ChemPLANT Competition

AixSTRAWdinary

Synthesis of Butadiene from Lignocellulosic Biomass

ABSTRACT

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The AixSTRAWdinary process:

- presents a **novel**, integrated process, combining cutting-edge technologies.
- uses cereal straw as an **innovative feedstock**, demonstrating its tremendous potentials.
- was **rigorously simulated** in Aspen Plus V14®, including a sensitivity analysis.
- is remarkably sustainable, with **CO_2e emissions** of $-8.76\,\mathrm{kg_{CO_2e}/kg_{BD}}$ (Scope 3, cradle-to-gate) and a meaningful **social impact** on local communities.
- constitutes an **economically viable** alternative, yielding a minimum selling price of $1.56\,€/\mathrm{kg_{BD}}$.

Introduction Buta-1,3-diene (BD) is an essential industrial chemical, widely used in the production of synthetic rubber and various other materials. As the overwhelming majority of BD is produced conventionally via naphtha cracking, it imposes significant environmental burdens, predominantly due to high direct CO_2 emissions (300 t/a) and energy-intensive unit operations. Our novel AixSTRAWdinary process presents a promising alternative to previous efforts, pioneering sustainable and economical BD production processes. To the best of our knowledge, this is the first work rigorously simulating the entire production pathway from biomass to BD using a chemocatalytic approach.

Innovative Feedstock Instead of fossil-based resources, the AixSTRAWdinary process uses cereal straw (CS), which has been recognized as a promising biomass source for several years. CS has the greatest theoretical potential of 30 Mt/a among biomass sources in Germany. In addition, its under-utilization causes low selling prices. In order to minimize transportation cost, Chemiepark Bitterfeld-Wolfen was chosen due to its high CS density in the adjacent areas and accessibility to industrial infrastructure. The surrounding fields around the plant location, as outlined in Figure 1, produce enough CS to meet the feedstock demand of the AixSTRAWdinary process.

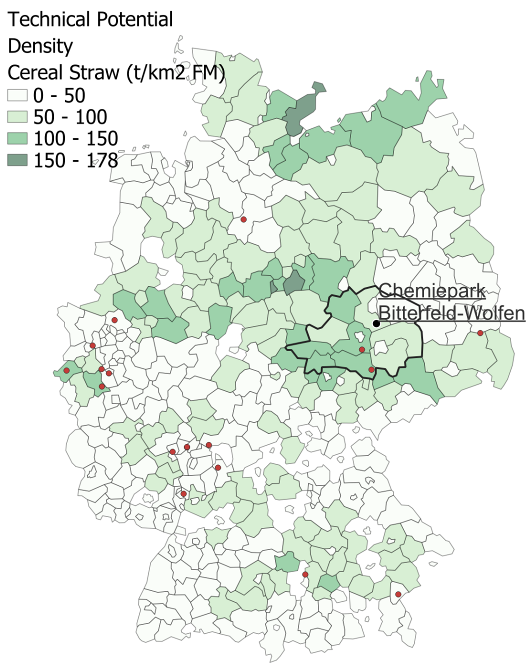

Figure 1: Cereal straw technical potential density (t/km^2) in Germany

AixSTRAWdinary Process Design The process was designed to be continuous to meet the production target of 50 kt/a of BD. The overall process was simulated rigorously in Aspen Plus V14® using the hybrid NRTL-RK thermodynamic model. An overview of the AixSTRAWdinary process is shown in Figure 2.

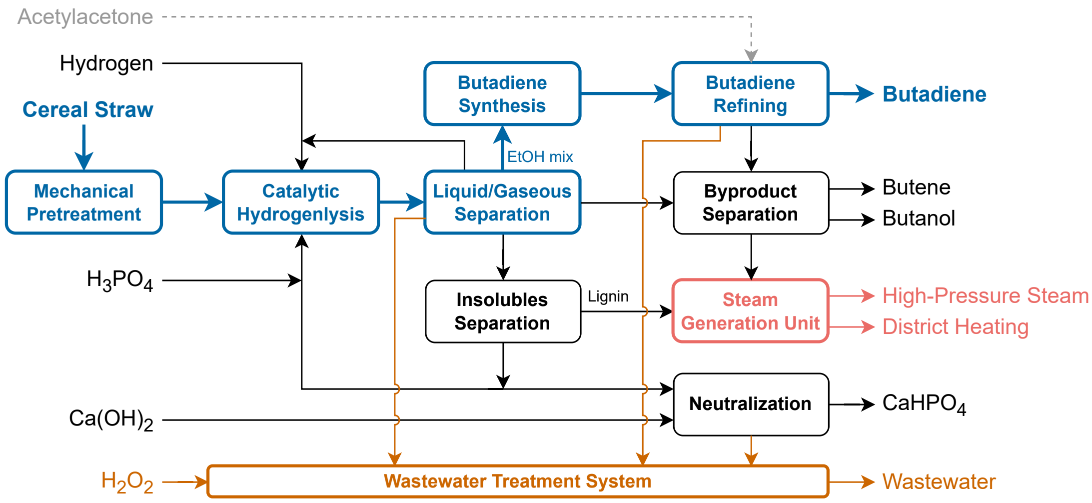

Figure 2: Overview of the AixSTRAWdinary process

The AixSTRAWdinary process centers around an innovative two-stage chemocatalytic synthesis, which consists of a direct conversion of lignocellulosic biomass to the intermediate ethanol and subsequent synthesis to BD. This is achieved without energy-intensive gasification or low-productivity fermentation steps.

