effect on flux. The effects A and B have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

3.2.3.2 Results for Design of Experiment: Separation Step 3 – MEK / BD / H_2O – Rejection Coefficient MEK

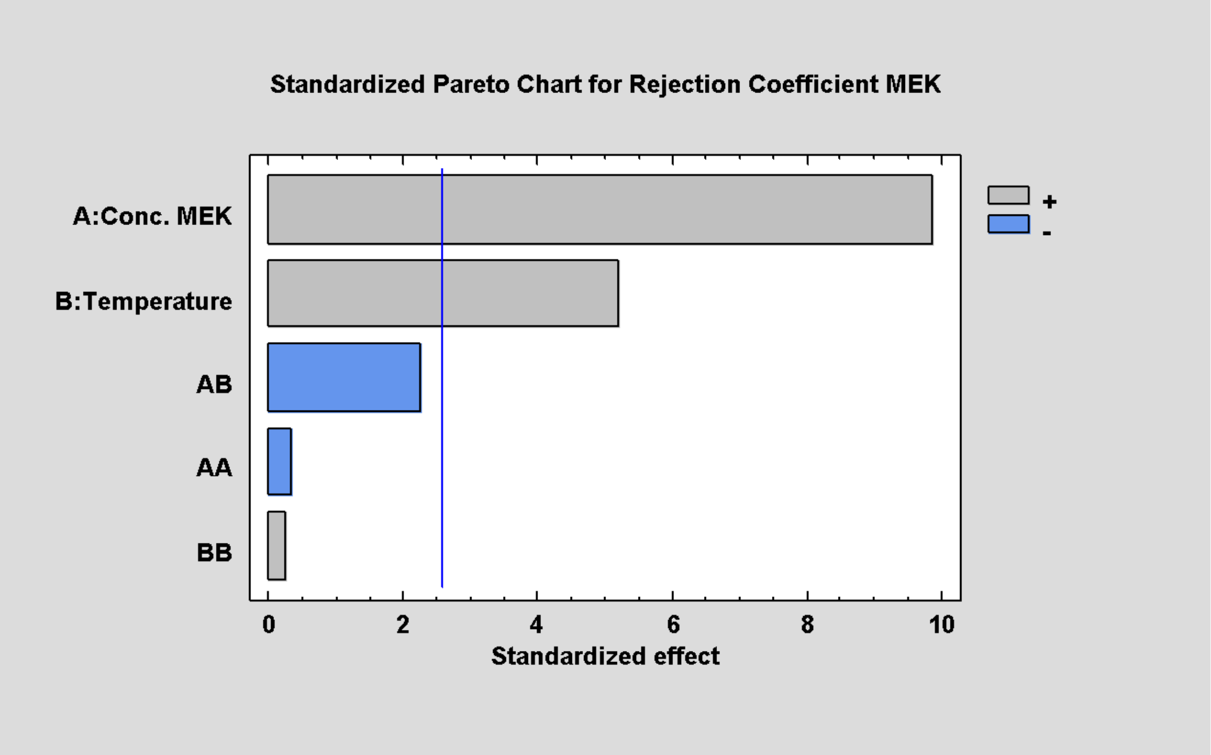

Figure 19: Standardized Pareto Chart for Rejection Coefficient MEK - the figure shows the standardized effect of factor A: Concentration of MEK and factor B: Temperature, on the response rejection coefficient MEK in the separation step 3 – MEK / BD / H_2O

Figure 19 shows the effect of the factors feed temperature and concentration of MEK in the feed on the response rejection coefficient MEK for the separation step MEK / BD / H_2O. The significant standardized effect on rejection coefficient MEK are:

- A, concentration of MEK: 9.88
- B, temperature: 5.21

That means, that the rejection coefficient MEK is rising with rising concentration of MEK and temperature. As MEK is the preferred permeate and the flux is rising at higher temperature and higher concentration of MEK, it's retention should be decreasing. The results lead back to the fact, that increasing temperature and concentration of MEK result in higher flux but conduct to less MEK in the permeate. There is no significant positive interaction between factor A and B. The factors AA and BB show no significant effect on rejection coefficient MEK. The effects A and B have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

3.2.3.3 Results for Design of Experiment: Separation Step 3 – MEK / BD / H_2O – Rejection Coefficient BD

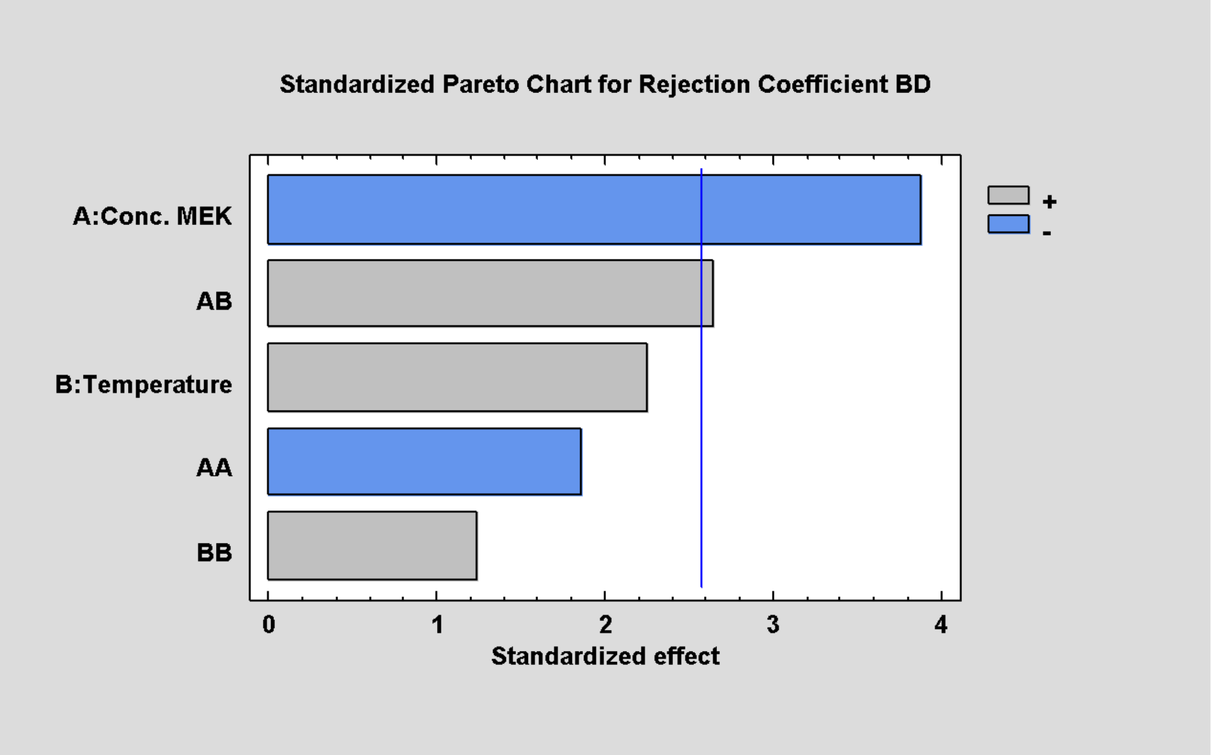

Figure 20: Standardized Pareto Chart for Rejection Coefficient BD – the figure shows the standardized effect of factor A: Concentration of MEK and factor B: Temperature, on the response rejection coefficient BD in the separation step 3 – MEK / BD / H_2O

Figure 20 shows the effect of the factors feed temperature and concentration of MEK in the feed on the response rejection coefficient BD for the separation step MEK / BD / H_2O. The significant standardized effects on rejection coefficient BD are:

- A, concentration of MEK: -3.89
- AB, interaction between concentration of MEK and temperature: 2.64

That means, that the rejection coefficient BD is decreasing with rising concentration of MEK. This result does encourage the result of rejection coefficient MEK, regarding to the effect of concentration of MEK. A higher concentration results in increasing flux, but also leads to unfavoured BD in the permeate. There is a significant positive interaction between factor A and B. That means, when temperature and concentration of MEK are increased, the rejection coefficient of BD is increasing and therefore can antagonize the negative effect of concentration of MEK. Since the effect AB is only slightly above the significance level and contradicts previous results, this result should be examined more closely in future studies. The factors B, AA and BB show no significant effect on rejection coefficient. The effects A and AB have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

3.2.3.4 Results for Design of Experiment: Separation Step 3 – MEK / BD / H_2O – Selectivity MEK

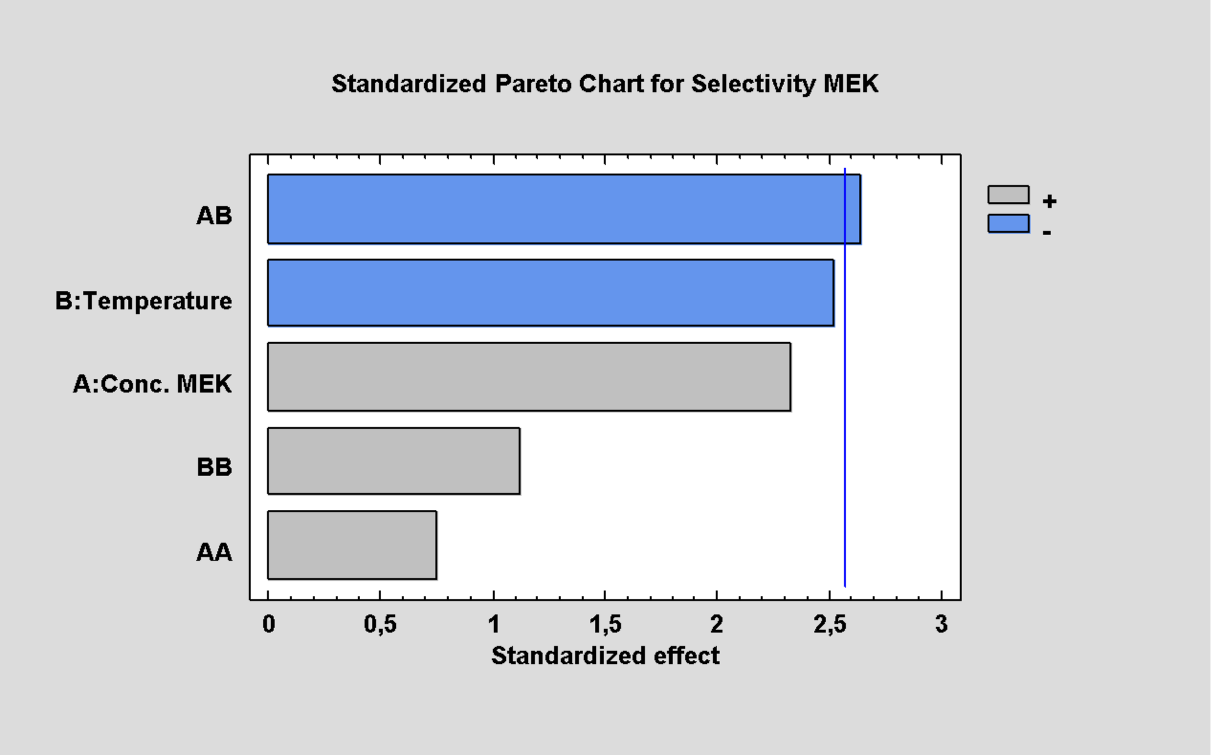

Figure 21: Standardized Pareto Chart for Selectivity MEK – the figure shows the standardized effect of factor A: Concentration of MEK and factor B: Temperature, on the response selectivity MEK in the separation step MEK / BD / H_2O

Figure 21 shows the effect of the factors feed temperature and concentration of MEK in the feed on the response selectivity MEK for the separation step MEK / BD / H_2O. The significant standardized effect on selectivity MEK is:

- AB, interaction between concentration of MEK and temperature: -2.64

That means, that there is a significant negative interaction between factor A and B. The factors A, B, AA and BB show no significant effect on selectivity MEK. The effect AB has a P-value less than 0.05, indicating that it is significant. The other effects show no significance.

