

The energy of exergy – analysis of different olefin production routes

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Keywords

exergy analysis, CO₂ reduction, chemical industry, olefin production

Abstract

In order to achieve the greenhouse gas emissions reduction targets, there must be a significant reduction in all sectors. The chemical and petrochemical sector was responsible for 7 % of worldwide CO₂ emissions and 10 % of worldwide industrial final energy demand in 2010. For this reason, efficiency potentials must be used or new production processes introduced. In the context of decarbonisation, the focus is often exclusively on the energy perspective, since this provides the relevant information for investment decisions in the field of energy or greenhouse gas efficiency. However, for industries in which energy carriers are used both energetically and materially, a purely energetic analysis can only have limited informative value with regard to the efficiency of the entire production process. An alternative to purely energetic analysis is exergy analysis, in which all relevant material flows for an analyzed process are included. In this context, an indicator for the efficiency of the overall process can be defined that combines energy and material flows. We therefore conduct such an analysis for the production of olefins by the steam cracking process. The required data is based on a virtual production plant according to the Best Available Techniques (BAT) document of the JRC. In addition, we analyze two possible future production processes and compare them with the current production process. The future production processes consider the production of Olefins either from waste or from hydrogen and CO₂. The exergy efficiency of the steam cracking process is around

56 %. The results show that the exergy efficiency cannot be increased with any of the possible future production processes we have investigated.

Introduction

The chemical and petrochemical sector was responsible for 7 % of worldwide CO₂ emissions and 10 % of worldwide industrial final energy demand in 2010 (IEA 2013). Conventional production processes such as steam crackers release large quantities of CO₂. In order to achieve the greenhouse gas reduction targets, efficiency potentials must be used or new production processes introduced. In the context of decarbonisation, the focus is often exclusively on the energy perspective, since this provides the relevant information for investment decisions in the field of energy or greenhouse gas efficiency. In the area of energy indicators, the Specific Energy Consumption (SEC) is usually used as an indicator for evaluating the energy efficiency of energy-intensive production process routes (Wilson 2012). In principle, the energy requirement of the process per tonne of manufactured product is shown here. However, increasing material efficiency within processes is also of great importance and in some cases can generate even greater savings than increasing energy efficiency (Skelton et al. 2013). An alternative to purely energetic analysis is exergy analysis, in which all relevant material flows for an analyzed process are included (Hernandez and Cullen 2016).

In the exergy analysis, both the energy sources and the material inputs and outputs of a system are assigned to exergies. Thus, the exergy analysis offers an integrated evaluation tool to consider the energetic as well as the material efficiency of a

process in an integrated way (Michalakakis et al. 2019). This means that the indicator of exergy efficiency considers both the energetic and the material components in one indicator. This approach has the advantage that waste materials are not only identified, but their value is also quantified in the form of “exergy content”. This applies both to waste streams that can be used for energy purposes (e.g. waste heat from hot flue gases) and to material waste streams (hot slags, etc.) (Szargut 1987). Another advantage is that the exergy analysis considers the working capacity of the thermodynamic system. This means that in addition to the quantity, the quality of the energy is also considered. The application of exergy analysis is widely used in the literature (Michalakakis et al. 2019, Hernandez and Cullen 2019, Xiang et al. 2015, Hajjaji et al. 2012, Luis et al. 2014).

A disadvantage of exergetic analysis is that the interpretation of the results is difficult. The results always depend on the system boundaries (see section Method) and the system configurations used. For this reason, the derivation of technical recommendations for action can also be different for each investigated system.

In our study, the exergetic consideration helps to identify unused efficiency potentials and to initiate possible improvements. Additional potentials in the area of material efficiency and energy efficiency can thus be identified under certain circumstances. In particular, the exergetic consideration helps in the evaluation of production processes with a material use of exergetically high-quality raw materials. For example naphtha is used in the current production of olefins, which is used both for energy but also predominantly for material purposes. The advantage of the exergetic evaluation (as carried out in this study) is that these plausibility considerations do not have to be carried out in the first place. During the evaluation, raw materials used (especially exergetically high-grade) are consistently and comprehensively included. In the previous example this leads directly to the fact that the exergetic efficiency of the two compared processes for olefin production is at a similar level. It can therefore be seen directly that the processes are similarly efficient in principle. The added value of exergy analysis, which results above all from the integrated consideration of material and energy flows, becomes particularly clear through this.

Many different production processes for the future production of olefins are currently presented in the literature (Bazzanella 2017; VCI 2019; Material Economics 2019). In our study we consider two of these possible future production processes. The literature has not yet conclusively decided which future production process is the most promising. For this reason, we are conducting an exergetic evaluation of the production processes to find out which production processes are most promising from an exergetic point of view and which should not be researched any further. This analysis has not yet been carried out in the literature.