Although few studies have investigated the intermediate synthesis stage, it was shown to be a viable alternative, achieving low overall CO_2 emissions. A Nickel-Carbon nanoparticles (Ni@C) catalyst in combination with phosphoric acid (H_3PO_4) was chosen due to its low cost, high ethanol yield, long-term stability, and ability to be immobilized by porous activated carbon pellets.

Ethanol (EtOH) is converted to BD with the one-step LEBEDEV process. While this process dates back to the 1930s, it was outperformed by naphtha stream cracking processes and not researched further until recently. We selected a K_2O:ZrO_2:ZnO/MgO – SiO_2 catalyst as it shows low catalytic performance losses in the presence of water, avoiding a costly purification of EtOH past its azeotropic point with water. The AixSTRAWdinary process meets the production target of 50 kt/a of BD with a purity of 99.68 wt.%.

Byproduct Valorization In addition to BD, other components such as butanol (99.9 wt.%), butene (97 wt.%), and dicalcium phosphate ($CaHPO_4$) (99.9 wt.%), can be sold as valuable byproducts.

Other remaining components such as, depolymerized lignin fragments, methane, and volatiles are energetically valorized in a steam generation unit (SGU). The including of the SGU and a heat pump enable the integration of 95 % of the overall process heat; in particular, no hot utilities are necessary. An excess of 215 t/h high pressure steam (HPS) can be supplied to nearby plants. In addition, the process provides district heating (DH) to nearby communities.

The process wastewater is pretreated through oxidation with hydrogen peroxide to meet the chemical oxygen demand requirements.

Sustainability Assessment A scope 3, cradle-to-gate carbon balance was performed and is depicted in Figure 3. The overall CO_2 equivalent (CO_2e) emissions of the AixSTRAWdinary process amount to $-8.76\,t_{CO_2e}/t_{BD}$, which is a significant improvement to the established naphtha-cracking process, which emits $1.7\,t_{CO_2e}/t_{BD}$. If the sold HPS is considered in the carbon balance, the overall emissions improve to $-14.7\,t_{CO_2e}/t_{BD}$.

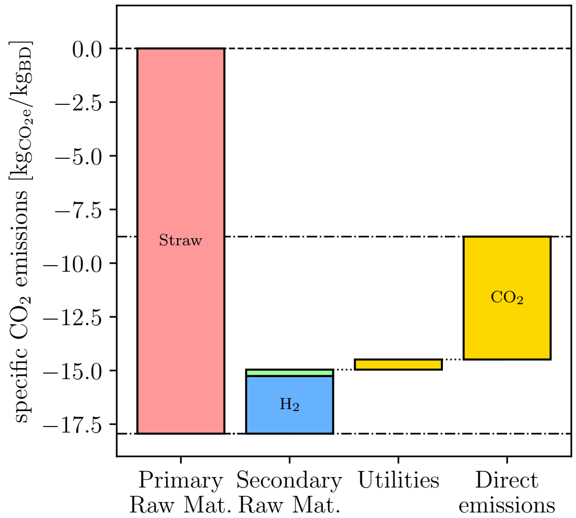

Figure 3: Breakdown of the CO_2e emissions

In addition to its ecological advantages, the AixSTRAWdinary process promotes social benefits by introducing new job opportunities to the region and supporting local farmers through the utilization of excess straw.

Economic Analysis A techno-economic analysis of the AixSTRAWdinary process was conducted to evaluate its economic viability. The total capital expenditures (CAPEX) of the process amount to 340.66 M€, while the operational expenditures (OPEX) are 178.75 M€. Figure 4 depicts the contribution of different key revenue sources to the overall financial structure. The revenue from the sale of BD, byproducts, and utilities such as HPS and DH amounts to 223.4 M€/a. Taking into account the net present value method, an interest rate of 5 %, and a plant lifetime of 20 years, we obtain a minimum selling price (MSP) of BD of 1.56 €/kg. A sensitivity analysis revealed that the MSP strongly correlates with the price of hydrogen (H_2) . Through heat integration and co-product valorization, BD can be sold for 1.90 €/kg, resulting in a net present value of 216 M€ and a payback period of 10 years. Our proposed selling price offers a distinct advantage over the reference bio-naphtha process, which has a market value of 2.00 €/kg. The results of the economic analysis indicate a strong profitability potential for the AixSTRAWdinary process.

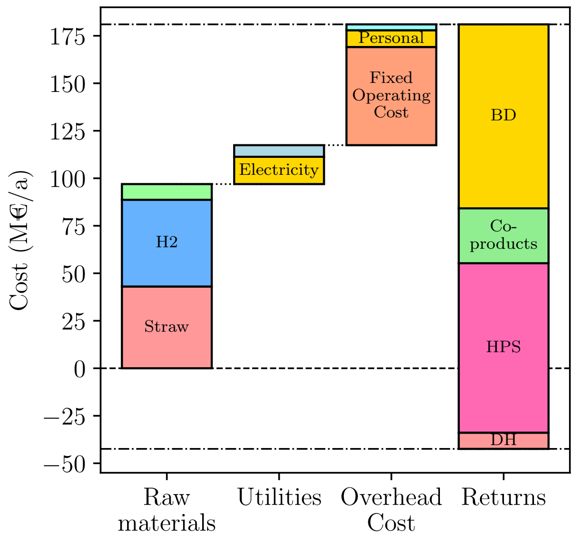

Figure 4: Breakdown of the per annum costs

Conclusion Due to its well-integrated design and novel approaches, the AixSTRAWdinary process constitutes very promising process both economically and ecologically. As H_2 prices are projected to decrease in the future, the price gap to the conventional naphtha-process could close, rendering the AixSTRAWdinary process even more competitive.