3.2.3.5 Results for Design of Experiment: Separation Step 3 – MEK / BD / H_2O – Selectivity BD

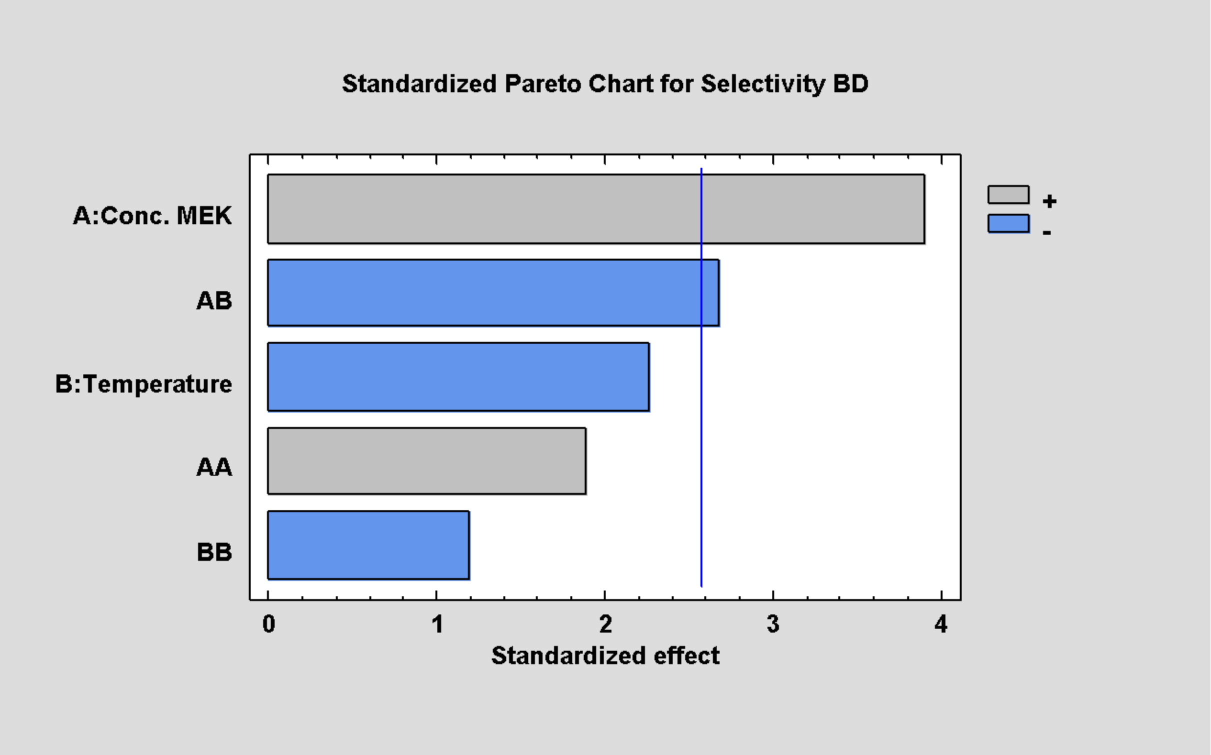

Figure 22: Standardized Pareto Chart for Selectivity BD – the figure shows the standardized effect of factor A: Concentration of MEK and factor B: Temperature, on the response Selectivity BD in the separation step MEK / BD / H_2O

Figure 22 shows the effect of the factors feed temperature and concentration of MEK in the feed on the response selectivity BD for the separation step MEK / BD / H_2O. The significant standardized effects on selectivity BD are:

- A, concentration of MEK: 3.89
- AB, interaction between concentration of MEK and temperature: -2.68

That means, that the selectivity BD is rising with higher concentration of MEK in the feed. There is a significant negative interaction between factor A and B. The factors B, AA and BB show no significant effect on selectivity BD. The effects A and AB have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

3.2.4 Results for Design of Experiment: Separation Step 4 – MEK / H_2O

The experimental design for the separation of MEK and water was undertaken with the Optimised Silica membrane. The variable factors are the concentration of MEK in the feed, with amounts between 5 wt.% and 15 wt.%, and the feed temperature from 25°C to 75°C. Table 24 shows the data for statistical analysis in statgraphics for the separation step 4 – MEK / H_2O. The results show, that the membrane was impermeable for MEK (except for experiment five, six and eleven), what describes the high values for the selectivity. The negative Rejection Coefficients H_2O means, that the concentration of H_2O in the permeate is higher than in the feed.

Table 24: Data for Statistical Analysis of Separation Step 4: MEK / H_2O

Experiment	Concentration MEK	Temperature	Flux	H_2O Permeate	Selectivity	Rejection Coefficient MEK	Rejection Coefficient H_2O
	[wt.%]	[°C]	[kg/m²h]	[wt.%]			
1	10.07	72.8	11.28	99.99	1119.98	1.00	-0.11
2	5.00	75.1	12.60	99.99	525.95	1.00	-0.05
3	10.03	51.3	4.04	99.99	1114.75	1.00	-0.11
4	9.99	50.3	3.83	99.99	1109.77	1.00	-0.11
5	15.04	50.2	3.71	99.43	1769.54	0.96	-0.17
6	10.20	24.5	0.31	99.43	1135.96	0.94	-0.11
7	4.99	50.3	4.04	99.99	524.73	1.00	-0.05
8	14.94	74.5	12.02	99.99	1756.30	1.00	-0.18
9	14.99	24.9	0.29	99.99	1762.58	1.00	-0.18
10	10.06	50.4	3.80	99.99	1118.71	1.00	-0.11
11	5.15	24.9	0.36	99.43	543.27	0.89	-0.05

3.2.4.1 Results for Design of Experiment: Separation Step 4 - MEK / H_2O – Flux

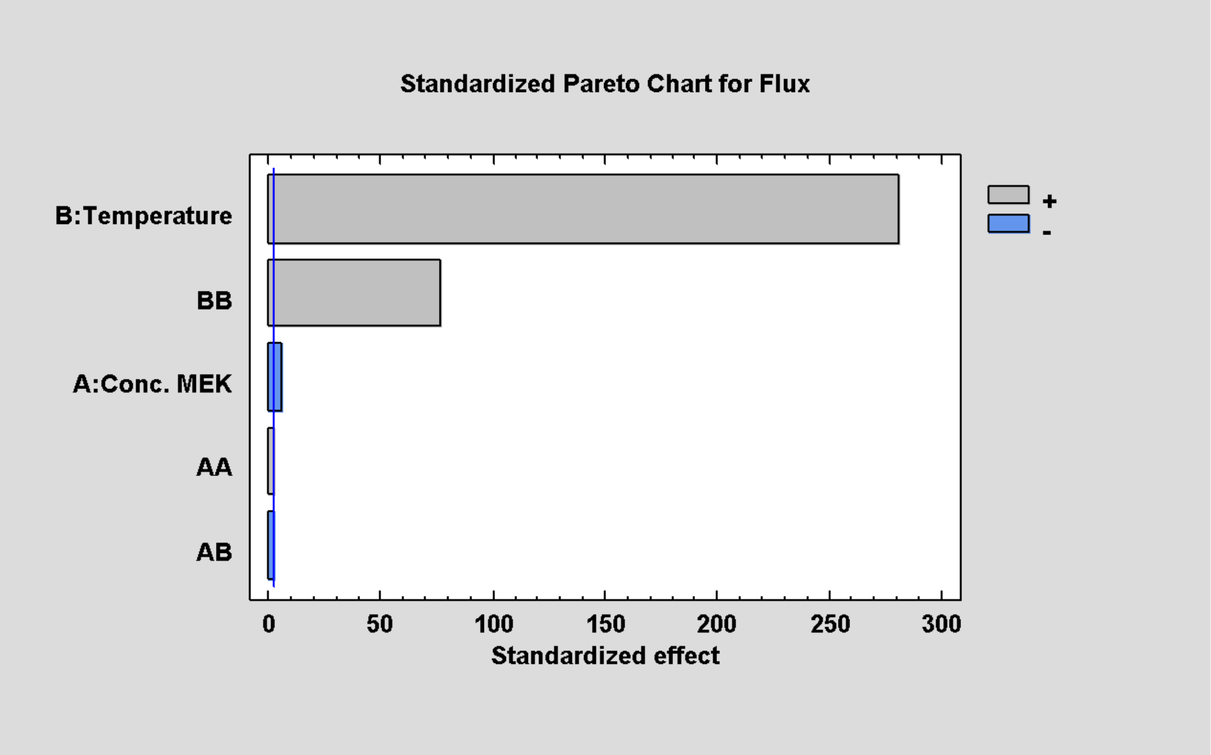

Figure 23: Standardized Pareto Chart for Flux - the figure shows the standardized effect of factor A: Concentration of MEK and factor B: Temperature, on the response flux in the separation step MEK / H_2O

Figure 23 shows the effect of the factors feed temperature and concentration of MEK in the feed on the response flux for the separation step MEK / H_2O. The significant standardized effects on Flux are:

- A, concentration of MEK: -5.50
- B, temperature: 280.95
- BB, the quadratic effect of temperature: 76.83

That means, that the flux is rising with higher temperature and decreasing with higher amount of MEK in the feed. The highest flux of 12.6 kg/m²h was achieved at 75.1 °C and 5 wt.% MEK. The factors AA and AB show no significant effect on flux. There is no significant interaction between factor A and B. The effects A, B and BB have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

