# Sample design problem and answers

## Comparison of ethanol and naphtha routes for but-1,3-diene production

The sample problem involves the comparison of a biobased and a petrochemical but-1,3-diene production process. The biobased process under consideration involves the production of but-1,3-diene from bioethanol over heterogeneous chemical catalysts 21, 22. This process is compared with its dominant petrochemical counterpart in which but-1,3-diene is produced by steam cracking of naphtha23. Further details for the processes can be found in the supporting information. The method is simultaneously applied to both processes and the individual parameter scores are normalized. The results for each of these parameters are examined in detail in the following sections.

## Parameter assessment results

Figure 4: Economic constraint comparison for but-1,3-diene from bioethanol and naphtha+

+ The scores presented in this figure have not been normalized

Figure 4 shows a comparison of the parameter “Economic constraint” for the two processes. It indicates feedstock costs for the process as a fraction of the market value of the products and co-products. The result is based on European market prices 24 for ethanol (0.78 €/kg), naphtha (0.63 €/kg), ethylene (0.98 €/kg) and but-1,3-diene (1.32 €/kg) in November 2010 and average 2010 prices 24 for other chemicals. The naphtha-based process offers greater economic leeway for processing, compared with the bioethanol-based process. However, it is important to note that the market prices change continuously based on supply and demand. A process developer needs to realize that an economic constraint above 1 does not necessarily mean that the process is not worth pursuing. An uncertainty and sensitivity analysis in conjunction with an evaluation of the market outlook should be used for decision-making based on this information. For example, if, even after considering theoretical yields and optimistic market scenarios, the economic constraint is above 1.5-2, that is a strong indication for exploring alternatives. In this particular case of but-1,3-diene production processes, there have been wide variations in the price of but-1,3-diene over time 24. On the supply side, greater steam-cracking capacity is expected to be put into operation in the Middle East. This capacity will be increasingly based on lighter feedstocks (ethane, propane). This could decrease co-production of C4s and thus but-1,3-diene. On the other hand, there is an increasing demand for but-1,3-diene from China, India and other growing markets. With this market outlook, one could expect favorable economic opportunities for an bioethanol-based but-1,3-diene process.

Figure 5: CED and GHG emissions for but-1,3-diene from ethanol and naphtha route

Figure 5 shows the comparison of the CED and GHG emissions associated with the bioethanol- and naphtha-based but-1,3-diene production processes. The CED and GHG emission data for raw materials is obtained from the Ecoinvent database 12 and EU directive 2009/28/EC 25. Bioethanol-based but-1,3-diene has a higher overall CED compared with naphtha-based but-1,3-diene. This is primarily due to the fact that the CED includes both renewable and non-renewable energy. The naphtha process has undergone extensive process and supply chain optimization in the past decades, thus making it more efficient. In comparison, the bioethanol process is relatively new and involves energy inputs to agriculture and the harvesting of crops in addition to chemical conversion. It is also more process-intensive to make a product from solid biomass compared with liquid crude oil. In a way, this higher CED also supports the opposite outcome observed for the PCEI (see Figure 6), since the energy inputs included in the CED occur outside of the system boundary of the PCEI. It is important to note that the allocation approach also plays a role in the final CED value for but-1,3-diene.

In contrast to the CED, the GHG emissions are higher in the case of naphtha-based but-1,3-diene. This deviation from the CED trend is observed because the emissions associated with the naphtha-based route include future emissions from fossil carbon embedded in the but-1,3-diene product, which will eventually be released into the atmosphere as CO2. The GHG emission value of ethanol is based on the EU directive 2009/28/EC 25 for biofuels. The value used is based on a mandated 35% reduction in GHG emissions of bioethanol compared with gasoline. In this directive, the current 35% reduction requirement is set to be reduced further to 60% by 2018. Thus further reductions in ethanol GHG emissions can be expected in the coming years.

