ChemPLANT Competition

# AixSTRAWdinary

## Synthesis of Butadiene from Lignocellulosic Biomass

FINAL REPORT


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# 1 Introduction

Buta-1,3-diene (BD) is an essential industrial chemical, widely used in the production of synthetic rubber and various other materials [1]. With global demand reaching 12 Mt/a and growing annually by 1 % to 2 % [2], the overwhelming majority (95 %) of BD production stems from naphtha cracking [1]. This conventional production method imposes significant environmental burdens, predominantly due to its high direct $CO_2$ emissions (300 t/a) [3] and energy-intensive processes [4]. Several alternatives have been proposed, aiming to improve the ecological footprint; however, due to their economical limitations, they are not yet feasible [3, 4].

The novel AixSTRAWdinary process presents a promising alternative to previous efforts, pioneering sustainable and economical BD production processes. BD is synthesized from cereal straw (CS), which has been recognized as a promising biomass source for several years [5]. The AixSTRAWdinary process centers around an innovative two-stage chemocatalytic process, which consists of a direct conversion of lignocellulosic biomass to ethanol and subsequent synthesis to BD. This is achieved without energy-intensive gasification or low-productivity fermentation steps [6]. Besides BD, the AixSTRAWdinary process produces various valuable co-products, high pressure steam (HPS) for neighboring chemical plants, as well as district heating (DH) for nearby communities. To the best of our knowledge, this is the first work to rigorously simulate the entire production pathway from biomass to BD using a chemocatalytic approach.

For the development of AixSTRAWdinary process, we carefully selected the feedstock (sec. 2.1 and 2.3) and determined the plant's location (sec. 2.2). Next, the process was developed according to the Douglas' hierarchy [7] and simulated in Aspen Plus V14® to ensure accurate and reliable results (sec. 3.1 and 3.2). Additional attention was put into heat integration (sec. 3.4) and wastewater treatment (sec. 3.3). To determine the process' viability, a comprehensive techno-economic analysis (sec. 4.2) was performed. Moreover, the social and ecological impact (sec. 4.1.1) were examined, calculating the $CO_2$ equivalent ($CO_2$e) balance. A sensitivity analysis (sec. 4.3) was then performed to scrutinize the validity of critical assumptions. Finally, current limitations and future opportunities were identified (sec. 5).

# 2 Preliminary Considerations

## 2.1 Feedstock

The main feedstock for the AixSTRAWdinary process is CS. According to the Deutsches Biomasseforschungszentrum gGmbH [8], it is the biomass with the greatest technical potential (30 Mt/a in 2015) and third-highest mobilizable potential (4.1 Mt/a in 2015) in Germany, and therefore associated with a low price [9]. Furthermore, it is currently underutilized, with approximately 86 % of CS in Germany decomposing on fields, emitting $CO_2$ in the process [5]. Despite its seasonality, it can be stored on unused fields for a sufficient amount of time at no extra cost to the farmer [10]. A key advantage of using CS as a feedstock is that it avoids negative environmental impacts of land

use change and does not compete with the food industry.

In addition to CS, the AixSTRAWdinary process requires hydrogen ($H_2$) as a feedstock. Here, grey $H_2$ produced by steam methane reforming was chosen. Blue $H_2$ was not used as the prices rose drastically while the environmental benefits remained negligible, while Green $H_2$ was determined to be economically infeasible and therefore also not used.

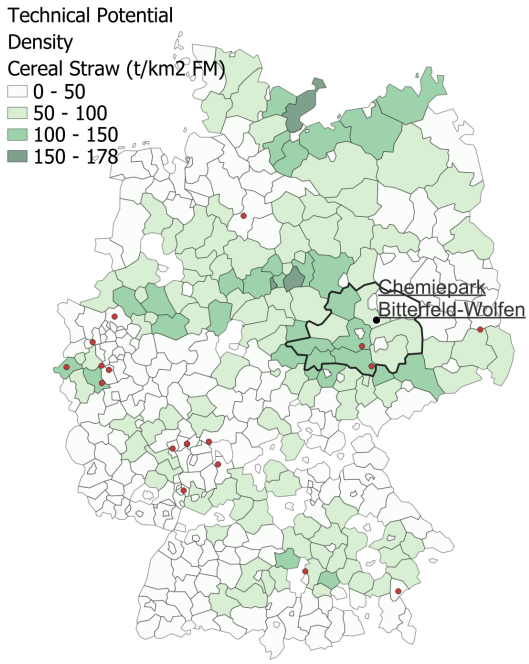



Figure 1: **Cereal straw technical potential in Germany.** Map of the cereal straw technical potential density (t/km$^2$) in Germany

In our concept paper, we considered supplementing the CS with brewer's spent grain, a waste product from beer production, to combat CS's seasonality and increase the plant's flexibility. However, CS can be stored on fallow land for free during winter and with minor cost during the remaining year [10], such that its seasonality is of no concern. Furthermore, including brewer's spent grain as a feedstock would also introduce some competition with the food industry, since it is currently primarily used to supplement animal feed [11].

The low density of CS and therefore costly transportation can be combated by minimizing the transportation distance from the fields to the production plant.

## 2.2 Plant Location

The BD production plant should be located in an area with a high CS density to minimize average transportation distances. Furthermore, to ensure access to centralized utilities, the plant must be located in an existing industrial park. Figure 1 shows the technical potential density in Germany as well as the locations of industrial parks. The Chemiepark Bitterfeld-Wolfen was selected as the plant location due to the high CS density in the surrounding area as well as for its extensive infrastructure. Furthermore, there is a $H_2$ production facility in the park [12], which would eliminate transport costs and emissions.

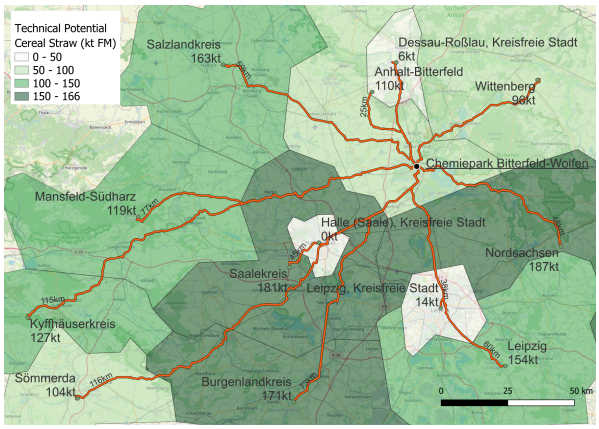



Figure 2: **Cereal straw technical potential near the plant.** Cereal straw technical potential (kt/a) of different districts in Saxony, as well as shortest transport distances to the centroids of the districts.

Figure 2 shows the transport distances from the centroids of the districts to the Chemiepark

Bitterfeld-Wolfen as well as the CS density in the surrounding areas. Considering a region of 13 districts, which are on average 59 km of road distance away from our site, the plant has access to a CS technical potential of 1430 kt/a fresh matter (FM). Recent geospatial data from 2018 shows that this technical potential remains currently underutilized in the selected region around Leipzig and Halle [13]. The region is therefore uniquely attractive as it combines large amounts of unharnessed CS potential with proximity to large scale industrial infrastructure.

The AixSTRAWdinary process requires approximately 510 kt/a dry matter (DM) of CS to produce 50 kt/a of BD. Assuming a moisture content of 41.5 wt.% at harvest [8], approximately 870 kt/a FM of CS is required. Therefore, the surrounding fields produce enough CS for the AixSTRAWdinary process, even if only a fraction of the total 1430 kt/a FM is accessible.

## 2.3 Price & Logistics

After a cereal crop harvest, the leftover CS must be gathered and compressed to square bales. This is accounted for, alongside storage costs and profit for the farmer, in the straw price of 77.7 €/t, which was calculated with the Straw Price Calculator from the Landwirtschaftskammer Niedersachsen [10]. CS has a density of approximately 150 $kg/m^3$ after being pressed into square bales [10]. A standard transport truck has a capacity of 90 $m^3$ [14], which leads to a capacity of 13.5 t of straw. The average cost per tonne of straw was calculated accounting for fuel, labor, tolls, and other fixed and variable costs according to Kotzagiorgis [15]. The straw transportation costs sum to 6.53 €/t, leading to an average total straw price of 84.23 €/t. The average emissions per tonne were taken from the German Umweltbundesamt [16]. They list an average emission of 0.253 $kg_{CO_2e}/(t\,km)$ for trucks over 12.5 t. Therefore, the average total emissions for the transportation of straw are 14.67 $kg_{CO_2e}/t$.