3.2.4.2 Results for Design of Experiment: Separation Step 4 – MEK / H_2O – Selectivity

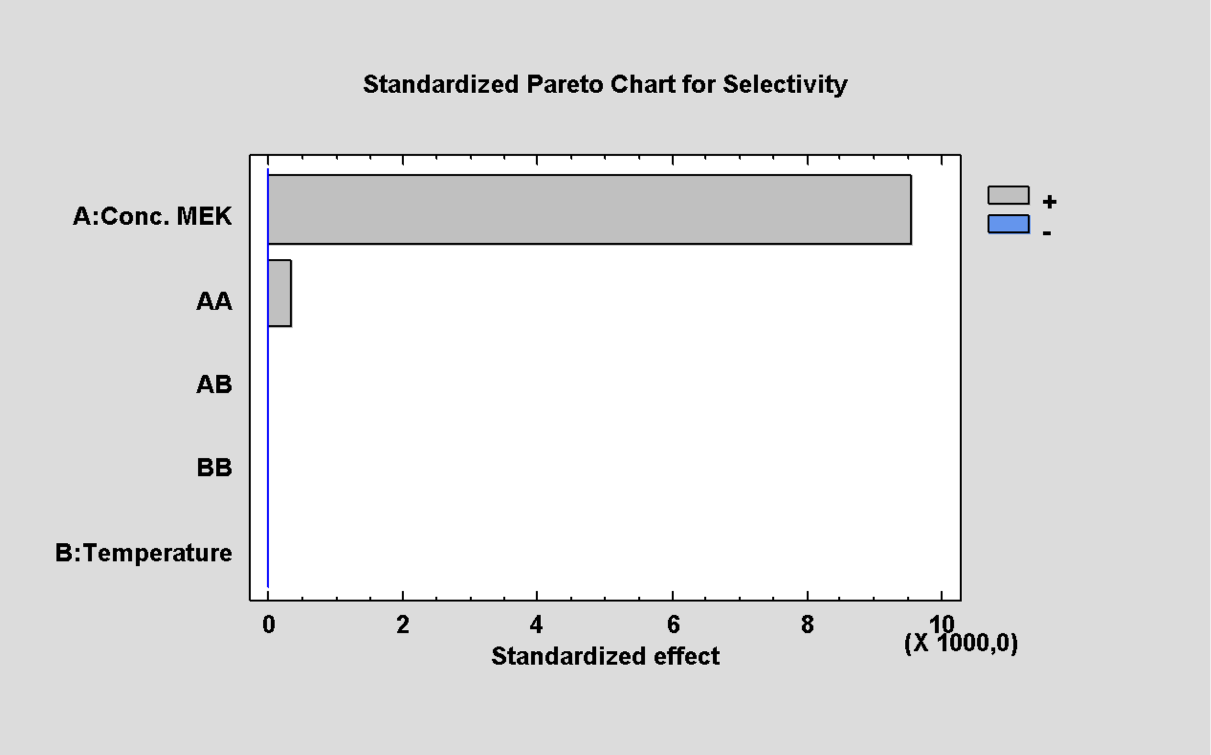

Figure 24: Standardized Pareto Chart for Selectivity – the figure shows the standardized effect of factor A: Concentration of MEK and factor B: Temperature, on the response selectivity in the separation step MEK / H_2O

Figure 24 shows the effect of the factors feed temperature and concentration of MEK in the feed on the response selectivity for the separation step MEK / H_2O. The significant standardized effects on selectivity are:

- A, concentration of MEK: 9568.50
- AA, quadratic effect of concentration of MEK: 337.56
- AB, interaction between temperature and concentration of MEK: 4.31

The factors BB and B show no significant effect on selectivity. That means, that the selectivity is rising with concentration of MEK. The effects A, AA and AB have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

3.2.4.3 Results for Design of Experiment: Separation Step 4 – MEK / H_2O – Rejection Coefficient MEK

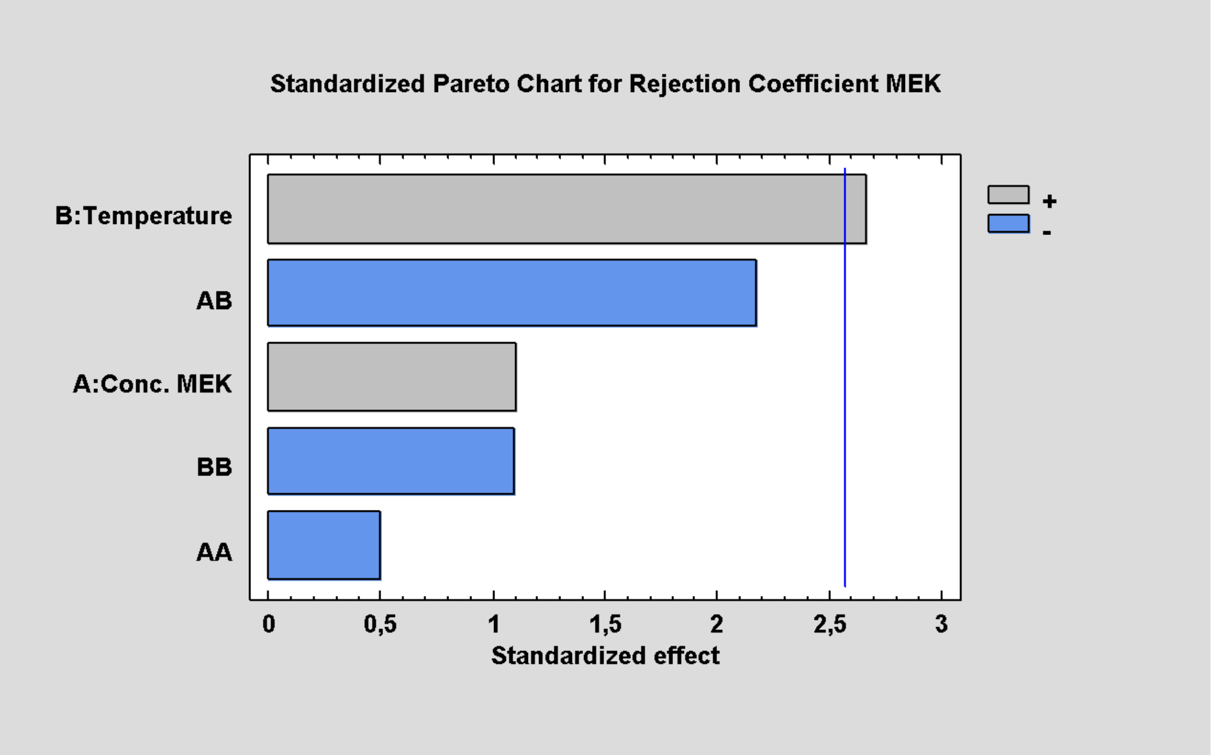

Figure 25: Standardized Pareto Chart for Rejection Coefficient MEK – the figure shows the standardized effect of factor A: Concentration of MEK and factor B: Temperature, on the response rejection coefficient MEK in the separation step MEK / H_2O

Figure 25 shows the effect of the factors feed temperature and concentration of MEK in the feed on the response rejection coefficient MEK for the separation step MEK / H_2O. The significant standardized effect on rejection coefficient MEK is:

- B, temperature: 2.67

That means, that the rejection coefficient MEK is rising with rising temperature. The factors AB, A, BB and AA show no significant effect on rejection coefficient MEK. The effect B has a P-value less than 0.05, indicating that it is significant. The other effects show no significance.

3.2.4.4 Results for Design of Experiment: Separation Step 4 – MEK / H_2O – Rejection Coefficient H_2O

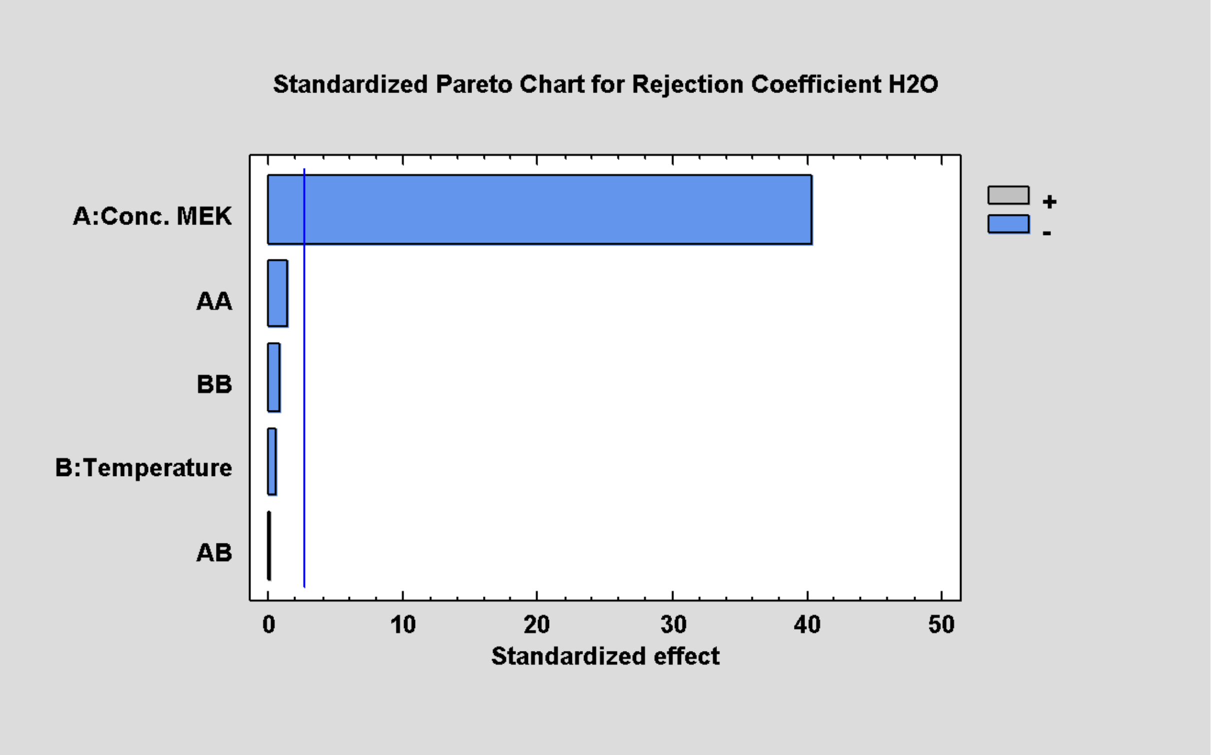

Figure 26: Standardized Pareto Chart for Rejection Coefficient H_2O – the figure shows the standardized effect of factor A: Concentration of MEK and factor B: Temperature, on the response rejection coefficient H_2O in the separation step MEK / H_2O

Figure 26 shows the effect of the factors feed temperature and concentration of MEK in the feed on the response rejection coefficient H_2O for the separation step MEK / H_2O. The significant standardized effect on rejection coefficient H_2O is:

- A, concentration of MEK: -40.32

That means, that the rejection coefficient H_2O is decreasing with rising concentration of MEK. The factors AA, BB, B and AB show no significant effect on rejection coefficient MEK. The effect A has a P-value less than 0.05, indicating that it is significant. The other effects show no significance.

