EarlySim module: Case study

Early stage assessment to find sustainable alternative routes to manufacture 1,3-butadiene.

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# Introduction

But-1,3-diene is a widely produced bulk chemical which is used in the production of rubber and a variety of other end products. In recent years the demand for but-1,3-diene has been steadily increasing owing to the growth in demand from emerging markets. Conventionally most of the but-1,3-diene has been produced as a co-product of ethylene/propylene production by steam cracking of petroleum naphtha. However, with recent market developments the feedstock for steam cracking to produce ethylene/propylene has been shifting to lighter feedstocks (ethane, propane). This could decrease co-production of C4s and thus but-1,3-diene. These market developments have opened up opportunities for alternative routes to produce but-1,3-diene.

There is also an increasing societal demand to reduce the environmental impact of chemicals production. A shift to new production routes for but-1,3-diene presents an opportunity to develop and commercialize alternative production routes that are not only economically viable but also environmentally more sustainable and safer.

In this case study, you will rapidly compare an alternative production route from ethanol with the conventional naphtha based production route. To enable a rapid analysis and comparison this case study relies on the process chemistry based early stage assessment methodology which has been convered in the presentation. For case study purpose the input data for the two routes has been provided. Once you understand the early stage assessment approach to compare the routes, you can then iterate to compare other alternative production routes. You can think of other catalysts or reaction schemes for ethanol conversion or you can test conversion of other feedstocks. Alternatively you can also test converting a feedstock to but-1,3-diene in in different world locations (e.g. by considering variations in prices and environmental impacts of feedstock).

The goal is to use your creativity and rapid early stage assessment to find promising alternative production routes that are economically viable, safer and more sustainable.

You can either construct an excel model to carry out the analysis or alternatively you can use the online Early Sim software module from SustAnalyze. Detailes for signing up are listed in the Get Started with online module document.

## 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.

In the biobased process, ethanol is converted to but-1,3-diene over heterogeneous catalyst in a gas phase reaction at around 400 oC. The table S1 shows the relevant process chemistry level inputs and outputs along with the stream mass fractions for this reaction that is considered in the preliminary assessment. The chemicals with zero fractions (e.g. ethoxyethane mass fraction in table S1) do not play a direct role in the presented results for the case study. However, they are included because some other routes (using different catalysts) for this conversion report the presence of these compounds.

Table S1: Ethanol to but-1,3-diene conversion reaction

|  |  |  |  |
| --- | --- | --- | --- |
| Inputs | | Outputs | |
| Chemical name | **Mass fraction (wt%)** | **Chemical name** | **Mass fraction (wt%)** |
| Ethanol | 100 | But-1,3-diene | 41.2 |
| Water | 0 | Ethene | 6.6 |
|  |  | Ethanal | 8.6 |
|  |  | Hydrogen | 1.9 |
|  |  | Ethoxyethane | 0 |
|  |  | But-1-ene | 0 |
|  |  | Ethanol | 10 |
|  |  | Water | 31.7 |

In the reference petrochemical process, but-1,3-diene is produced as a co-product in steam cracking of naphtha at around 800 oC to produce ethene. The table S2 shows the relevant inputs and outputs for this conversion.

Table S2: Steam cracking of naphtha

|  |  |  |  |
| --- | --- | --- | --- |
| Inputs | | Outputs | |
| Chemical name | **Mass fraction (wt%)** | **Chemical name** | **Mass fraction (wt%)** |
| Naphtha | 100 | Ethene | 32.4 |
|  |  | Propene | 16.8 |
|  |  | But-1,3-diene | 5.0 |
|  |  | Benzene | 10.4 |
|  |  | Hydrogen | 1.1 |
|  |  | Methane | 13.9 |
|  |  | Other C4 (Butane, But-1-ene, 2-Methylpropene) | 6.2 |
|  |  | Other aromatics (Methylbenzene, dimethylbenzene) | 0 |
|  |  | Pentane, Hexane | 4.0 |
|  |  | C7+ non aromatics (Heptane) | 1.2 |
|  |  | Fuel oil | 9.0 |

## Raw material environmental impact inputs

*Bio-Ethanol*

Considering the context of this but-1,3-diene case study, the bioethanol being used for this assessment is assumed to be produced in the European Union (EU). Hence, a general European feedstock mix for bioethanol is used for this assessment. This feedstock mix is based on the process ‘Ethanol (at distillation, RER/U, biomass)’ in the ecoinvent database12 and the input values are as mentioned in the article by Patel et al.