# 3 AixSTRAWdinary Process Design

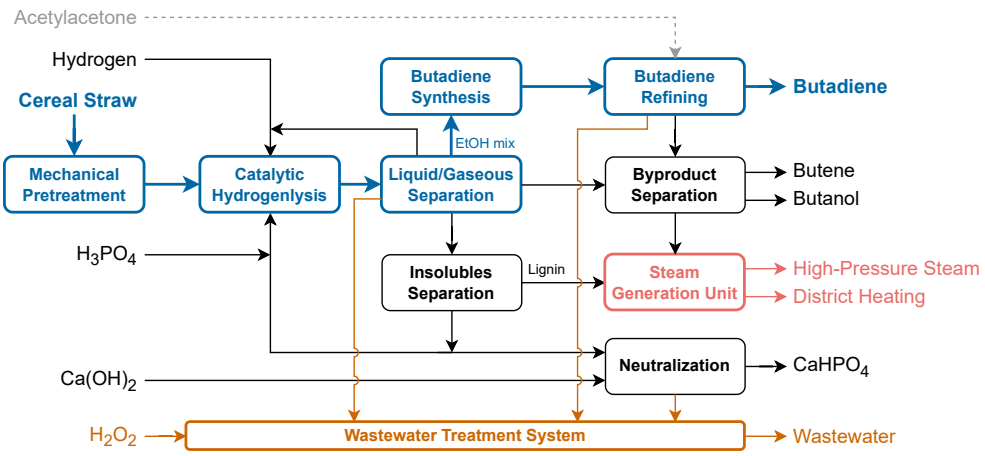



Figure 3: **Overview of the AixSTRAWdinary process.**

In this section, we present AixSTRAWdinary, our innovative chemocatalytic two-step BD production process. An overview of the full process is shown in Figure 3. It can be split conceptually into two main parts: 1) Synthesis of the intermediate ethanol from CS, and 2) Subsequent synthesis of the product BD from ethanol (EtOH).

Based on the process requirements and economical and ecological objectives, a flow chart synthesis was carried out according to the Douglas decision hierarchy [7]. The process was designed as a continuous process due to high volume flows resulting from the production target of 50 kt/a BD. This design choice ensures optimal efficiency and scalability, handling large quantities of feedstock and products while maintaining consistent operational performance.

The overall process was simulated in Aspen Plus V14® using the hybrid NRTL-RK thermodynamic model, which is well-suited to address the non-ideality and operating conditions of our process. The interactions between incomplete functional groups were estimated using the UNIFAC model, which predicts activity coefficients and phase behavior in non-ideal liquid mixtures.

## 3.1 Ethanol Production

For the large-scale production of ethanol, we combined novel approaches for the chemocatalytic conversion of lignocellulose [17, 18, 19, 20, 21]. The approach has a set of distinct advantages over the conventional yeast fermentation route, promising space-time-yields of up to 29 g/(L h) compared to 4.5 g/(L h) for fermentation [18]. In addition, the use of ethanol as an intermediate allows for the supplementation of bioethanol from third parties, increasing the flexibility of the process. In the AixSTRAWdinary process, CS is pretreated before being chemocatalytically converted to ethanol. The ethanol is subsequently purified to meet requirements for optimal butadiene synthesis.

### 3.1.1 Biomass Pretreatment

CS comprises a complex structure of cellulose, hemicellulose, lignin, ash, and moisture. For our simulation, it was modeled in Aspen Plus V14® using the ASPESV140-Databank. In this database, CS consists of cellulose (42 wt.%), xylan (35 wt.%), lignin (11 wt.%), and water (12 wt.%). The inherent recalcitrance of lignocellulosic biomass [22] poses a challenge for efficient chemocatalytic reactions, hence the cellulose must be made accessible to the catalyst by appropriate pretreatment.

In the AixSTRAWdinary process, this is performed by drying and shredding the CS in order to separate the fibers, increasing the surface area and exposing the cellulose [23]. The drying process was simulated as a conveyor belt with a hot air inlet [6]. The shredder's particle size distribution was estimated with fitted ROSIN-RAMMLER parameters [24].

### 3.1.2 Ethanol Synthesis

A previous techno-economic analysis found a chemocatalytic conversion process to be superior to gasification and fermentation [6]. However, it relied on an expensive platinum-based catalyst with an unspecified recovery process [19]. Since then, significantly cheaper transition metal (TM) catalysts with higher ethanol yields, such as Nickel-Carbon nanoparticles (Ni@C), have been developed [18, 25]. We designed a process to convert pretreated lignocellulose directly to ethanol using a Ni@C catalyst in combination with phosphoric acid ($H_3PO_4$).

The Ni@C nanoparticle catalyst shares four distinct properties in contrast to other TM catalysts:

Table 1: **Biomass hydrogenolysis yields.** Yields of the Ni@C+$H_3PO_4$ catalyzed cellulose hydrogenolysis at 50 g/L cellulose concentration, 200 °C, 5.5 MPa, and $t_r$ = 3 h. Adapted from Liu et al. [18].

| **Conversion [%]** | **Yield [C-mol%]** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | EtOH | $CH_4$ | BuOH | Glu | PG | IPA | HMF | EG | Sor | FA | LA |
| 91.2 | 49.6 | 21.0 | 7.5 | 3.8 | 3.4 | 3.2 | 3.2 | 1.4 | 0.4 | 0.2 | 0.1 |

EtOH: ethanol; $CH_4$: methane; BuOH: *n*-butanol; Glu: glucose; PG: propane-1,2-diol; IPA: isopropanol; HMF: hydroxy methyle furfural; Sor: sorbitol; EG: ethylene glycol; FA: formic acid; LA: levulinic acid

- It can be immobilized onto porous active carbon pellets [26].
- The catalyst itself has been shown to be stable [18].
- It is magnetic [27] and thus even leached nanoparticles can be efficiently recovered using a magnetic field [28].
- The synthesis process of the catalyst is straight forward and well described by the authors [18].

The reaction takes place in ten parallel continuously stirred tank reactors (CSTRs) at 200 °C and 5.5 MPa, each with a volume of 150 $m^3$. A suspension of shredded straw and $H_3PO_4$ is fed into the reactors such that the cellulose concentration amounts to 50 g/L. To enable the hydrogenation reaction, compressed hydrogen is supplied via a sparger.

The cellulose-to-catalyst and $H_3PO_4$-to-catalyst mass ratios were taken from Liu et al. [18] With an average residence time of $t_r$ = 3 h, ethanol as well as ten byproducts are formed. The reaction was implemented in Aspen Plus V14® using an `RYield` reactor with yields reported by Liu et al. [18], as shown in Table 1. It was observed that the primary gaseous reaction product was methane ($CH_4$) [18]. In order to balance the reaction stoichiometry, $CH_4$, $H_2$, and water were used accordingly.

### 3.1.3 Separation and Purification

From the top of the reactor `REC-1`, the gas phase is drawn and purified in the gaseous separation system. The liquid phase is drawn from the bottom of the reactor and fractionated in the liquid separation system.

**Gaseous Separation** The gas phase, consisting mainly of unreacted $H_2$ and $CH_4$, is first cooled to 35 °C and then separated in a flash unit (`FLASH-1`). Hereby, the majority of the remaining alcohols in the gas phase are condensed. The gaseous stream from `FLASH-1` is further purified via adsorption to recycle $H_2$ back to the reactor, reducing the required $H_2$ mass flow by 78 %. Two alternately-operated parallel adsorbers (`AD-1`) are loaded with activated carbon [29], effectively removing residual water, alcohols, and methane ($CH_4$). All components except for $H_2$ are desorbed [30] and sent to the steam generation unit (`SGU`) for energetic valorization.

**Liquid Separation** The liquid phase from `FLASH-1` is mixed with the liquid product stream from reactor `REC-1` before the liquid products are separated by distillation. In the first distillation column (`DEST-1`), the heavy boilers, including $H_3PO_4$, are separated along with 99 wt.% of the water, which constitutes the

largest volumetric component of the DEST-1 feed stream. This separation step therefore significantly reduces the flow rates at the top of the column and avoids the evaporation of large quantities of water, which would be energy-intensive.