4. Discussion

4.1 Discussion of Design of Experiment

4.1.1 Discussion of Separation Step 1: BD / H_2O

The highest flux achieved is 13.25 kg/m²h in the separation step BD / H_2O with the Optimised Silica membrane at 75°C and 1.51 wt.% BD in the feed. All experiments showed, that the flux increases with higher feed temperature, hence a high feed temperature is generally recommended. According to manufacturer data, the operation limit for the Optimised Silica Membrane is 95°C. Thus, further experiments with temperatures from 75-95°C are recommended, as in our experiments the highest feed temperature was 75°C. Due to the low boiling point of MEK (79.5°C) a maximum temperature of 75°C was set for all experiments to create uniform conditions.

As expected due to the results of the membrane screening, the Optimised Silica membrane showed no permeability for BD and 100 wt.% H_2O as permeate. That's why rejection coefficient and selectivity could not be analysed.

None of the membranes preferred BD as permeate, therefore it was treated as retentate in the design of experiment. This finding is encouraged by results of previous studies. As mentioned before by Shao and Kumar (2009), according to the solution-diffusion theory neither the hydrophilic nature nor the big molecular size of BD favours its permeation trough the membrane when separating it from fermentation broth with a PDMS membrane. What would be desirable is a membrane that is permeable for BD. So that the hypothetical serial process combination could be performed as planned. Since the concentration of BD in the fermentation broth is very low, it is much more laborious and energy-intensive if BD is treated as retentate. If no suitable membrane can be found, other methods should also be considered. As mentioned in chapter 1.2.2.2 Conventional and Alternative Downstream of BD, a combination of liquid-liquid extraction and pervaporation or salting-out seem also promising (Shao and Kumar 2009) (Xie et al. 2016).

Since already higher BD yields can be achieved with fermentation, further research should be carried out with BD concentration up to 10 wt.% in the feed.

4.1.2 Discussion of Separation Step 2: MEK / BD

The flux of separation step 2: MEK / BD is positively affected by rising MEK concentration and temperature. The operation limit for the PDMS membrane is 70°C and short term 80°C according to manufacturer data. Because of decreasing selectivity at temperatures over 55°C in earlier experiments, our experiments with the PDMS membrane were not conducted at higher temperatures.

According to the statistical evaluation of our results, the temperature has no significant effect on rejection coefficient or selectivity when separating MEK and BD with the PDMS membrane. Still, the highest permeate purity of 99.33 wt.% MEK was achieved at the lowest temperatures (25.18, 24.91 and 24.85°C). Thus, the effect of temperature on selectivity and rejection coefficient should be studied further, to possibly enable higher purity of MEK. The results for the separation of MEK / BD with the PDMS membrane also show that a rising MEK concentration seems to promote the permeability of BD. Hence, the standard specification purity of 99.5 wt.% MEK was not achieved.

In this separation step, it should be reconsidered if pervaporation is suitable. Due to the high volatility and low boiling point of MEK, distillation could maybe achieve higher purity of MEK with low energy intake.

4.1.3 Discussion of Separation Step 3: MEK / BD / H_2O

As in the other separation steps, the flux of separation step 3 is rising with increasing temperature and concentration of MEK. It was already mentioned in discussion of separation step 2, that the operation limit for the PDMS membrane is 70°C and short term 80°C according to manufacturer data, but because of decreasing selectivity at temperatures over 55°C in earlier experiments, our experiments with the PDMS membrane were not conducted at higher temperatures.

The same problem with permeability of BD as in separation step 2 also occurs in the separation of MEK / BD / H_2O with the PDMS membrane. An interaction between rising temperature and rising concentration of MEK seems to have a significant negative effect on selectivity. Also, a rising concentration of MEK has a negative effect on rejection coefficient BD. In this separation step BD is treated as retentate and MEK and H_2O are treated as permeate.

The results show, that amounts up to 2.48 wt.% BD were found in the permeate. Subsequently to separation step 3, MEK is separated from remaining water with the Optimised Silica membrane in separation step 4. As MEK is treated as retentate in this separation step and the Optimised Silica membrane is not permeable for BD, undesirable BD would remain in MEK. These facts indicate further research for the separation step MEK / BD / H_2O. This result encourages the observation of unfavourable diffusion of BD in the PDMS membrane from Shao and Kumar (2009).

Alternatively, MEK and H_2O could be separated from BD via distillation. As MEK builds an azeotrope with water, with a boiling point at 73.4°C, distillation could be energy-efficient in this case. Afterwards pervaporation could be used to break the azeotrope of MEK and H_2O.

4.1.4 Discussion of Separation Step 4: MEK / H_2O

Earlier studies separated MEK from water via pervaporation with a silicalite membrane and achieved a flux up to 0.36 kg/m²h at 15.4 wt.% (Smetana, Falconer, and Noble 1996). Like in similar studies, MEK was always treated as permeate (Chen et al. 2008) (Thiyagarajan, Ravi, and Bhattacharya 2011) (Smetana, Falconer, and Noble 1996).

Due to the fact, that MEK was treated as retentate in our research, the flux values cannot be compared to the previous studies. As in this study the separation step MEK / H_2O provides to separate remaining water from MEK it is better to treat MEK as retentate. Due to the results from the prior separation step MEK / BD / H_2O it is expected that MEK is the main component in the MEK / H_2O feed and therefore the separation occurs faster when water is treated as permeate

In our research the maximum achieved flux, when separating MEK from water with the Optimised Silica membrane, was 12.6 kg/m²h at 5 wt.% MEK and 75.1°C. As in the other separation steps, the flux is rising with higher temperature and further research should be conducted at higher temperatures.

The results show, that the membrane was nearly impermeable for MEK. With a permeate purity up to 99.99 wt.% water a Rejection Coefficient MEK of 1 and Selectivity of 1769.54 were reached.

Another positive conclusion of the operated separation of MEK / H_2O is that unlike distillation, the Optimised Silica membrane separated beyond the azeotrope of 88.7 wt.% MEK.

4.2 Discussion of Hypothetical Process Combinations

4.2.1 Discussion of Serial Process Combination

Figure 27 shows the hypothetical continuous serial process. In a bioreactor BD is produced by fermentation from *E. Coli*. The first connected membrane separation step should separate BD from the fermentation broth, so that BD can be directly used for chemical catalysis. Then MEK is produced via catalytical dehydration of BD. Afterwards, a second membrane should separate MEK from the remaining BD. The results show that the hypothetical continuous serial process is not possible with the tested membranes. As none of the membranes prefer BD as permeate, it is not possible to head from the BD / H_2O separation step directly into chemical catalysis.

According to the results, the serial process must be separated into a two-step discontinuous process (see figure 28). The first step is the separation of BD from water with the Optimised Silica Membrane. This step was operated with a flux up to 13.26 kg/m²h and 100 wt.% H_2O permeate. After all the water is removed, BD can be used for chemical catalysis. The second step contains chemical catalysis of BD to MEK and connected separation of MEK from BD with the PDMS membrane with a flux up to 7.84 kg/m²h. The retentate is transferred back into chemical catalysis. The maximal achieved amount of MEK in the permeate was 99.33 wt.%. This value does not match the standard specification purity of min. 99.5 wt.% MEK and therefore further studies are required to increase the selectivity in the separation step MEK / BD. This should be possible with further optimization of the process parameters.

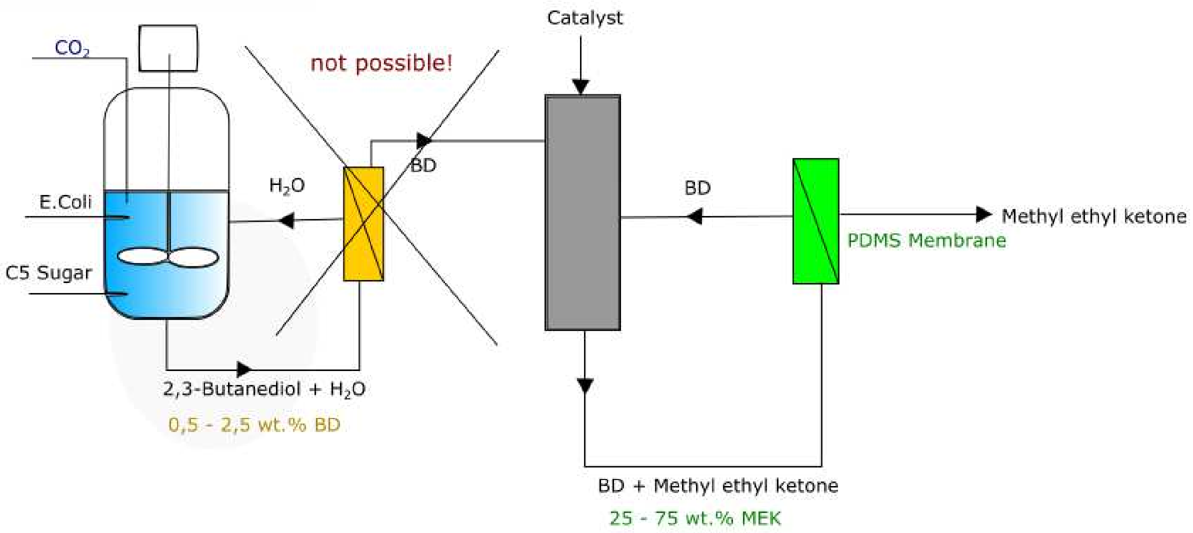

Figure 27: Hypothetical Continuous Serial Process – Separation of BD from fermentation broth and subsequent catalysis to MEK (not possible). Afterwards separation of MEK from remaining BD.

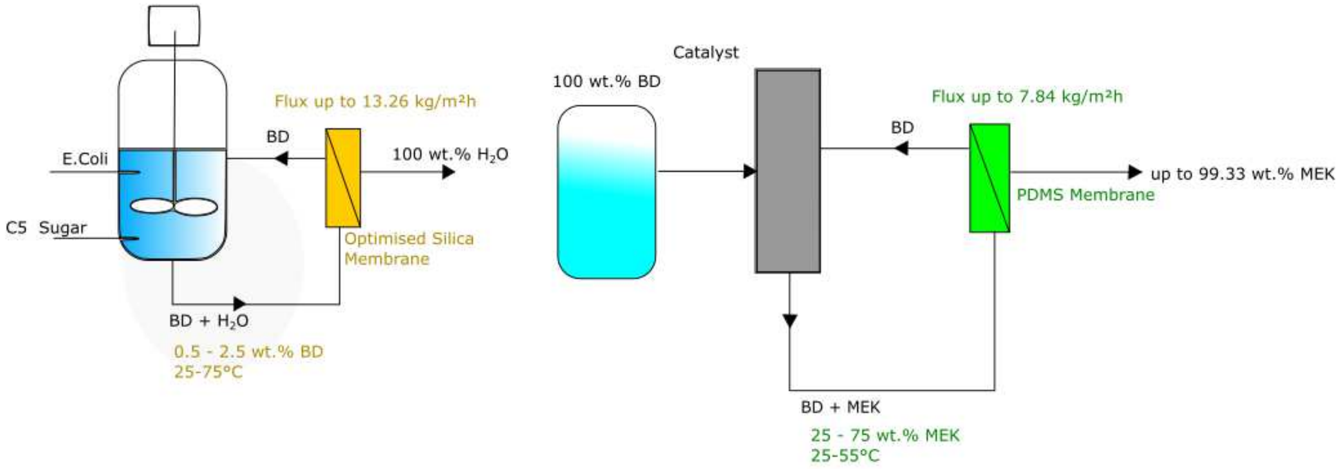

Figure 28: Discontinuous Serial Process in Two Steps – At first separation of water from BD. After all the water is removed, BD can be used for chemical catalysis. Subsequently MEK is separated from remaining BD.