Figure 6: PCEI scores for bioethanol- and naphtha-based but-1,3-diene processes

Figure 6 shows a comparison of potential process costs and environmental impacts for but-1,3-diene production based on the energy loss index and the various contributing factors. In this case, both processes are based on only one reaction and a subsequent separation step. The scores compared in figure 6 are raw scores for each process and have not been normalized. The bioethanol-based process involves one reaction step and three co-products. This makes it a relatively simple conversion process with lower separation requirements. The naphtha-based process involves a large number of products (>9), some with fairly close boiling points, which need to be separated. On a mass basis, but-1,3-diene is only 5% of the output stream from the steam cracker. In general, steam cracking is also a strongly endothermic reaction, thus demanding large additional energy inputs. In line with expectations, the model indicates that the naphtha-based process needs relatively more intensive processing compared with the bioethanol-based process. Thus relatively lower processing costs and environmental impacts can be expected in the case of an ethanol-based but-1,3-diene process.

Figure 7: Comparison of process hazards for bioethanol- and naphtha-based but-1,3-diene

Figure 7 shows the comparison of the EHS index (EHSI), which is based on the hazard scores of the processes as allocated to the but-1,3-diene product. It is evident that the naphtha-based but-1,3-diene process carries a moderately higher hazard compared with the ethanol-based but-1,3-diene process. The hazard index is based on the specific mass flows of the chemicals per unit of product within the process. Both processes lead to one metric ton of but-1,3-diene, which carries an identical hazard potential in both cases. The difference in scores shown in figure 7 therefore originates from the hazard potential of the respective inputs and other co-products. The more hazardous characteristics of naphtha and steam-cracking co-products compared with ethanol explain the higher EHS index.

Figure 8: Risk aspects index comparison

In this method, we also assess certain risk aspects associated with a conversion process. Figure 8 shows a comparison of this parameter for the two routes of but-1,3-diene production. In figure 8, not all the indicators are displayed on the bar chart, since some indicators have a score of 0 for the processes being compared. Given the timeframe considered, both feedstocks can be expected to be widely available in large quantities. The market value of but-1,3-diene is higher than the value of ethanol for fuel use. Thus there is a good probability that bioethanol will be available for processing to but-1,3-diene through an economically feasible process. This indicates a low feedstock supply risk (therefore zero score for both routes).

But-1,3-diene has a well-established commodity-scale market that is expected to grow further. Thus we expect a low market risk. In the case of the ethanol-based process, new infrastructure and logistics will need to be developed for processing, which entails additional risks. In comparison, the addition of new capacity based on existing naphtha-based technology has considerably lower risks.

This particular analysis has been considered from the perspective of implementation of the process in Europe. In the case of naphtha, large-scale availability in the EU will be dependent upon imports from countries outside the EU, which would more or less be classified under free markets. However, ethanol production in the EU is increasing, which will enable the benefits of regional feedstock availability for but-1,3-diene production. In this case, since the target molecule is same, the technical aspects associated are similar.

Overall, based on the weighting factors, the bioethanol-based process has a comparatively lower score for this parameter. For the given timeframe and context, this parameter gives a good indication of the risk aspects associated with the biobased process. For different contexts, such an indicator or the respective weights can be modified accordingly and used to incorporate external qualitative information in the assessment scheme.

## Integrated score

Integrating the scores for each parameter, Figure 9 shows the overall comparison of bioethanol- and naphtha-based but-1,3-diene processes using the baseline weights which are indicated in parenthesis. As lower scores are better, the figure indicates that the bioethanol-based process has an edge over the petrochemical process. Table 4 shows the raw scores for each of the parameters considered. For an ethanol-based process, one can expect comparatively lower processing costs, process hazards and marginally lower risks. However, the ethanol-based process has a comparatively higher economic constraint and a similar environmental impact of raw materials. The total score of the ethanol-based route is 0.81 compared with 0.90 for the naphtha route. Thus the index ratio for the ethanol-based process is 0.90. This indicates that the bioethanol-based process may be beneficial. Apart from its use for evaluating and improving the new process, the index ratio can also be used to rank different process options. If one were to evaluate the potential benefits in terms of magnitude of contribution to the society, then in addition to the beneficial index ratio, the market size of the product could also be explicitly considered.