The mixture of EtOH (65 wt.%), *n*-butanol (BuOH) (8 wt.%), isopropanol (IPA) (4 wt.%), and water (23 wt.%) at the top of column DEST-1 is further purified in column DEST-2. Here, it is important to note that all present alcohols form azeotropes with water. Water-BuOH (91.5 °C) forms a high-boiling heteroazeotrope, while water-EtOH (78.1 °C) and water-IPA (80.1 °C) form low-boiling azeotropes. This characteristic can be exploited to fractionate the mixture by distillation in column DEST-2 [31]. The EtOH-water mixture is concentrated in the top stream to the azeotropic point, with 5.0 wt.% IPA additionally present. EtOH exits the separation system from the top of DEST-2 at a purity of 87.9 wt.%, with further sequestration of IPA impractical due to the similar boiling points.

The heteroazeotropic BuOH-water mixture in the bottom stream forms a liquid-liquid equilibrium [31]. BuOH is further purified in a distillation-decanter system. The aqueous phase, which is seperated in a decanter (DEC-2), is purified in DEST-4, where water is separated at the bottom as a high boiling component and added to the wastewater stream. The BuOH-rich phase is purified in DEST-3. BuOH is separated at the bottom of the column, achieving a purity of 99.9 wt.%. In both columns, the low-boiling heteroazeotropic BuOH-water mixture is separated at the top and returned to Dec-2 to minimize the loss of BuOH. To prevent the accumulation of light boilers (EtOH and IPA), 5 % of the top stream of DEST-4 is purged. The purified butanol is then sold as a byproduct.

**Insolubles Separation** The exact behavior of lignin in our reactor has not been studied in literature. However, several structurally similar components were shown to depolymerize at 200 °C using Nickel-based catalysts [32]. The depolymerisation products were primarily hydrophobic long-chain alcohols, forming a second phase in aqueous solutions[32]. The complex structure of lignin, with its high molecular weight and hydrophobic aromatic rings, further reduces its solubility in aqueous solutions [33]. This aspect was not considered in the experimental studies due to the complexity of accurately replicating lignin [32]. These findings indicate that the phenolic monomers formed due to lignin depolymerization as well as non-depolymerized fragments are poorly soluble in aqueous solutions. Therefore, the presumption was made that the lignin residue is non-soluble in water. A decanter (DEC-1) is used to separate the organic compounds from the aqueous solution. The separated organic compounds are sent to the SGU to be energetically valorized, providing heat for the overall process. 90 wt.% of the aqueous phase is recycled back to the reactor to reduce water and $H_3PO_4$ consumption.

The $H_3PO_4$ in the remaining aqueous phase is neutralized with calcium hydroxide ($Ca(OH)_2$), forming dicalcium phosphate ($CaHPO_4$) [34]. $CaHPO_4$ has the very low solubility of $1.2 \times 10^{-7}$ $g/kg_{H_2O}$ in water and is insoluble in the organic phase [35]. It therefore fully precipitates out of the solution and is then separated via filtration (FLT-1) to be sold as a byproduct. It can be used as a feedstock supplementation for livestock or as a source of phosphorus in fertilizers [36].

## 3.2 Butadiene Synthesis

In the second part of the AixSTRAWdinary process, the EtOH stream is synthesized to the main product BD and the byproduct butene. Although this is an established production pathway dating back to the 1930s [37], many new catalysts are being developed [38, 39, 40] to improve its feasibility. For the synthesis of BD, the one-step LEBEDEV process was selected, since it is reported to be more sustainable and to have lower operating costs than the two-step OSTROMISLENSKY [40].

### 3.2.1 Butadiene Synthesis

The feed to the BD synthesis reactor contains 88 wt.% EtOH, 7 wt.% water, and 5 wt.% IPA. A low $x_{EtOH}$ incurs high CAPEX and OPEX due to the large amount of inert gas that must be compressed in the feed and recycle streams [41], hence maximizing $x_{EtOH}$ was seen as a key criterion. A high catalytic performance in the presence of water was also considered important to prevent energy-intensive EtOH purification past the EtOH-water azeotrope. The $K_2O$:$ZrO_2$:ZnO/MgO – $SiO_2$ catalyst studied by Da Ros et al. [42] was chosen as it combines a high BD selectivity with a high $x_{EtOH}$ of up to 0.8. Furthermore, simulations by Bozga et al. [43] revealed a minimal reduction in EtOH conversion and BD yield with an azeotropic EtOH-water mixture instead of a pure EtOH feed. Therefore, we presume negligible performance losses of this catalyst caused by the presence of water in the feed.

The kinetic model developed by Brosteanu et al. [44] was implemented using the `Rplug` model. As shown in Figure 4, this model considers the production of BD via acetaldehyde (AcH) and crotonaldehyde (Croton), forming butene, $H_2$, and water as side products. With this kinetic model, we achieved an EtOH conversion of 99.8 % and a BD yield of 83.9 %. The feed stream in our process contains 5 mol% IPA. Due to insufficient literature on the interactions between IPA and this catalyst, it was assumed to be inert. Otherwise, further byproduct formation is possible, necessitating additional separation steps. No allenes or alkynes are produced as side products in this reaction.

The reactor design by Bozga et al. [43], who use the same catalyst and kinetic model, has a feed rate of 3800 kg/h. A scaleup was conducted based on their work to produce approximately 50 kt of BD annually. Hence a heated multitube reactor (`REC-2`) with $n_t = 700$ tubes, each with a diameter $d_t = 80$ mm, was dimensioned, resulting in a residence time of $t_r = 10.0$ s. The catalyst is present as spherical particles with diameter 3 mm with a bed void fraction of 50 %. The liquid phase reactants are first pressurized to 3 bar and subsequently preheated to 200 °C.

### 3.2.2 Butadiene Separation and Purification

To separate the BD from the byproducts, first heavy boilers, such as water, IPA, EtOH, and Croton are predominantly sequestered by distillation in `DEST-5`, with the bottom stream being sent to wastewater treatment. Next, the head product is washed with cold water in `EXT-1`, removing most of the butene as well as other impurities. The butene-rich stream is then sent to a stripping column (`STRP-1`), where the butene is recovered from the effluent. Finally it is sent through an adsorption column (`AD-2`) loaded with silica beads, where water [45, 46] and other polar molecules such as AcH [47], EtOH [48], IPA [48], etc. are removed in various degrees. The final butene stream has a mass flow rate of 1087 kg/h and a purity of 97 wt.%.

Conversely, the top stream of EXT-1, containing 94.5 wt.% BD, is compressed to 4 bar to aid the following purification steps. The BD-rich stream is sent through an adsorption column (AD-3) analogous to the the impurity removal of the butene stream. Finally, the BD is brought to the required purity by extraction (EXT-2) using acetylaceton (AcA) as the extractant, as it was shown to achieve the highest extraction efficiency [49]. Here, the hot unpurified BD stream is washed with cold AcA in a stripping column, with the head product sent to the SGU. Lastly, the BD is separated by distillation (DEST-6) and the extractant is recycled.

The resulting liquefied BD achieves a purity of 99.68 wt.%, with the impurities comprising 2409 mg/kg butene, < 1 mg/kg alcohols and carbonyles, and < 1 mg/kg water. No detectable amounts of allenes, alkynes, or sulfur are present in the final product, hence all requirements are fulfilled.

## 3.3 Wastewater Treatment

The AixSTRAWdinary process produces 77.4 kt/h of wastewater with the primary pollutants comprising 0.95 wt.% IPA and 0.13 wt.% butene. As the theoretical chemical oxygen demand (COD) amounts to 33 642 ppm, it must be reduced to comply with wastewater regulations. In a clarification basin (WWT), the pollutants are oxidized to $CO_2$ and water, requiring 0.5 mol of hydrogen peroxide ($H_2O_2$) per mole of IPA [50]. To ensure complete oxidation of both IPA and butene, the four-fold amount of $H_2O_2$ is added. The clarification basin was dimensioned to ensure a residence time of $t_r$ = 3 h [50]. The pretreated wastewater has a theoretical COD of 8472 wppm [51] and is sent to the centralized wastewater treatment.