4.2.2 Discussion of One Pot Integration

The one pot process combination (figure 29) is realisable as planned in the hypothesis. The bioreactor where BD is produced through fermentation already contains the catalyst for MEK production via catalytical dehydration of BD. MEK should be separated from the ternary mixture consisting of MEK / BD / H_2O directly afterwards. As expected two membranes are necessary for this step. First MEK and H_2O are separated from BD with the PDMS membrane. A Flux up to 2.74 kg/m²h was achieved in this separation step. As mentioned in chapter 4.1.3. Discussion of Separation Step 3: MEK / BD / H_2O, p. 46, the standard specification purity of 99.5 wt.% MEK may not be achieved because of unfavourable diffusion of BD into the permeate. Further research is required for this problem. In the next step remaining H_2O is separated from MEK with the Optimised Silica membrane. A Flux up to 12.6 kg/m²h was achieved in this step with permeate consisting of up to 99.99 wt.% H_2O.

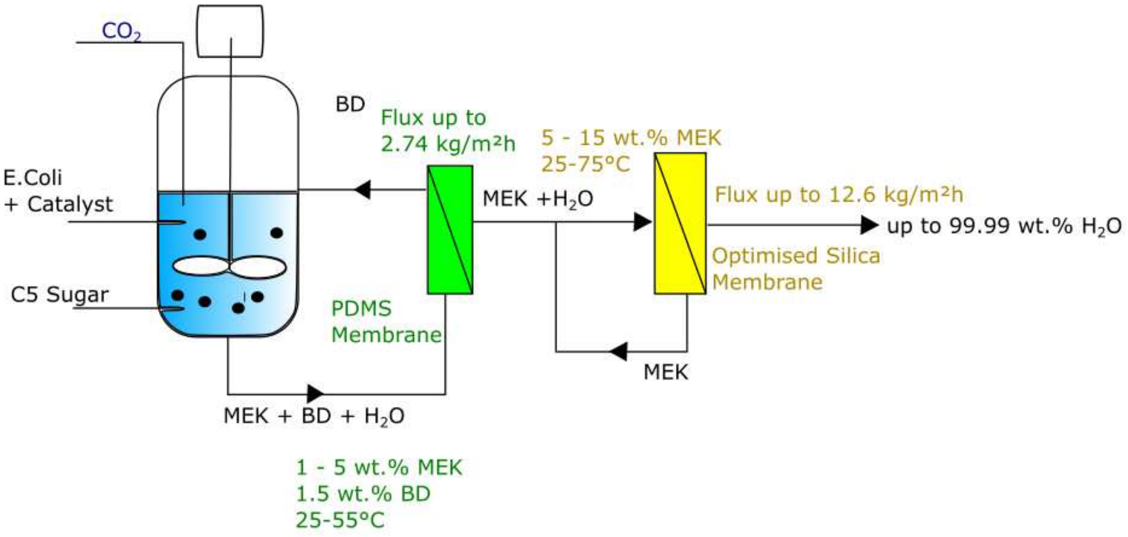

Figure 29: One Pot process - separation of MEK and water from the ternary mixture (MEK / BD / H_2O) with the PDMS membrane and following separation of water from MEK with the Optimised Silica Membrane

5. Conclusion & Outlook

Six different pervaporation membranes were tested for their suitability to connect the fermentation of 2,3-butanediol (BD) with following chemical catalysis to methyl ethyl ketone (MEK). There are two potential process combinations: Serial process combination and one pot integration. First, a membrane screening was undertaken to find one suitable membrane for each separation step. HybSi standard, HybSi dense, HybSi open, Optimised Silica and PDMS were screened for their ability to separate BD from water, MEK from BD, MEK from water and a ternary mixture of MEK, BD and water into their components. The Optimised Silica membrane was chosen for the separation of water from MEK and water from BD. The PDMS membrane was chosen to separate the organic mixture of MEK / BD and the ternary mixture of MEK / BD / H_2O. None of the membranes preferred BD as permeate, so BD was treated as a retentate in all separation steps. Next a Design of Experiment was established for each separation step. With variation of feed composition and feed temperature, the effect on flux, selectivity and rejection coefficient was studied.

All experiments and separation steps showed, that the flux is increasing with higher feed temperature. The highest flux achieved is 13.25 kg/m²h in the separation step BD / H_2O with the Optimised Silica membrane at 75°C and 1.51 wt.% BD in the feed. When separating H_2O from MEK a maximum flux of 12.6 kg/m²h was achieved at 75.1°C and 5 wt.% MEK in the feed. With the PDMS membrane a flux of 7.84 kg/m²h was achieved when separating MEK and BD at 55.8°C and 75 wt.% MEK in the feed. For the separation step MEK / BD / H_2O the maximum flux is 2.74 kg/m²h at 54.7°C and 4.99 wt.% MEK. In the separation steps MEK / BD and MEK / BD / H_2O the flux was increasing with higher concentration of MEK in the feed, too. In this separation steps the increase of concentration of MEK also caused decrease in selectivity and rejection coefficient of BD. This unfavourable effect caused BD to permeate through the PDMS membrane and inhibits a complete separation of MEK from BD. After the separation of the ternary mixture, undesirable BD probably remains in MEK when removing water with the Optimised Silica membrane When separating MEK from BD with the PDMS membrane, a permeate purity from 95.15-99.33 wt.% MEK was detected. Although the standard specification purity of min. 99.5 wt.% MEK was not achieved in this separation step, the quality can possibly be improved with further research. In contrast, the separation step BD / H_2O with the Optimised Silica membrane showed no permeability for BD and 100 wt.% H_2O as permeate. In the separation step MEK / H_2O with the Optimised Silica membrane selectivity and rejection coefficient MEK were positive affected by rising concentration of MEK and temperature. The permeate purity reached from 99.43 to 99.99 wt.% H_2O.

Alternative separation methods should be considered for separation step one, two and three. According to literature a combination of liquid-liquid extraction and pervaporation or salting-out seem promising for the separation of BD from water (Shao and Kumar 2009) (Xie et al. 2016). Due to the high volatility and low boiling point of MEK, distillation could maybe achieve higher purity of MEK with low energy intake for the separation of MEK and BD. An alternative process for the separation of MEK / BD / H_2O could be the separation of MEK and H_2O from BD via distillation. As MEK builds an azeotrope with water, with a boiling point at 73.4°C, distillation could be energy-efficient in this case. Afterwards pervaporation could be used to break the azeotrope of MEK and H_2O.

The results show that the hypothetical continuous serial process is not possible, because none of the membranes prefers BD as permeate. Hence the serial process must be split into two steps instead. The hypothetical one pot integration seems feasible with combination of PDMS and Optimised Silica membrane. The PDMS membrane separates MEK and water from BD and a downstream installed Optimised Silica membrane separates water from MEK. As the standard specification purity of 99.5 wt.% MEK was not achieved, further research is necessary to improve selectivity of the PDMS membrane or to find a membrane that fulfils the demands of the needed separation steps. It must be pointed out, that all experiments were undertaken with synthetic feed mixtures that did not contain bacteria or by-products of fermentation or chemical catalysis. Further research with fermentation broth is necessary.

This scientific work shall build a base for further research to combine biotechnological BD production and subsequent chemical catalysis to MEK via pervaporation membranes. According to the results following further research is reasonable in the future to build on this scientific work:

- Tests with fermentation broth and BD concentrations up to 10 wt.% to simulate realistic conditions
- Tests with higher feed temperature (>55°C for PDMS, >75°C for Optimised Silica) to increase flux
- Optimization of process parameters to reach the standard specification purity of 99.5 wt.% MEK

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7. Appendix

7.1 Design of Experiment for Separation Step 3: MEK / BD / H_2O - BD variable

A factorial design was created: a 2^3 design which will study the effects of three factors in eleven runs (see figure 30). The experiments for the separation MEK / BD / H_2O are undertaken with the PDMS membrane. The responses are flux and selectivity. The constant adjustments for the experiments are shown in table 12, page 20. The variable factors (see table 25) are the concentration of MEK in the feed, with amounts between 1 wt.% and 5 wt.%, the concentration of BD with amounts from 0.5 wt.% to 2.5 wt.% and a feed temperature from 25°C to 75°C.

Table 25: Variable Adjustments for Design of Experiment MEK / BD / H_2O – BD variable

Membrane	PDMS
Experimental Design	Screening Design
Feed composition	1-5% MEK and 0.5-2.5 % 2,3-Butanediol in H_2O
Temperature	25-75°C

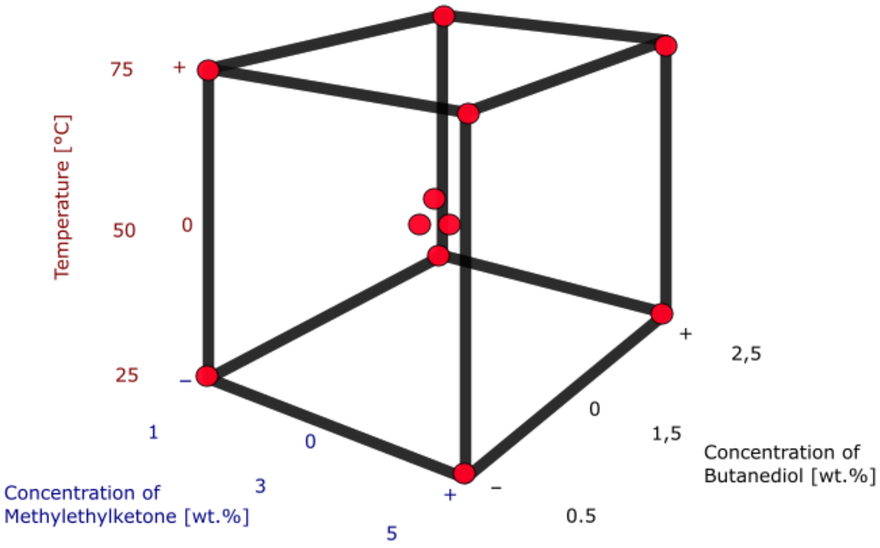

Figure 30: Experimental Design for Separation Step 3: MEK / BD / H_2O – BD variable - the red dots show the testing points, 2^3 Screening Design with eleven testing points, including three central points

7.1.1 Results for Design of Experiment: Separation Step 3 – MEK / BD / H_2O – BD variable

The experimental design for the separation step of MEK, BD and water was undertaken with the PDMS membrane. An experimental screening design was created and eleven experiments in randomized order were undertaken to determine flux, and selectivity. To show the effect of the factors at the responses, a Standardized Pareto Chart for each response was created. The constant adjustments for the experiments are shown in table 23. The variable factors are the concentration of MEK and 2,3-butanediol in the feed and the feed temperature from 25°C to 75°C.