Figure 9: Bioethanol- and naphtha-based but-1,3-diene process comparison

Table 4: Bioethanol- and naphtha-based but-1,3-diene process scores for each parameter

|  |  |  |
| --- | --- | --- |
| Parameters+ | Ethanol- based | Naphtha- based |
| Economic constraint (index) | 1.00 | 0.83 |
| Environmental impact of raw materials (normalized index)# | 0.81 | 0.76 |
| Process cost and environmental impact (index) | 1.93 | 3.60 |
| EHS hazard potential (index) | 1.95 | 2.67 |
| Risk aspects (index) | 0.14 | 0.15 |

+ Lower values are better for the respective processes.

# Cumulative energy demand ( MJ/kg but-1,3-diene): 118.96 (bioethanol); 61.17 (naphtha).

# GHG emissions (kgCO2 eq./ kg but-1,3-diene): 2.45 (bioethanol); 3.98 (naphtha).

## Uncertainty and sensitivity analysis

The index ratio gives a good first indication of the sustainability of a biobased process option. To evaluate the robustness of this result and aid in decision-making, an uncertainty and sensitivity analysis has been carried out. A 20% decrease in the yield from ethanol would lead to an index ratio of 0.91. In the case of theoretical yields of but-1,3-diene from ethanol, the resulting index ratio is 0.89. The relatively minor change in the index ratio can be attributed to the fact that the combined value of all the products and co-products from the reaction is considered. Thus a 20% yield decrease for but-1,3-diene production results in a corresponding increase in production of co-products. It is important to note that this change depends on the value of the co-products. If the co-products produced are of low economic value, then a change in yields can lead to significant variations in the index ratio.

Figure 10: Histogram of Monte Carlo simulation results for base-case weighting set (N = 10000)

Table 5: Results of Monte Carlo analysis for base-case weighting set

|  |  |
| --- | --- |
| Parameter | Value |
| Mean | 0.87 |
| Standard deviation | 0.10 |
| Minimum | 0.60 |
| Maximum | 1.46 |
| Kurtosis | 4.3 |

Figure 10 and table 5 show the results of the Monte Carlo analysis based on the uncertainty in the estimated environmental impact and economic feasibility. The uncertainty in parameters such as yields, the CED and GHG emissions has been incorporated. In the case of economic data, the uncertainty in prices for bioethanol, naphtha, ethene, propene and but-1,3-diene has been used. Quarterly prices from January 2007 to November 2010 have been taken into account 24, 26. This range incorporates the wide variation in chemical and fuel prices that was experienced during this time frame. The results indicate that in terms of the index ratio, the ethanol-based process can be expected to provide benefits in 90% of the scenarios. These statistics support the outcome, which indicates that ethanol-based but-1,3-diene can provide certain benefits compared with the naphtha-based process.

Figure 11: Histogram of Monte Carlo simulation results with variation in weighting sets and default parameter set for ethanol to but-1,3-diene (N = 1000)

However, the uncertainty analysis reported in figure 10 is based on a particular weighting set, which represents a viewpoint in a general context. As an example in some regions of the world, the risk aspects might carry a high weight. Figure 11 shows the distribution of the index ratio for a wide range of randomly selected different weighting sets, within specified ranges. These index ratios are estimated for the default set of parameter values. The mean value of this distribution is 0.92, while the standard deviation is 0.05. This reaffirms the validity of the outcome over a wide range of different viewpoints.

## System boundary discussion



Figure 12: Information flows using a smaller system boundary



**Figure 13: Information flows using an extended system boundary**

For this assessment method one could use different system boundaries, which involves consideration regarding which raw material to start with and where it lies along the value chain. To assess the effect of a change in system boundaries on the model’s outcome, we consider the biobased but-1,3-diene production process. The two respective system alternatives have been shown in figures 12 and 13. In both figures, solid dark arrows represent quantitative information based on the market data or detailed modeling efforts. The hatched arrows represent qualitative information based on indices, which is used in the absence of quantitative information. The width of an arrow represents the weight assigned to that particular aspect. The bubbles represent information that is implicitly incorporated in the information carried by the arrows and the model in general. We combine these information flows using weights into a total score.