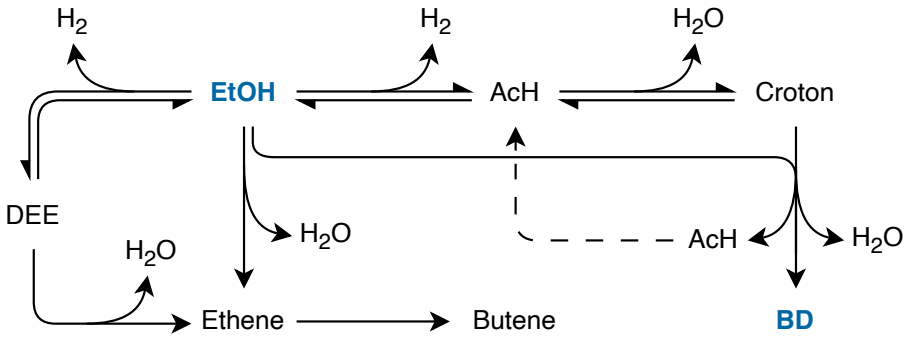



Figure 4: **BD synthesis pathways.** Reaction pathways of the BD synthesis, adapted from [44]

## 3.4 Heat Integration

Since heat integration resembles an important process characteristic, careful consideration was put into integrating as much heat as possible. The composite curve analysis was performed using Aspen Plus V14® Energy Analyzer.

Within the main synthesis pathway, the highest heat consumption is contributed to heating the cellulose solution to the required temperatures for EtOH formation with $\dot{Q}_{\text{HX-1}}$ = 78.6 MW. Conversely, cooling down the products of this reaction yields $\dot{Q}_{\text{HX-2}}$ = 27.1 MW for the gas phase and $\dot{Q}_{\text{HX-3}}$ = 74.0 MW for the liquid

phase. In addition, the distillation columns DEST-1 and DEST-2 have high condenser and reboiler duties due to the large water mass flow and high reflux ratio required. Without heat integration, the utility cost would amount to 180 M€/a, rendering the process economically infeasible.

To provide the thermal energy to the plant, the waste lignin residue from the biomass-to-EtOH reaction as well as most off gases are energetically valorized in a SGU, providing a total heat duty of $\dot{Q}_{\mathrm{SGU}} = 138\,\mathrm{MW}$. The SGU comprises a biomass boiler, flue gas cleaning system, ash pan, and conveyor system. The off gases are used to maintain a continuous and controllable flame in the boiler. In a closed heat transfer loop, the BD reactor REC-2 is heated with a portion of the thermal energy. The remaining heat is used to generate HPS, which is in part supplied to the production plant as a hot utility and in part sold to the site's utility network. With this approach, a heat integration of 75.7 % can be achieved, eliminating the need for hot utilities entirely and lowering the utility costs considerably to 9 M€/a. However, 141.1 MW of low temperature heat still remain unutilized.

Industrial heat pumps are an emerging field promising great integration benefits and were successfully engineered for heating duties up to 120 MW at similar temperature ranges [52, 53]. Hence, in order to improve heat utilization and valorize the remaining low temperature heat, a heat pump was added to elevate its temperature. Thus 68.74 MW of low temperature heat were lifted from $T_{\mathrm{low}} = 64\,^{\circ}\mathrm{C}$ to $T_{\mathrm{high}} = 135\,^{\circ}\mathrm{C}$, enabling a theoretical coefficient of performance (COP) of $\mathrm{COP}_{\mathrm{th}} = 5.83$. Assuming a technical efficiency of $\eta = 85\,\%$, the COP is reduced to 4.96, hence a power input of $P_{\mathrm{el}} = 17.37\,\mathrm{MW}$ is required.

With the integrated heat pump, the high temperature heat from the SGU $\dot{Q}_{\mathrm{SGU}}$ can be harnessed to produce an excess of 215 t/h of HPS. This is supplied to the utility network, cutting the overall costs and carbon emissions of the industry park. In addition, this allows for the integration of a DH network, providing $\dot{Q}_{\mathrm{DH}} = 16.67\,\mathrm{MW}$ at $T_{\mathrm{DH}} = 120\,^{\circ}\mathrm{C}$ to the nearby cities Halle and Leipzig, which already have the necessary infrastructure [54]. If the DH cannot be sold due to seasonal demand fluctuations, the impact on the process performance is limited, as further discussed in Section 4.3.

With the aforementioned approach to heat integration including lignin residue and off gas valorization and heat pump integration, up to 95 % of the process heat is integrable, reducing carbon emissions of utility usage by more than 98 % compared to the unintegrated case. Moreover, accounting for the added the electricity demand, the produced HPS and DH yield a net profit of 83.3 M€/a.

# 4 Process Analysis

To evaluate the AixSTRAWdinary process' performance, a sustainability assessment and economical analysis were carried out, to evaluate its viability.

## 4.1 Sustainability Assessment

In recent years, Environmental, Social, and Governance (ESG) criteria of process evaluation have become increasingly relevant, hence careful consideration was put into analyzing these aspects of the AixSTRAWdinary process.

### 4.1.1 $CO_2$ equivalent balance

This analysis focuses on calculating the $CO_2e$ emissions of the AixSTRAWdinary process. We consider all scope 1 emissions (direct emissions from the process), scope 2 emissions (indirect emissions from utilities), as well as scope 3, cradle-to-gate emissions (indirect emissions from raw materials, including transportation) [55]. The specific $CO_2e$ emissions for each material and utility are shown in Table 3.

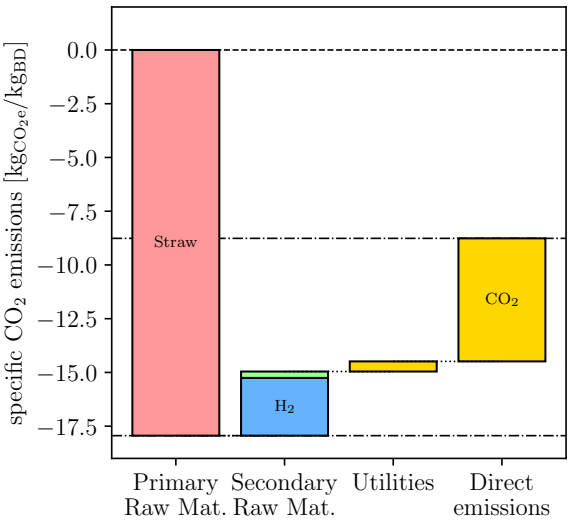



Figure 5: **$CO_2e$ balance.** Composition of the product carbon footprint, entailing cradle-to-gate emissions

The main educt, CS, is assigned a negative value of $-1.79\,kg_{CO_2e}/kg$ as it has already bound $CO_2$ from the atmosphere. This value was calculated with the assumption that the only carbon source during growth is bound $CO_2$, adding the emissions from straw transportation mentioned in Chapter 2.2.

To estimate the cost and $CO_2e$ emissions for the low temperature cooling utility, the compressor duty of the refrigeration unit powered by green electricity was considered. The specific emissions for all other educts and utilities were either given in the ChemPLANT task description or found in literature. Emissions from transportation of $H_2$ have a low impact on the overall emissions whencompared to emissions from production and were therefore neglected [56]. There is also a $H_2$ production plant located in the Chemiepark Bitterfeld-Wolfen [12], which could supply the AixSTRAWdinary process with $H_2$ to prevent transportation emissions and costs. The emissions from the transportation of all other raw materials were neglected due to the relatively small amounts required when compared to straw and water. The overall emissions of the AixSTRAWdinary process are $-8.76\,t_{CO_2e}/t_{BD}$, a considerable improvement over the conventional naphtha-cracking process emitting $1.7\,t_{CO_2e}/t_{BD}$. Since the indirect emissions of products were not considered, the HPS produced in the SGU was assigned a value of $0\,kg_{CO_2e}/t$. If the HPS is considered with a value of $-169\,kg_{CO_2e}/t$, as given in the ChemPLANT task description, the overall emissions improve to $-14.7\,t_{CO_2e}/t_{BD}$.

### 4.1.2 Social Impact

Besides clear economic and ecologic advantages, our approach has multiple social benefits. First of all, the region discussed in Section 2.3 will benefit from multiple new direct as well as indirect jobs, as shown in Section 2. Moreover, the farmers will be able to sell their excess straw, which is currently often unused [57], at a decent price. A large and diverse group of stakeholders, including farmers, is already strongly in favor of establishing a strong straw market [57]. Similar policies promoting an emerging straw market have already been successfully implemented in Denmark, demonstrating its practicability. [57]

The choice of CS as the feedstock as well as our choice in site location in a large industrial park enable an economically viable and sustainable BD production process and will benefit local actors in the area.