Table 26: Experimental Design for Separation Step 3 – MEK / BD / H_2O – BD variable

Membrane	PDMS
Experimental Design	Screening Design
Feed composition	1-5% MEK and 0.5-2.5 % 2,3-Butanediol in H_2O
Temperature	25-75°C

Table 27: Data for Statistical Analysis: Separation Step 3 – MEK / BD / H_2O – BD variable

Experiment	**Concentration MEK**	**Concentration BD**	**Temperature**	**Flux**	**Selectivity**
	[wt.%]	**[wt.%]**	**[°C]**	**[kg/m²h]**	
1	2.97	1.48	51.6	1.98	22.8
2	2.97	1.49	51.8	1.86	33.5
3	2.98	1.50	51.0	1.98	20.5
4	1.00	0.51	25.6	0.35	50.3
5	4.93	0.49	25.3	0.94	9.1
6	1.05	2.49	25.1	0.15	45.1
7	1.00	0.52	75.5	3.08	13.9
8	4.94	2.46	24.9	0.91	7.3
9	4.92	0.51	74.9	4.55	13.8
10	1.00	2.49	74.9	2.86	15.7
11	4.94	2.47	74.4	4.53	14.2

7.1.1.1 Results for Design of Experiment: Separation Step 3 – MEK / BD / H_2O – BD variable – Flux

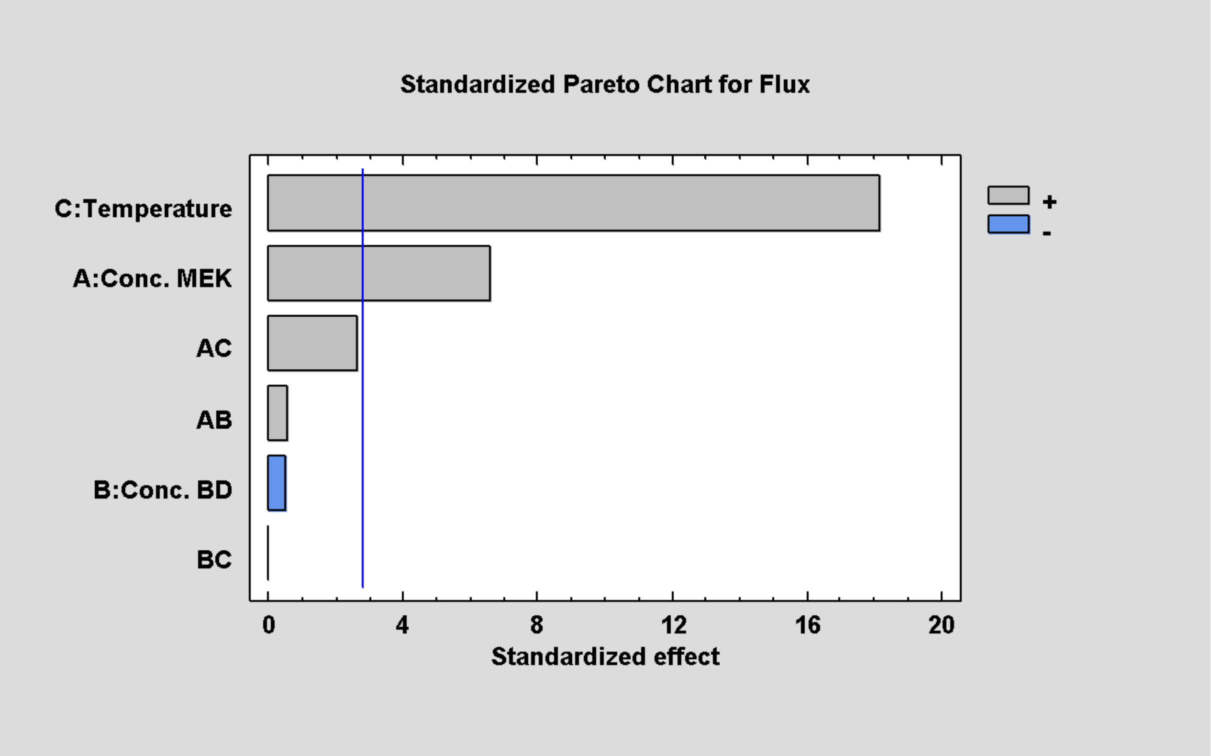

Figure 31: Results for Design of Experiment: Separation Step 3 – MEK / BD / H_2O – BD variable – Flux – Standardized Pareto Chart for Flux

Figure 31 shows the effect of the factors feed temperature, concentration of MEK and concentration of BD in the feed on the response flux for the separation step MEK/BD/H_2O – BD variable. The significant standardized effects on flux are:

- C, temperature: 18.17
- A, concentration of MEK: 6.59

That means, that the flux is increasing with rising concentration of MEK and temperature. There is no significant interaction between the factors. The factor B, concentration of BD shows no significant effect on flux. That's why the response surface design for the separation step MEK/BD/H_2O was undertaken with a constant concentration of BD.

The effects A and C have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

7.1.1.2 Results for Design of Experiment: Separation Step 3 – MEK / BD / H_2O – BD variable – Selectivity

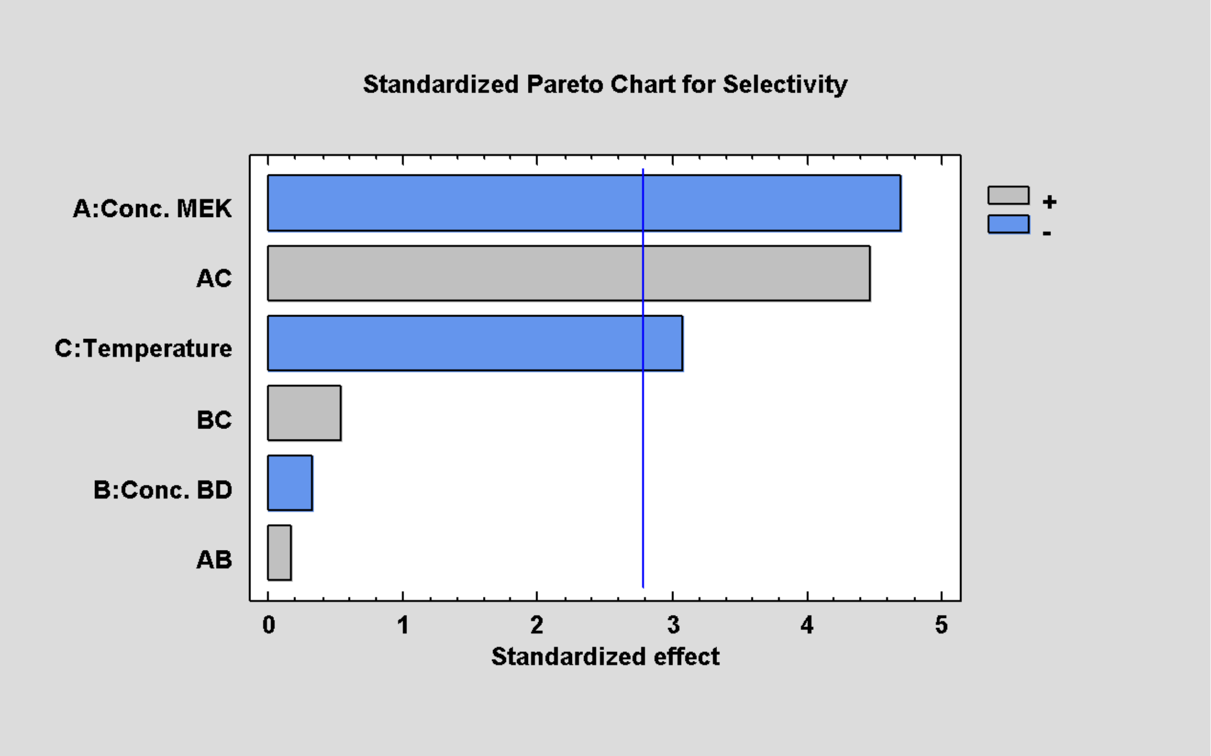

Figure 32: Results for Design of Experiment: Separation Step 3 – MEK / BD / H_2O – BD variable – Selectivity – Standardized Pareto Chart

Figure 32 shows the effect of the factors feed temperature, concentration of MEK and concentration of BD in the feed on the response selectivity for the separation step MEK / BD / H_2O – BD variable. The significant standardized effects on selectivity are:

- A, concentration of MEK: -4.69
- AC, interaction between concentration of MEK and temperature: 4.47
- C, temperature: -3.07

That means, that the selectivity is decreasing with rising concentration of MEK and temperature. There is a significant positive interaction between concentration of MEK and temperature. There is no significant interaction between factor A and B and factor B and C. The factor B, concentration of 2,3-butanediol shows no significant effect on selectivity. That’s why the response surface design for the separation step MEK/BD/H_2O was undertaken with a constant concentration of BD.

The effects A, C and AC have P-values less than 0.05, indicating that they are significant. The other effects show no significance.

7.2 Analysis of Variance (ANOVA) for Design of Experiment

7.2.1 ANOVA of Separation Step 1: BD / H_2O

7.2.1.1 ANOVA of Separation Step 1: BD / H_2O – Flux

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration of 2,3-Butanediol	0.00048477	1	0.00048477	0.00	0.9778
B:Temperature	220.989	1	220.989	390.08	0.0000
AA	0.059561	1	0.059561	0.11	0.7589
AB	0.153619	1	0.153619	0.27	0.6248
BB	20.5599	1	20.5599	36.29	0.0018
Total error	2.8326	5	0.566519		
Total (corr.)	239.756	10			

R-squared = 98.8186 percent

R-squared (adjusted for d.f.) = 97.6371 percent

Standard Error of Est. = 0.752675

Mean absolute error = 0.375508

Durbin-Watson statistic = 1.30392 (P=0.1262)

Lag 1 residual autocorrelation = 0.253793

The StatAdvisor

The ANOVA table partitions the variability in Flux into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level. The R-Squared statistic indicates that the model as fitted explains 98.8186% of the variability in Flux. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 97.6371%. The standard error of the estimate shows the standard deviation of the residuals to be 0.752675. The mean absolute error (MAE) of 0.375508 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.2.1.2 ANOVA of Separation Step 1: BD / H_2O – Selectivity

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration of 2,3-Butanediol	67490.7	1	67490.7	560972.60	0.0000
B:Temperature	0.12463	1	0.12463	1.04	0.3555
AA	3.3263	1	3.3263	27.65	0.0033
AB	0.0345129	1	0.0345129	0.29	0.6152
BB	0.287122	1	0.287122	2.39	0.1830
Total error	0.601551	5	0.12031		
Total (corr.)	69057.3	10			