A GHG emission value of 1.46 kg CO2/kg bioethanol is used for the case study. It should be noted that this value represents only the fossil CO2 emissions from the bioethanol production process. The biogenic CO2 emissions are not considered since the biogenic CO2 is recycled into biomass in a rather short time frame.

The cumulative energy demand (CED) associated with bioethanol is derived from the mean value associated with the above mentioned ‘Ethanol (at distillation, RER/U, biomass)’ process in the ecoinvent database12. Based on this reference a value of 71.4 MJ/kg is used for the case study.

*Naphtha*

Considering the EU context, the GHG emissions and CED associated with naphtha production are based on the process ‘Naphtha (at refinery, RER/U)’ in the ecoinvent database12. This represents an average for naphtha production in the EU. The corresponding mean values for GHG emissions and CED are 0.42 kg CO2/kg naphtha and 53.1 MJ/kg naphtha respectively.

As evident, the GHG and CED values for a feedstock are based on benchmarked or average data. Hence, the inherent uncertainty needs to be considered in the uncertainty analysis.

## Sensitivity analysis

A sensitivity analysis can help you determine the sensitivity of the overall outcome (sustainability index ratio in this case) to variation in the underlying data inputs. As an example in this case study, test the sensitivity of the outcome to a 20% variation in the price of ethanol. You can also use the online software for sensitivity analysis.

## Uncertainty parameters

An uncertainty analysis can play a crucial role in decision making by allowing you to construct a probability distribution of the outcome based on the probability of variation in data inputs. At this point the uncertainty analysis cannot be created using the online software. However, if you choose to model in excel, you can use an excel plugin (if you have access) from Crystal Ball, @Risk and others. In such cases you can use the uncertainty data inputs listed in the table below. This table shows the probability of variation and the values that are possible for a particular data input. These are based either on histrorical data or values from different data sources or world regions. A key benefit of uncertainty analysis is that it allows you to consider wide variations for all the data inputs, which means that if a production route is not viable with any of the variations, then there is a very less chance that it will be viable in future.

Table S4: Uncertainty analysis data

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Units | Distribution | Mean | Std. Dev. | Max | Min |
| CEDethanol | MJ/kg | Normal | 71.4 | 8.92 |  |  |
| CEDnaphtha | MJ/kg | Normal | 53.1 | 1.66 |  |  |
| GHGethanol | kgCO2/kg | Lognormal | 1.46 | 0.52 |  |  |
| GHGnaphtha | kgCO2/kg | Normal | 0.42 | 0.04 |  |  |
| SelectivityEtOH2butadiene |  | Triangular | 0.78 |  | 0 | 1 |
| Prices |  |  |  |  |  |  |
| Ethylene | Euro/MT | Normal | 951 | 182 |  |  |
| Butadiene | Euro/MT | Normal | 1292 | 498 |  | 0(trunc) |
| Naphtha | Euro/MT | Normal | 679 | 208 |  | 0(trunc) |
| Propylene | Euro/MT | Normal | 767 | 213 |  |  |
| Benzene | Euro/MT | Normal | 927 | 288 |  |  |
| Ethanol | Euro/MT | Normal | 666 | 71.6 |  |  |

## Scenario analysis

A scenario analysis is used test the outcome in a specific future scenario which you deem more probable. For this case study, assess the outcome for a future scenario in which lignocellulosic ethanol with a price of 650 USD/metric tonne, CED of 48 MJ/kg ethanol and GHG emissions of - 0.219 kgCO2 eq./kg ethanol is available. This can be implemented by changing the data input in the online software or excel and testing the outcome.

## Case study assessment results

The assessment results listed in the sections below are based on the provided data inputs. Kindly check your data inputs if you reach different assessment results. However, do go ahead and be creative in trying out new ideas and new iterations for the processes.

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

+ The scores presented in this figure have not been normalized

Figure 1 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 2: CED and GHG emissions for but-1,3-diene from ethanol and naphtha route

Figure 2 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 3), 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 3: PCEI scores for bioethanol- and naphtha-based but-1,3-diene processes

Figure 3 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 4: Comparison of process hazards for bioethanol- and naphtha-based but-1,3-diene

Figure 4 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 5: Risk aspects index comparison

In this method, we also assess certain risk aspects associated with a conversion process. Figure 5 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 6 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 6: Bioethanol- and naphtha-based but-1,3-diene process comparison

Table 1: 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 7: Histogram of Monte Carlo simulation results for base-case weighting set (N = 10000)

Table 2: 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 8: 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.

# 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.

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