## 4.2 Economic Analysis

Based on the simulation results, a techno-economic analysis of the AixSTRAWdinary process was conducted to evaluate its economic viability.

### 4.2.1 CAPEX Evaluation

The total investment $C_\mathrm{I}$ for the process was estimated using a conventional factor method. First, the total equipment cost $C_\mathrm{e}$ of the plant was determined. Based on average multiplication factors $f_{i,n}$ according to Peters et al. [58], the total capital costs $C_{\mathrm{I},i}$ for the equipment $i$ are then calculated using the equation (1). These factors take into account both direct investment costs such as installation costs, infrastructure costs, as well as indirect investment costs and working capital.

$$C_{\mathrm{I},i} = C_{\mathrm{e},i} \cdot \left(1 + \sum_{n=1}^{N} f_{I,n}\right) = C_{e,i} \cdot 5.93 \quad (1)$$

The sizing of the equipment and the associated costs were grouped by process areas and evaluated based on their characteristic sizes, as illustrated in Table 4. Investment costs were determined using Aspen Process Economic Analyzer (APEA) and supplemented by a literature review based on mass and energy balances as well as equipment specifications. Due to the high volumetric flow rate and the required residence time of $t_\mathrm{r} = 3\,\mathrm{h}$ in `Rec-1`, the reactor was divided into 10 identical parallel units and scaled according to the APEA results. The system was scaled using a digression coefficient of $n = 0.45$ since the CAPEX for reactors scale non-linearly with volume [59]. We ensured that the sizing was technically feasible and industrially available through online research, considering the prevailing high pressure of 55 bar in the reactors [60]. The equipment costs for the adsorption and desorption columns were estimated based on the required amount of adsorbent [29, 45], the adsorbent costs [61, 62], and the total volume. Using a safety factor of 1.5 for the volume, the costs were extrapolated degressively ($n = 0.7$) [59] from a distillation tower as dimensioned in APEA.

Since we did not model the SGU in detail within Aspen Plus V14®, we estimated the investment costs correlating the specific investment costs to its thermal power. According to the results of the IEA Task 32 Report [63], we calculated the specific investment costs, which include the biomass boiler, the flue gas cleaning system, the ash pan, and the conveyor system. Since the study considers a combined heat and power plant (CHP), we excluded the costs associated with electricity production to obtain an estimate of the plant costs for providing only HPS. In total, the specific investment costs amount to 970 €/kW. Taking into account the thermal output of the SGU of 140 MW, the investment costs result in 135 M€.

Similarly, we estimated the investment costs for the heat pump by linear extrapolation using 3367 €/kW to approx. 23.1 M€ [64].

The amount of catalyst required for both the straw-to-EtOH and EtOH-to-BD reactions were calculated with the residence time, educt mass flow in the feed, and catalyst-to-educt mass ratio. The estimation of the catalyst cost was based on the prices of the raw materials required for their synthesis. The required materials and their amounts were given by Liu et al. [18] for the Ni@C catalyst and Da Ros et al. [42] for the $K_2O$:$ZrO_2$:ZnO/MgO–$SiO_2$ catalyst. Due to missing data on the lifetime of the catalysts, we assumed a 30 % annual catalyst loss.

The CAPEX for the wastewater treatment unit were estimated based on the total volume of

232 $m^3$ according to Gillot et al. [65] with a linear digression coefficient of $n = 0.7$ [59].

In total, the CAPEX amount to 340.66 M€. All CAPEX were adjusted for inflation to the year 2022. The EtOH reaction system, followed by the distillation columns for EtOH purification, are the most capital-intensive components in the BD production process aside from the SGU and heat pump.

#### 4.2.2 OPEX Evaluation

In addition to the total CAPEX, OPEX are critical for assessing the process' economic viability. Annual operating costs include investment-related expenses and direct production costs. A plant lifetime $T_L = 20$ a, $T_0 = 8300$ h operating hours per year, an interest rate of $i = 5$ %, and a residual value of 0 M€ were used as economic parameters.

To estimate the operational labor requirements, we use the empirical equation [66]:

$$N_P = \left(6.29 + 31.7 \cdot SP^2 + 0.23 \cdot FP\right)^{0.5} \quad (2)$$

where $N_P$ represents the number of workers needed per shift. This is calculated based on the number of processing steps involving solids (SP) and the number of process steps (FP) that do not involve solids. For the Aixstrawdinary process, with SP = 4 and FP = 35, we obtain a required labor capacity of 22.8 workers per shift. Considering that the plant operates 24 hours a day for 346 days a year, with three 8-hour shifts per day, this results in 1038 shifts per year. Each worker works for 48 weeks per year at 40 hours per week, covering 240 shifts per year. Thus, 4.32 shift groups are needed. Consequently, the total required number of workers is $N_P = 98$. With personnel costs of 90 k€/a per worker, we estimate the operation labor cost to be approximately 8.82 M€/a.

The quantities and costs of raw materials, utilities, and waste treatment are detailed in Table 3. All prices were adjusted for inflation to the year 2024. The OPEX, calculated based on the data in Table 2, amount to a total of 178.7 M€/a. The raw material costs account for approximately 53 % of the OPEX, with the most significant expenses being the purchase and transportation of CS and the procurement of $H_2$. By implementing heat integration, we achieve a reduction of 117 % in OPEX. Figure 7 presents a comparative analysis of the revenue breakdown, highlighting key revenue sources and their contributions to the overall financial structure. The annual revenue from the sale of BD, byproducts, and utilities such as HPS and DH amounts to 223.4 M€/a.

#### 4.2.3 Evaluation of Process Profitability

Considering the annual revenue from the sale of products and the Aixstrawdinary process OPEX, the cash flow sums to 44.7 M€/a. To assess the profitability of the process, the standard net present value (NPV) method was applied [66]. This dynamic investment appraisal discounts future payments to their present values [67]. Sustainable BD production via bio-naphtha stream cracking has a BD market price of approximately 2.00 €/kg. Due to great heat integration and byproduct valorization, the BD produced with Aixstrawdinary process can be sold for 1.90 €/kg, leading to a NPV of 216 M€. Since the NPV is positive, the investment is considered profitable. The payback time of the investment is 10 years, as indicated in Figure 6, which reflects the discounted cumulative cash flow over time.

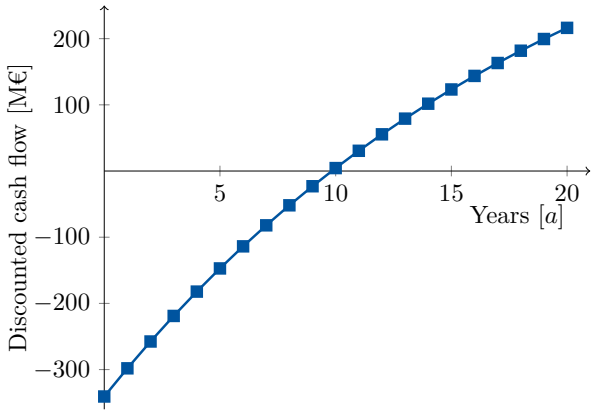



Figure 6: **Discounted cash flow.** Progression of the discounted cash flow over the lifetime of the plant

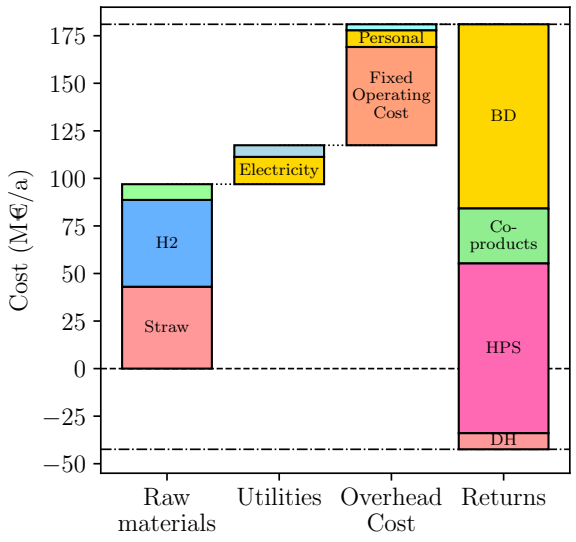



Figure 7: **Annual process costs.** Composition of annual costs for the full process

In addition, we have calculated the minimum selling price (MSP) of BD, which represents the critical selling price at which the process breaks even: NPV = 0. The MSP is calculated as the difference between the CAPEX, OPEX, and the annual revenues excluding BD (REV*) divided by the annual production quantity of BD:

$$\mathrm{MSP} = \frac{1}{\dot{m}_{BD} \cdot T_0} \cdot \left( \mathrm{CAPEX} \cdot \frac{(1+i)^n \cdot i}{(1+i)^n - i} + \mathrm{OPEX} - \mathrm{REV}^* \right) \tag{3}$$

The MSP is calculated to be 1.56 €/kg. The results of the economic feasibility analysis indicate a strong profitability potential for the Aixstrawdinary process. These findings are consistent with other techno-economic analyses of BD production from biomass, which report similar MSP values between 1.4 €/kg to 2.6 €/kg [68, 3]. Compared to the bio-naphtha-based process, the Aixstrawdinary process can produce BD more cost-effectively.