R-squared = 99.9991 percent

R-squared (adjusted for d.f.) = 99.9983 percent

Standard Error of Est. = 0.346858

Mean absolute error = 0.209258

Durbin-Watson statistic = 2.24449 (P=0.6347)

Lag 1 residual autocorrelation = -0.138354

The StatAdvisor

The ANOVA table partitions the variability in Selectivity into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 99.9991% of the variability in Selectivity. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 99.9983%. The standard error of the estimate shows the standard deviation of the residuals to be 0.346858. The mean absolute error (MAE) of 0.209258 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level

7.2.2 ANOVA of Separation Step 2: MEK / BD

7.2.2.1 ANOVA of Separation Step 2: MEK / BD – Flux

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	24.0142	1	24.0142	275.86	0.0000
B:Temperature	16.4869	1	16.4869	189.39	0.0000
AA	2.24983	1	2.24983	25.85	0.0038
AB	8.7417	1	8.7417	100.42	0.0002
BB	0.000193552	1	0.000193552	0.00	0.9642
Total error	0.435254	5	0.0870508		
Total (corr.)	53.5393	10			

R-squared = 99.187 percent

R-squared (adjusted for d.f.) = 98.3741 percent

Standard Error of Est. = 0.295044

Mean absolute error = 0.176834

Durbin-Watson statistic = 3.12577 (P=0.9880)

Lag 1 residual autocorrelation = -0.598927

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The ANOVA table partitions the variability in Flux into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 4 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 99.187% of the variability in Flux. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 98.3741%. The standard error of the estimate shows the standard deviation of the residuals to be 0.295044. The mean absolute error (MAE) of 0.176834 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.2.2.2 ANOVA of Separation Step 2: MEK / BD – Selectivity

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	279662.0	1	279662.0	7410.45	0.0000
B:Temperature	0.169874	1	0.169874	0.00	0.9491
AA	106462.00	1	106462.00	2821.02	0.0000
AB	0.170903	1	0.170903	0.00	0.9490
BB	1.0135	1	1.0135	0.03	0.8762
Total error	188.695	5	37.7389		
Total (corr.)	393912.00	10			

R-squared = 99.9521 percent

R-squared (adjusted for d.f.) = 99.9042 percent

Standard Error of Est. = 6.1432

Mean absolute error = 3.1046

Durbin-Watson statistic = 1.56592 (P=0.1930)

Lag 1 residual autocorrelation = 0.0642495

The StatAdvisor

The ANOVA table partitions the variability in Selectivity into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 99.9521% of the variability in Selectivity. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 99.9042%. The standard error of the estimate shows the standard deviation of the residuals to be 6.1432. The mean absolute error (MAE) of 3.1046 is the average value of the residuals.

7.2.2.3 ANOVA of Separation Step 2: MEK / BD – Rejection Coefficient MEK

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	10.7007	1	10.7007	32040.40	0.0000
B:Temperature	0.0000434436	1	0.0000434436	0.13	0.7331
AA	1.30484	1	1.30484	3907.01	0.0000
AB	0.0000985787	1	0.0000985787	0.30	0.6103
BB	5.7533E-7	1	5.7533E-7	0.00	0.9685
Total error	0.00166987	5	0.000333974		
Total (corr.)	12.1543	10			

R-squared = 99.9863 percent

R-squared (adjusted for d.f.) = 99.9725 percent

Standard Error of Est. = 0.018275

Mean absolute error = 0.00975471

Durbin-Watson statistic = 1.65594 (P=0.2439)

Lag 1 residual autocorrelation = 0.0934761

The StatAdvisor

The ANOVA table partitions the variability in Rejection Coefficient MEK into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 99.9863% of the variability in Rejection Coefficient MEK. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 99.9725%. The standard error of the estimate shows the standard deviation of the residuals to be 0.018275. The mean absolute error (MAE) of 0.00975471 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.2.2.4 ANOVA of Separation Step 2: MEK / BD – Rejection Coefficient BD

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	0.0139925	1	0.0139925	16.23	0.0100
B:Temperature	0.0000115299	1	0.0000115299	0.01	0.9124
AA	0.000362142	1	0.000362142	0.42	0.5455
AB	0.00000128333	1	0.00000128333	0.00	0.9707
BB	0.000260897	1	0.000260897	0.30	0.6059
Total error	0.00431117	5	0.000862233		
Total (corr.)	0.0188182	10			

R-squared = 77.0904 percent

R-squared (adjusted for d.f.) = 54.1808 percent

Standard Error of Est. = 0.0293638

Mean absolute error = 0.0152984

Durbin-Watson statistic = 1.31677 (P=0.0865)

Lag 1 residual autocorrelation = 0.103765

The StatAdvisor

The ANOVA table partitions the variability in Rejection Coefficient BD into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 1 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 77.0904% of the variability in Rejection Coefficient BD. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 54.1808%. The standard error of the estimate shows the standard deviation of the residuals to be 0.0293638. The mean absolute error (MAE) of 0.0152984 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.2.3 ANOVA of Separation Step 3: MEK / BD / H_2O

7.2.3.1 ANOVA of Separation Step 3: MEK / BD / H_2O – Flux

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	1.48019	1	1.48019	209.90	0.0000
B:Temperature	4.00553	1	4.00553	568.01	0.0000
AA	0.0195977	1	0.0195977	2.78	0.1564
AB	0.0180257	1	0.0180257	2.56	0.1708
BB	0.0128799	1	0.0128799	1.83	0.2345
Total error	0.0352593	5	0.00705185		
Total (corr.)	5.46809	10			

R-squared = 99.3552 percent

R-squared (adjusted for d.f.) = 98.7104 percent

Standard Error of Est. = 0.0839753

Mean absolute error = 0.0381624

Durbin-Watson statistic = 1.46906 (P=0.1429)

Lag 1 residual autocorrelation = 0.0485165

The StatAdvisor

The ANOVA table partitions the variability in Flux into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 99.3552% of the variability in Flux. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 98.7104%. The standard error of the estimate shows the standard deviation of the residuals to be 0.0839753. The mean absolute error (MAE) of 0.0381624 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.2.3.2 ANOVA of Separation Step 3: MEK / BD / H_2O – Rejection Coefficient MEK

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	219.181	1	219.181	97.55	0.0002
B:Temperature	60.8989	1	60.8989	27.10	0.0034
AA	0.237226	1	0.237226	0.11	0.7584
AB	11.1886	1	11.1886	4.98	0.0760
BB	0.142254	1	0.142254	0.06	0.8114
Total error	11.2345	5	2.2469		
Total (corr.)	293.959	10			

R-squared = 96.1782 percent

R-squared (adjusted for d.f.) = 92.3564 percent

Standard Error of Est. = 1.49897

Mean absolute error = 0.815806

Durbin-Watson statistic = 1.78036 (P=0.3176)

Lag 1 residual autocorrelation = -0.0735062

The StatAdvisor

The ANOVA table partitions the variability in Rejection Coefficient MEK into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 96.1782% of the variability in Rejection Coefficient MEK. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 92.3564%. The standard error of the estimate shows the standard deviation of the residuals to be 1.49897. The mean absolute error (MAE) of 0.815806 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.2.3.3 ANOVA of Separation Step 3: MEK / BD / H_2O – Rejection Coefficient BD

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	1.98939	1	1.98939	15.08	0.0116
B:Temperature	0.663209	1	0.663209	5.03	0.0750
AA	0.454744	1	0.454744	3.45	0.1225
AB	0.922521	1	0.922521	6.99	0.0457
BB	0.199946	1	0.199946	1.52	0.2730
Total error	0.659441	5	0.131888		
Total (corr.)	5.44729	10			

R-squared = 87.8942 percent

R-squared (adjusted for d.f.) = 75.7883 percent

Standard Error of Est. = 0.363164

Mean absolute error = 0.20507

Durbin-Watson statistic = 1.41712 (P=0.1211)

Lag 1 residual autocorrelation = 0.143187

The StatAdvisor

The ANOVA table partitions the variability in Rejection Coefficient BD into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 87.8942% of the variability in Rejection Coefficient BD. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 75.7883%. The standard error of the estimate shows the standard deviation of the residuals to be 0.363164. The mean absolute error (MAE) of 0.20507 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.2.3.4 ANOVA of Separation Step 3: MEK / BD / H_2O – Selectivity MEK

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	85491.60	1	85491.60	5.42	0.0675
B:Temperature	100223.00	1	100223.00	6.35	0.0532
AA	8842.62	1	8842.62	0.56	0.4879
AB	109662.00	1	109662.00	6.95	0.0462
BB	19759.90	1	19759.90	1.25	0.3141
Total error	78933.30	5	15786.70		
Total (corr.)	470021.00	10			

R-squared = 83.2064 percent

R-squared (adjusted for d.f.) = 66.4128 percent

Standard Error of Est. = 125.645

Mean absolute error = 67.9511

Durbin-Watson statistic = 1.71202 (P=0.2734)

Lag 1 residual autocorrelation = 0.133552

The StatAdvisor

The ANOVA table partitions the variability in Selectivity MEK into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 1 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 83.2064% of the variability in Selectivity MEK. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 66.4128%. The standard error of the

estimate shows the standard deviation of the residuals to be 125.645. The mean absolute error (MAE) of 67.9511 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.2.3.5 ANOVA of Separation Step 3: MEK / BD / H_2O – Selectivity BD

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	2.08449	1	2.08449	15.18	0.0115
B:Temperature	0.702454	1	0.702454	5.11	0.0732
AA	0.486479	1	0.486479	3.54	0.1186
AB	0.984566	1	0.984566	7.17	0.0440
BB	0.195773	1	0.195773	1.43	0.2860
Total error	0.686672	5	0.137334		
Total (corr.)	5.74129	10			

R-squared = 88.0398 percent

R-squared (adjusted for d.f.) = 76.0795 percent

Standard Error of Est. = 0.370587

Mean absolute error = 0.209129

Durbin-Watson statistic = 1.4063 (P=0.1168)

Lag 1 residual autocorrelation = 0.152011

The StatAdvisor

The ANOVA table partitions the variability in Selectivity BD into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 88.0398% of the variability in Selectivity BD. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 76.0795%. The standard error of the estimate shows the standard deviation of the residuals to be 0.370587. The mean absolute error (MAE) of 0.209129 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.2.4 ANOVA of Separation Step 4: MEK / H_2O

7.2.4.1 ANOVA of Separation Step 4: MEK / H_2O – Flux

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	0.0801668	1	0.0801668	30.23	0.0027
B:Temperature	209.35	1	209.35	78933.55	0.0000
AA	0.016692	1	0.016692	6.29	0.0539
AB	0.0142563	1	0.0142563	5.38	0.0682
BB	15.6554	1	15.6554	5902.73	0.0000
Total error	0.0132612	5	0.00265224		
Total (corr.)	218.356	10			