The results presented earlier for the ethanol-to-but-1,3-diene process (figure 9) are represented by the system shown in figure 12. Alternatively, instead of using ethanol as our starting point, we could start with glucose. This second alternative is represented in figure 13. In this case, we analyze the glucose-to-ethanol *and* the ethanol-to- but-1,3-diene conversion steps. The integrated scores for the comparative assessment of glucose-based and naphtha-based but-1,3-diene are shown in figure 14. The total scores in this case are 0.82 and 0.95, respectively, for the glucose- and naphtha-based processes. Thus the index ratio works out to 0.87. Please refer to the electronic supplementary information (ESI) for additional explanation about the interaction and interdependence of different parameters in reference to the system boundary.

Figure 14: Glucose- and naphtha-based but-1,3-diene process comparison

The key question here is how to select the system boundary. Life-cycle assessment follows the approach of extending the system back to the cradle in order to include the environmental impacts of the entire process chain; a more complete analysis ensures more accurate results. Based on this example, one may consider the approach in figure 13 with an extended system boundary to be more accurate than the one in figure 12. However, the opposite is valid for this assessment because we utilize a mix of background and foreground information. The approach for this method is based on the assumption that the price, the CED and the GHG emissions of raw materials carry quantitative information regarding the costs, hazards and environmental impacts involved in the production of the raw materials. For the extended system represented by figure 13, quantitative and rather accurate information is obtained for the glucose raw material. This information is then complemented with qualitative and semi-quantitative information (PCEI, EHSI) for the glucose-to-ethanol and ethanol-to-but-1,3-diene conversion steps. In the case of the system represented by figure 12, quantitative and again relatively accurate information is obtained for the ethanol raw material. This information is then complemented with qualitative and semi-quantitative information for only the ethanol-to-but-1,3-diene conversion step. Hence in the case of a smaller system boundary, the assessment relies more on external quantitative information and less on qualitative and semi-quantitative information about the process.

As an example, to get an indication of the energy demands of but-1,3-diene production from ethanol, both the CED value for ethanol and the energy loss index (ELI) are used. The latter can be seen as a proxy (qualitative information) for the energy requirements related to the conversion of ethanol to but-1,3-diene. The combination of this information with the CED of ethanol can be seen as a proxy for the CED of but-1,3-diene. The CED for ethanol represents definite information based on detailed modeling efforts and data. This information is complemented with indicative information using the energy loss index for the process cost and environmental impact to get an indication of the CED of but-1,3-diene without detailed modeling. In the case of an extended system boundary, however, in addition to quantitative information on the CED of glucose, the outcome relies on two sets of proxies (qualitative information): first for the glucose-to-ethanol and then for the subsequent ethanol-to-but-1,3-diene conversion step. Thus a smaller system boundary ensures that the outcome from the model is based on higher-quality quantitative information. Hence a system boundary representing exclusively the conversion of ethanol to but-1,3-diene (figure 12) should provide the most accurate evaluation. However, in the case of a category such as EHS hazards, there is a tradeoff involved in having a smaller system boundary. To some extent, it can be assumed that hazard costs are estimated and priced into the product price through insurance and investments into hazard control mechanisms. However, the internalization of hazard costs into the price of the product depends on local governmental laws and the regulatory framework in the region where the product is produced. If there is only limited legal enforcement in countries representing a substantial part of global production, this could explain lower production costs and hence lower prices; in this case, prices would not properly reflect good practice in hazard control. It also relies on the very definition of hazards, which can vary across regions. Some aspects might not be viewed as hazards in some regions, while they might be classified as hazards in others. In such a scenario, a smaller system boundary can be less desirable because it increases the reliance of the outcome on externally estimated hazards built into prices rather than on concrete hazard indices estimated within the model. Nevertheless, given the uncertainty in hazard classification and estimation, combined with the weight for each hazard category, we believe the outcome from the model would be more plausible in the case of a smaller system boundary.

# Design problems for homework

1. Compare the production of biobased route to propylene glycol from glycerol to that petrochemical route from propylene and report on the results
2. Find 2 different catalytic conversion routes from literature, to convert natural gas to methanol and compare with the existing route.