## 4.3 Sensitivity Analysis

The sensitivity analysis is used to investigate the effect of different parameters on the MSP of BD. Key parameters include the prices of CS, $H_2$, electricity, the heat pump power, the yearly fraction of DH demand and the selling price of HPS. We have calculated the change in MSP for changes in these parameters ranging from −30 % to 30 %.

Figure 8 indicates that the selling price of HPS has the biggest impact on the MSP: as the HPS selling price decreases, the MSP increases significantly. The $H_2$ and CS selling prices also exhibit a major impact, while the electricity cost and DH demand have a lower impact. Hence, even if DH demands are less than expected, the process remains profitable. Increasing the heat pump duty enables more DH to be generated, while having a minor impact on MSP. On the other hand, lowering the heat pump duty reduces the available heat for HPS generation, thus substantially elevating the MSP.

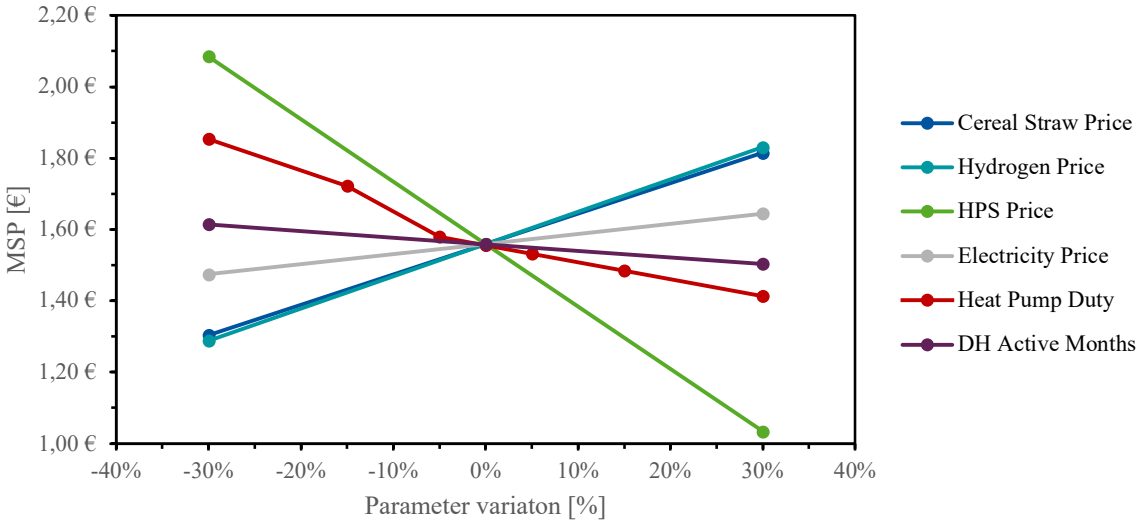



Figure 8: **Sensitivity Analysis.** Influence of various process parameters on the butadiene minimal selling price.

Table 2: **Detailed breakdown of the AixSTRAWdinary process OPEX.**

| **Cost type** | **Calculation** | **Value [M€/a]** |
|---|---|---|
| **Fixed Production Costs** | | |
| Depreciation | $\frac{\text{CAPEX}}{T_\text{L}}$ | 17.03 |
| Imputed interest | $i \cdot \frac{\text{CAPEX}}{2}$ | 8.52 |
| Maintenance and repair | $0.05 \cdot \text{CAPEX}$ | 17.03 |
| Property insurance | $0.01 \cdot \text{CAPEX}$ | 3.41 |
| Property Taxes | $0.01 \cdot \text{CAPEX}$ | 3.41 |
| **Subtotal** | | **49.40** |
| **Variable Production Costs** | | |
| Raw materials $C_\text{RM}$ | | 93.40 |
| Utilities $C_\text{U}$ | | 17.37 |
| Waste treatment $C_\text{W}$ | | 6.65 |
| Operating labor $C_\text{OL}$ | | 8.82 |
| Direct supervisory and clerical labor | $0.15 \cdot C_\text{OL}$ | 1.32 |
| Patents | $0.01 \cdot \text{OPEX}$ | 1.79 |
| **Subtotal** | | **129.35** |
| **Total Cost** | | **178.75** |

Table 3: **Prices and $CO_2$e emissions for materials and utilities.**

| | **Amount** | **Price** | | **$CO_2$e-Emissions** | |
|---|---|---|---|---|---|
| | kt/a | €/t | M€/a | $kg_{CO_2e}/kg$ | $kt_{CO_2e}/a$ |
| **Educts and Auxiliaries** | | | | | |
| Cereal straw | 510.9 | 84.23 [10] | 43.034 | -1.79 | -914.5 |
| Hydrogen | 15.21 | 3000 [69] | 45.636 | 9.00 [70] | 136.9 |
| Phosphoric acid | 2.922 | 900 [71] | 2.630 | 0.95 [72] | 2.8 |
| Acetylacetone | 0.156 | 5000 [73] | 0.778 | 1.90[1] [74] | 0.3 |
| Water | 530.5 | 2.00[2] | 1.061 | 0.0035[2] | 1.9 |
| Calcium hydroxide | 2.279 | 100 [75] | 0.228 | 0.92 [76] | 2.1 |
| Hydrogen peroxide | 6.686 | 530 [77] | 3.544 | 1.20 [77] | 8.0 |
| Catalyst loss | 30 %/a | | 0.035 | - | - |
| **Subtotal** | | | **96.946** | | **-762.3** |
| **Products** | | | | | |
| BD | 50.97 | 1900 | 96.847 | - | - |
| Butene | 8.949 | 1200 [78] | 10.739 | - | - |
| Dicalcium phosphate | 4.179 | 465 [79] | 1.943 | - | - |
| Butanol | 12.82 | 1265 [80] | 16.212 | - | - |
| **Subtotal** | | | **125.741** | | |
| **Waste** | | | | | |
| Carbon dioxide | 292.1 | - | - | 1.00 | 292.1 |
| Wastewater | 620.9 | 5[2] | 3.105 | 0.35[2] | 0.2 |
| **Subtotal** | | | **3.105** | | **292.3** |
| | GW h/a | €/(MW h) | M€/a | $kg_{CO_2e}/(MW\,h)$ | $kt_{CO_2e}/a$ |
| **Consumed Utilities** | | | | | |
| Green electricity | 143.6 | 100[2] | 14.360 | 40[2] | 5.7 |
| Refrigeration | 25.14 | 29 | 0.720 | 11.45 | 0.3 |
| Cooling water | 332.1 | 6.9[3] | 2.291 | 53.5[2] | 17.8 |
| **Subtotal** | | | **17.371** | | **23.8** |
| **Produced Utilities** | | | | | |
| District heating[4] | 161.4 | 70 [81] | 8.473 | - | - |
| High pressure steam | 841.7 | 106.0[5] | 89.225 | - | - |
| **Subtotal** | | | **97.698** | | |
| **Total** | | | **97.706** | | **-446.2** |

[1] Generic value for organic chemicals

[2] Given in the Chemplant task description

[3] Calculated based on a selling price of 0.08 €/$m^3$ as given in the Chemplant task description