R-squared = 99.9939 percent

R-squared (adjusted for d.f.) = 99.9879 percent

Standard Error of Est. = 0.0514999

Mean absolute error = 0.030387

Durbin-Watson statistic = 1.41092 (P=0.2201)

Lag 1 residual autocorrelation = 0.120228

The StatAdvisor

The ANOVA table partitions the variability in Flux into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 3 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 99.9939% of the variability in Flux. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 99.9879%. The standard error of the estimate shows the standard deviation of the residuals to be 0.0514999. The mean absolute error (MAE) of 0.030387 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.2.4.2 ANOVA of Separation Step 4: MEK / H_2O – Selectivity

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	2.2729E6	1	2.2729E6	91556168.40	0.0000
B:Temperature	0.000270331	1	0.000270331	0.01	0.9209
AA	2828.69	1	2828.69	113944.09	0.0000
AB	0.461637	1	0.461637	18.60	0.0076
BB	0.152288	1	0.152288	6.13	0.0561
Total error	0.124126	5	0.0248253		
Total (corr.)	2.27756E6	10			

R-squared = 100.0 percent

R-squared (adjusted for d.f.) = 100.0 percent

Standard Error of Est. = 0.15756

Mean absolute error = 0.0842929

Durbin-Watson statistic = 0.839998 (P=0.0233)

Lag 1 residual autocorrelation = 0.513321

The StatAdvisor

The ANOVA table partitions the variability in Selectivity into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 3 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 100.0% of the variability in Selectivity. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 100.0%. The standard error of the estimate shows the standard deviation of the residuals to be 0.15756. The mean absolute error (MAE) of 0.0842929 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is less than 5.0%, there is an indication of possible serial correlation at the 5.0% significance level. Plot the residuals versus row order to see if there is any pattern that can be seen.

7.2.4.3 ANOVA of Separation Step 4: MEK / H_2O – Rejection Coefficient MEK

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	0.000803671	1	0.000803671	1.22	0.3194
B:Temperature	0.0046774	1	0.0046774	7.11	0.0446
AA	0.000164193	1	0.000164193	0.25	0.6386
AB	0.00311484	1	0.00311484	4.73	0.0816
BB	0.000786973	1	0.000786973	1.20	0.3240
Total error	0.00328999	5	0.000657997		
Total (corr.)	0.0132909	10			

R-squared = 75.2463 percent

R-squared (adjusted for d.f.) = 50.4927 percent

Standard Error of Est. = 0.0256515

Mean absolute error = 0.0139848

Durbin-Watson statistic = 1.43756 (P=0.2356)

Lag 1 residual autocorrelation = 0.257126

The StatAdvisor

The ANOVA table partitions the variability in Rejection Coefficient MEK into separate pieces for each of the effects. It then tests the

statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 1 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 75.2463% of the variability in Rejection Coefficient MEK. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 50.4927%. The standard error of the estimate shows the standard deviation of the residuals to be 0.0256515. The mean absolute error (MAE) of 0.0139848 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.2.4.4 ANOVA of Separation Step 4: MEK / H_2O – Rejection Coefficient H_2O

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Concentration MEK	0.0240353	1	0.0240353	1625.44	0.0000
B:Temperature	0.00000388001	1	0.00000388001	0.26	0.6303
AA	0.0000276571	1	0.0000276571	1.87	0.2297
AB	2.28506E-7	1	2.28506E-7	0.02	0.9059
BB	0.0000111498	1	0.0000111498	0.75	0.4249
Total error	0.0000739348	5	0.000014787		
Total (corr.)	0.0241636	10			

R-squared = 99.694 percent

R-squared (adjusted for d.f.) = 99.388 percent

Standard Error of Est. = 0.00384538

Mean absolute error = 0.00219652

Durbin-Watson statistic = 1.45196 (P=0.2442)

Lag 1 residual autocorrelation = 0.248226

The StatAdvisor

The ANOVA table partitions the variability in Rejection Coefficient H_2O into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 1 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 99.694% of the variability in Rejection Coefficient H2O. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 99.388%. The standard error of the estimate shows the standard deviation of the residuals to be 0.00384538. The mean absolute error (MAE) of 0.00219652 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

7.3 Membrane Datasheets

PERVATECH

Datasheet: Hybrid Silica AR Membranes

Hybrid Silica AR membranes have hydrophilic characteristics, meaning that the water content of the feed passes preferentially through the membrane.

Membrane elements:

Dimensions:	1-channel tube 250 x 10 x 7 mm, effective area 0,005 m^2
	1-channel tube 500 x 10 x 7 mm, effective area 0,01 m^2
	4-tube assembly 1200 x 25 mm, effective area 0,1 m^2
	4-tube assembly 600 x 25 mm, effective area 0,05 m^2
Substrate material:	α-Al_2O_3
Top layer:	Hybrid Silica AR (Open, Standard or Dense)
Coating position:	Inside of the tube

Limits of operation

Temperature:	150 °C
Pressure:	max. 10 bar
pH:	0,5-8,5

Handling, storage and cleaning

Handling

Always wear clean gloves when handling the membranes in order to prevent contamination with fungi. **Warning:** The membranes are brittle and cannot withstand shock, excessive vibration nor mechanical bending forces.

Storage

The membranes can be stored in a dry place under ambient conditions. To prevent the risk of fungi growth on the ceramic element the relative humidity should not exceed 60%.

Cleaning

At the end of the standard dehydration process flush the element with clean solvent or demineralized water (max. 50 °C). CIP the element with appropriate means. This is either with its own solvent or typically 0,5% to 1% enzymatic neutral non-ionic detergent. In some cases special CIP procedures might be applicable. Sterilize with Formaldehyde (1%) or Sodium Azide (<0.01%) or equivalent. Please consult Pervatech for more information or consult the separate cleaning datasheet.

Possible applications with hydrophilic membranes

- Breaking of azeotrope
- Removal of water from organics e.g. alcohols, a-protic solvents, DMAc, DMSO, DMF, NMP, Phenol, THF, ACN, esters, acetates, ketones or acids
- In situ dehydration of condensation reactions
- Dehydration of essential oils
- Separation of low Mw from higher Mw solvents (purification)

Datasheet: Optimised Silica Membranes

Optimised Silica membranes have hydrophilic characteristics, meaning that the water content of the feed passes preferentially through the membrane.

Membrane construction

Element sizes:	500 x 10 x 7 mm, effective area 0,01 m^2 (standard),
	250 x 10 x 7 mm, effective area 0,005 m^2 (knock-out testing only)
Substrate material:	α-Al_2O_3
Intermediate layer:	Gamma alumina
Top layer:	Optimised Silica coated on inside of the support tube

Limits of operation

Temperature:	95 °C
Pressure:	max. 10 bar
pH:	2-8

Storage and cleaning

Cleaning

At the end of the standard dehydration process flush the element with clean solvent, in case water is the solvent flush with warm water (max. 50 °C). Continue flushing until “clean” water is coming out of the system.

After flushing the element, CIP the element with appropriate means. This is either with its own solvent or with typically 0,5% to 1% enzymatic neutral non-ionic detergent.

Flush out thoroughly the element with clean solvent of the application or with RO water.

Sterilize with Formaldehyde (1%) or Sodium Azide(<0.01%) or equivalent.

Storage

No special storage is required. Keep the elements clean and dry.

For more details refer to the separate cleaning datasheet.

Possible applications with hydrophilic membranes

- Breaking of azeotrope
- Removal of water from organics like Alcohols, A-protic solvents, DmAc, DMSO, DMF, ethyl acetate, NMP, Phenol, THF, AcN
- In situ dehydration of condensation reactions
- Dehydration of essential oils
- Separation of low mw from higher mw solvents (purification)

Datasheet: PDMS Membranes

PDMS (Poly Di Methyl Siloxane) membranes have hydrophobic/organophilic characteristics, in which the organic constituent of the feed passes preferentially through the membrane.

Membrane elements:

Dimensions: 1-channel tube 250 x 10 x 7 mm, effective area 0,005 m^2
1-channel tube 500 x 10 x 7 mm, effective area 0,01 m^2
4-tube assembly 1200 x 25 mm, effective area 0,1 m^2
4-tube assembly 600 x 25 mm, effective area 0,05 m^2
Substrate material: α-Al_2O_3
Top layer: PDMS
Coating position: Inside of the tube

Limits of operation

Temperature: 70 °C (short-term 80 °C)
Pressure: max. 10 bar
pH: 1-12
pre-filtration: 10 µ cartridge filter

Storage and cleaning

Storage before use: Out of direct sunlight
Room temperature
< 70% RH
Storage after use (short) : In a solution of water and 10-15% IPA or water with 2500 ppm Sodium Meta Bisulfite
Storage after use (long): In a solution of water with 0.7% Benzalkonium
Cleaning: The element can be cleaned by flushing with water to which a non-ionic detergent (10 ppm KOH) is added. Also enzymatic solutions dependent on the feed composition may be used. In case of food & additives processing contact us for alternatives.

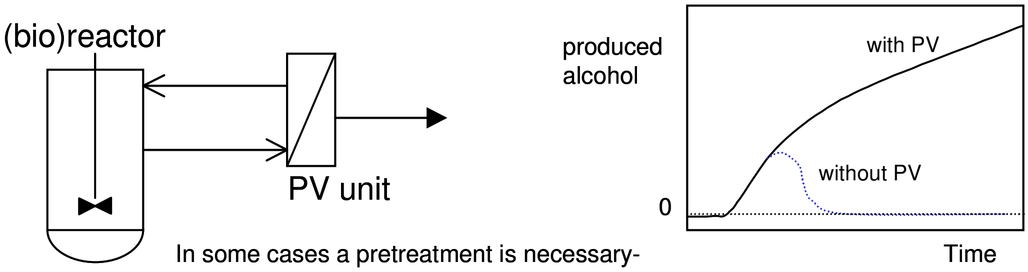
Sterilization options

Steam: 106-108°C
Flushing: With ethylene oxide or 100% ethanol

Possible applications with hydrophobic/organophilic membranes

- Recovery or extraction of organics from natural feed like fruit juices, wine, beer, coco-nut oil, essential oils (carvon, limonene) and in combination with fermentation.
- recovery of organics in biotech or biotech related food applications such as in natural feed like fruit juices, wine, beer, coco-nut oil, essential oils (carvon, limonene) and in combination with fermentation.
- Removal of ethyl alcohol (and other alcohols) from wine and beer
- Upgrading reverse osmosis permeate in juice production.
- Combination with bioreactors in production of alcohols (ethanol, IPA, butanol), ABE (acetone, butanol, ethanol), aldehydes, flavor production as well as acid production.
- Removal of VOC

Typical example of PV process in combination with bioreactors:



In some cases a pretreatment is necessary-
PDMS membranes are stable and insensitive to fouling

Principle of membrane reactor for continuous recovery of product (alcohols, aromas)
The system with PV continues to produce alcohol while other systems stop when inhibiting amounts of alcohol (or other inhibitor) have been reached.