[4] Assumed to be sold three quarters of the year due to seasonality

[5] Calculated based on a selling price of 50 €/t as given in the Chemplant task description

Table 4: **Detailed breakdown of the AixSTRAWdinary process CAPEX.**

| Equipment | Quantity | Specification | | Investment cost $C_I$ [M€] |
|---|---|---|---|---|
| **Mechanical Pretreatment** | | | | |
| Dryer | 1 | | APEA | 8.39 |
| Shredder | 1 | | APEA | 3.68 |
| Heat exchanger | 1 | | APEA | 0.07 |
| **Ethanol Production** | | | | |
| Pump | 1 | | APEA | 5.84 |
| Heat exchanger | 7 | | APEA | 9.22 |
| Reactor | 10 | 150 $m^3$ | APEA[1] | 87.89 |
| Catalyst[2] | - | | | 0.46 |
| Flash | 1 | | APEA | 0.47 |
| Distillation column | 4 | | APEA | 24.73 |
| Decanter | 2 | | APEA | 1.71 |
| Adsorption column | 2 | 162 $m^3$ | [29] | 6.76 |
| Filter | 1 | | APEA | 0.44 |
| **Butadiene Production** | | | | |
| Heat exchanger | 9 | | APEA | 2.57 |
| Reactor | 1 | | APEA | 5.84 |
| Catalyst[3] | - | | | 0.23 |
| Distillation column | 5 | | APEA | 9.71 |
| Adsorption column | 4 | 1.5 $m^3$ to 3 $m^3$ | [45] | 0.63 |
| Compressor | 1 | | APEA | 6.51 |
| **Heat Integration** | | | | |
| Steam generation unit | 1 | 970 €/kW | [63] | 135.00 |
| Heat pump | 1 | 3367 €/kW | [64] | 23.14 |
| **Wastewater Treatment** | | | | |
| Wastewater treatment unit | 1 | | [65] | 7.37 |
| **CAPEX** | | | | **340.66** |

[1] APEA calculations were performed for a single reactor and scaled up as detailed in Section 4.2.1

[2] See [82, 83, 84] for material costs

[3] See [85, 86, 87, 88, 89, 90, 91] for material costs

# 5 Limitations & Future Opportunities

A major limitation of the overall process is the substantial quantity of water involved. The reactants are diluted in an aqueous solution to enable the target yield with high selectivity [18, 25]. However, this poses a challenge for downstream processing, as a great amount of heat is required to heat the educts for EtOH formation as well to aid their subsequent separation. Further investigation into reducing the amount of water and its effects on the space-time yield of the overall process is therefore necessary. Additionally, research into novel low-cost catalysts with superior performance compared to the current Ni@C could present an attractive option for improving the overall process efficiency.

As outlined in Chapter 3.4, the AixSTRAWdinary process utilizes the waste lignin and off gases for HPS generation in the SGU, enabling considerable heat integration efficiency improvements. To minimise the exergy losses, the addition of a CHP, providing HPS as well as electricity, could increase the efficiency and profitability even further. The ratio of produced steam and power could be adjusted to the demand in order to account for demand fluctuations. That way even if the produced amount of HPS exceeds the sites current demand, the surplus can be converted to electricity, which can be directly used on-site to supply the heat pump, or sold to the public electricity grid.

Hydrogen plays a key role in the economic and ecologic performance of the AixSTRAWdinary process, as shown in the sensitivity analysis (Figure 8). As hydrogen prices are projected to reduce significantly in the coming years [92], the MSP of BD is conservatively estimated. Therefore, the price gap to the naphtha-process would close, rendering the AixSTRAWdinary process even more competitive. The BD reaction produces large amounts of $H_2$, which is currently sent to the SGU. Hence, recovering and recycling this surplus $H_2$ from the off gas stream could improve the profitability considerably if hydrogen prices stagnate. Future research could also also focus on the potential for on-site $H_2$ production via electrolysis, utilizing electricity generated from lignin valorization in a CHP.

To avoid the use of organic solvents, metal organic frameworks were successfully tested to separate butene and BD [93]. Integrating these findings could improve the CAPEX and $CO_2$e emissions of the process. Further research is required to examine the feasibility of this approach.

# 6 Conclusion

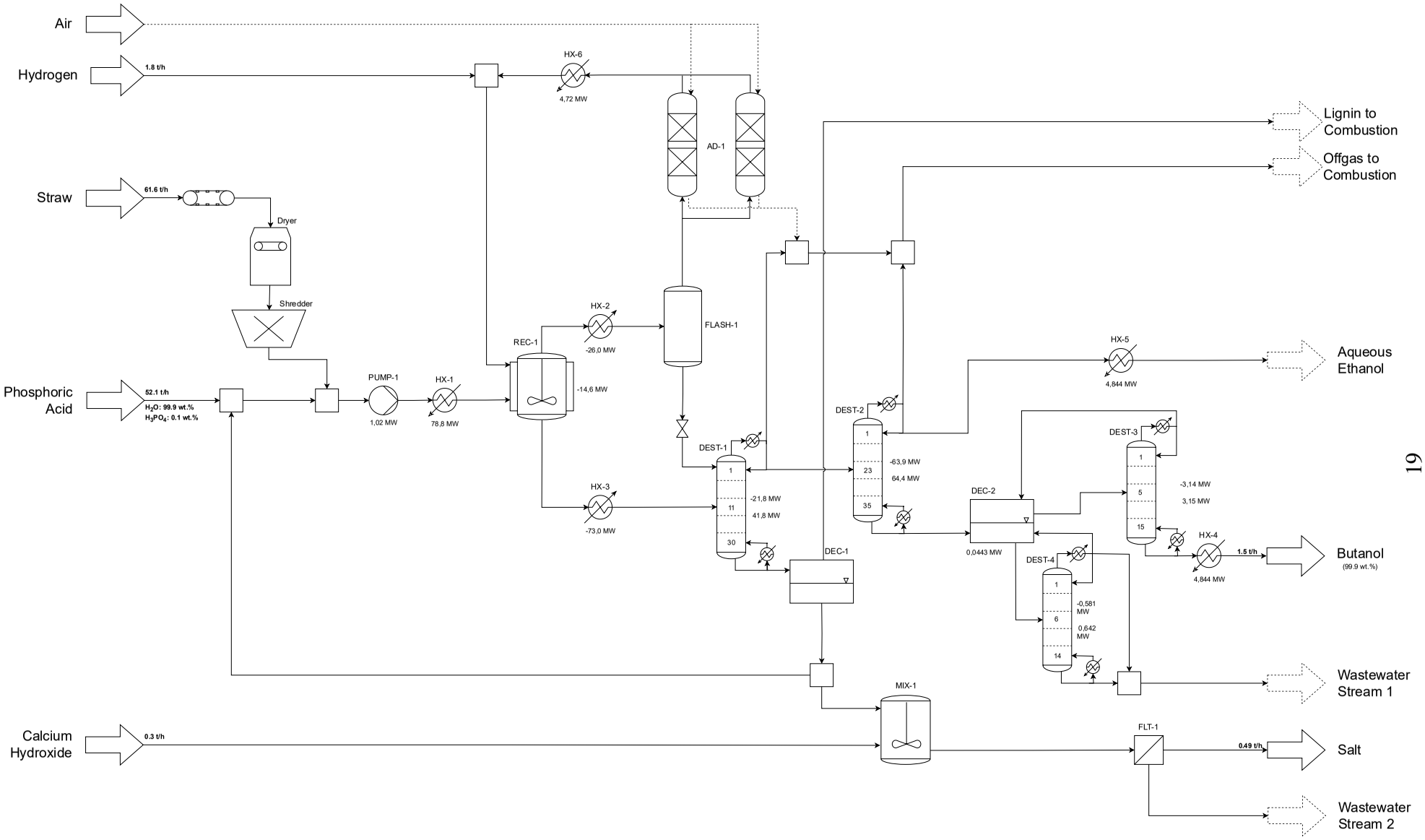
In this work we have developed the AixSTRAWdinary process, a large scale process for the production of 50 kt of buta-1,3-diene per year. Cereal straw was selected as a novel feedstock due to its low price, high technical potential, and underutilization. Furthermore, it is highly sustainable due to the lack of land-use change or competition with the food industry. The plant was placed in the Chemiepark Bitterfeld-Wolfen as it is located in an area with sufficient amounts of CS as well due to its the large existing infrastructure. This was followed by rigorous process design and simulation including heat integration and byproduct valorisation. In addition to BD, the AixSTRAWdinary process produces BuOH, butene, and $CaHPO_4$

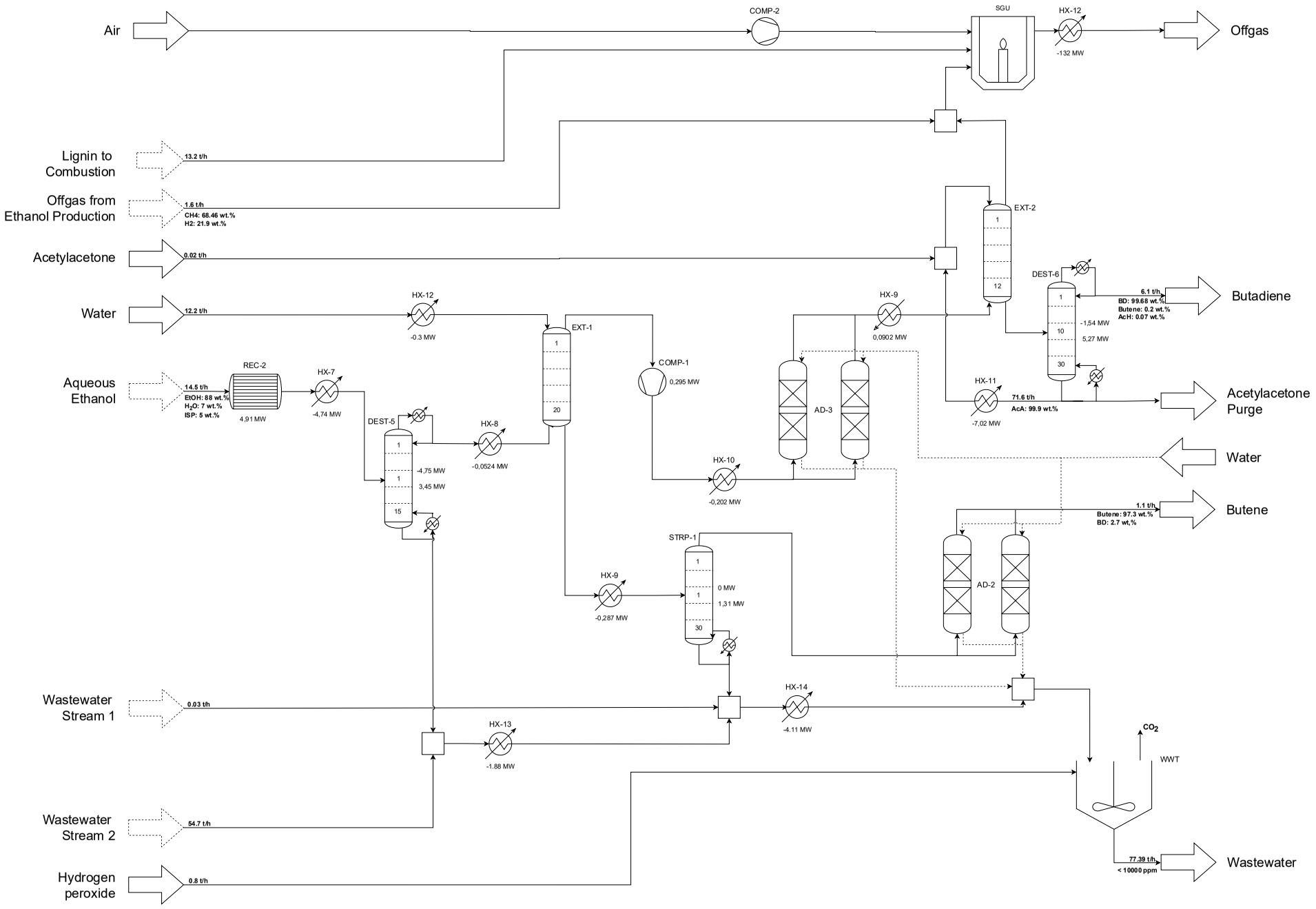
and is able to supply nearby plants with an abundance of HPS as well as district heating to nearby communities.

A sustainability assessment and techno-economic analysis provided insights into the overall performance of the process. We determined a scope 3, cradle-to-gate product carbon footprint of $-8.76\,t_{CO_2e}/t_{BD}$. If the negative emissions of exported HPS are considered , this value improves to $-14.7\,t_{CO_2e}/t_{BD}$. Fossil-based steam-cracking processes, on the other hand, emit $1.7\,t_{CO_2e}/t_{BD}$. Although the selling price is higher than that of conventional fossil-based processes, the AixSTRAWdinary process is far more sustainable. Additionally, the AixSTRAWdinary process provides tangible social benefits by promoting an emerging straw market in the region, which would support local actors, in particular farmers by providing them with a secondary source of income.

Based on our economical analysis, we propose a BD selling price of 1.90 €/kg, leading to a payback time of 10 years. This is notably lower than the reference synthetic naphtha-based process with a selling price of 2.00 €/kg. Sensitivity analysis revealed that the cost of HPS, CS, and $H_2$ are the most impactful cost factors, hence future opportunities relating to these factors were evaluated. In particular, improved catalytic performance, the integration of a CHP, and predicted reductions in $H_2$ price or $H_2$ recycling would significantly improve the AixSTRAWdinary process performance.

We conclude that the AixSTRAWdinary process is a superior alternative to BD production processes based on synthetic naphtha. Furthermore, it could compete with traditional fossil-based BD production processes in the future.


Air
Hydrogen
1.8 t/h
HX-6
4,72 MW
AD-1
Lignin to Combustion
Offgas to Combustion
Straw
61.6 t/h
Dryer
Shredder
HX-2
-26,0 MW
FLASH-1
REC-1
-14,6 MW
HX-5
4,844 MW
Aqueous Ethanol
Phosphoric Acid
52.1 t/h
$H_2O$: 99.9 wt.%
$H_3PO_4$: 0.1 wt.%
PUMP-1
1,02 MW
HX-1
78,8 MW
DEST-2
1
23
35
-63,9 MW
64,4 MW
DEST-3
1
5
15
-3,14 MW
3,15 MW
DEST-1
1
11
30
-21,8 MW
41,8 MW
HX-3
-73,0 MW
DEC-2
0,0443 MW
HX-4
4,844 MW
1.5 t/h
Butanol
(99.9 wt.%)
DEC-1
DEST-4
1
6
14
-0,581 MW
0,642 MW
Wastewater Stream 1
MIX-1
Calcium Hydroxide
0.3 t/h
FLT-1
0.49 t/h
Salt
Wastewater Stream 2


Air
COMP-2
SGU
HX-12
-132 MW
Offgas
Lignin to Combustion
13.2 t/h
Offgas from Ethanol Production
1.6 t/h
CH4: 68.46 wt.%
H2: 21.9 wt.%
Acetylacetone
0.02 t/h
EXT-2
1
12
DEST-6
Water
12.2 t/h
HX-12
-0.3 MW
EXT-1
1
20
COMP-1
0,295 MW
HX-9
0,0902 MW
6.1 t/h
BD: 99.68 wt.%
Butene: 0.2 wt.%
AcH: 0.07 wt.%
Butadiene
1
10
30
-1,54 MW
5,27 MW
Aqueous Ethanol
14.5 t/h
EtOH: 88 wt.%
H2O: 7 wt.%
ISP: 5 wt.%
REC-2
4,91 MW
HX-7
-4,74 MW
DEST-5
1
1
15
-4,75 MW
3,45 MW
HX-8
-0,0524 MW
AD-3
HX-11
-7,02 MW
71.6 t/h
AcA: 99.9 wt.%
Acetylacetone Purge
HX-10
-0,202 MW
Water
1.1 t/h
Butene: 97.3 wt.%
BD: 2.7 wt.%
Butene
STRP-1
1
1
30
0 MW
1,31 MW
HX-9
-0,287 MW
AD-2
Wastewater Stream 1
0.03 t/h
HX-14
-4.11 MW
HX-13
-1.88 MW
CO2
WWT
Wastewater Stream 2
54.7 t/h
Hydrogen peroxide
0.8 t/h
77.39 t/h
< 10000 ppm
Wastewater

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