PRODUCTION PROCESS DESCRIPTION

In this paper we investigate different production processes of olefins in the chemical sector. The term olefins covers many different products. In this paper and following the definition of “high value chemicals (HVC)” in Brunke (2017), olefins include the substances ethylene (C_2H_4), propylene (C_3H_6) and butadiene (C_4H_6). Depending on the reference source, BTX are also counted as HVC. In this paper we investigate the follow-

ing current and possible future production processes for the production of olefins.

1. The steam cracking process.
2. Olefin production with waste-to-methanol (WTM) and methanol-to-olefins (MTO).
3. Olefin production with methanol synthesis (CO_2 & H_2) and methanol-to-olefins (MTO) (olefins from CO_2 & H_2).

We have selected the possible future production processes for the analyses based on expert interviews in 2016. There are also other possible future production processes. Other potentially promising processes are for example methane pyrolysis or pyrolysis from waste. A brief description of these production processes is given below. Based on this, the system boundaries of the analysis and the life cycle inventories determined are described.

Steam Cracker:

About 98 % of the global production of ethylene is carried out in steam crackers. The production of olefins using the steam cracking process can be divided into three main steps:

First, the raw materials (hydrocarbons: naphtha, ethane, propane, butane and gas oils) are cracked in the steam cracking furnace into short-chain olefins (alkenes: ethylene, propylene and butadiene, among others) (Fleiter et al. 2013). The starting raw materials are first mixed with hot steam and heated to approx. 600 °C. The mixture of hydrocarbons and steam is then briefly heated to 750–875 °C and thereby split (Brunke 2017). Second, the cracked gas is quenched to avoid secondary reactions (Zimmermann and Walzl 2012). Then the cracked gas is cooled down to ambient temperature in washing towers. During this process different fractions (e.g. pyrolysis oil and pyrolysis gasoline) are separated. The resulting cracked gas is first compressed step by step and further fractions (including water) are separated. The water is then used again for steam generation. Third, the cracked gas is fractionated into the desired products (olefins). This process varies depending on the set process configurations (Falcke et al. 2017/BREF LVOC). A possible process control consists in the separation of methane and hydrogen from the cracked gas by cryogenic separation (low-temperature separation: -150 °C). Afterwards a further decomposition of the fission gas takes place to produce the desired products. Rectification processes are used in particular.

With regard to the energy consumption of the described process, the cracking furnace, which is responsible for about 65 % of the total energy consumption, as well as the cooling for cryogenic separation are particularly relevant (Brunke 2017; Fleiter et al. 2013; Romero and Linares 2014; Zimmermann and Walzl 2012).

Waste to Methanol (WTM)

Methanol can be produced from waste (in the literature also referred to as the Waste to Methanol (WTM) process). The carbon content of the waste and thus the composition of the waste is of great importance. A possible process variant is described in Iaquaniello et al (2017). The process described there can be divided into five main steps: First, the waste is gasified to synthesis gas in a high-temperature gasifier. Second, the synthesis gas produced is cooled and purified in a cooling tower. Third, any hydrogen sulphide present in the synthesis gas is

separated and the synthesis gas is stored temporarily. Fourth, carbon monoxide (CO) is partially removed from the synthesis gas. For this purpose, a water gas shift reaction is performed in which excess carbon monoxide (CO) is reacted with water (H_2O) to form carbon dioxide (CO_2) and hydrogen (H_2). This is necessary because a certain ratio of hydrogen (H_2) and carbon monoxide (CO) in the gas must be set for the conversion of the temporarily stored synthesis gas to methanol. Fifth, the synthesis gas is converted to methanol in a reactor.

Methanol production from CO_2 and H_2 (methanol synthesis)

In possible future production processes, methanol can be produced by the synthesis of carbon dioxide (CO_2) and hydrogen (H_2). A possible process variant is described in Pérez-Fortes et al (2016). In this work, energy and mass balances are given for the entire process. The process variant of Pérez-Fortes et al. (2016) is divided into the following four main steps: First, CO_2 is compressed by several compressors and then mixed with hydrogen. The hydrogen is obtained within the production process by electrolysis of water. Second, the methanol synthesis of CO_2 and H_2 takes place in a reactor. Third, the emerging gas stream is cooled down, which allows an almost complete condensation of the methanol. Fourth, the methanol is distilled to separate the water in the condensate.

Methanol-to-olefins (MTO)

The Methanol to Olefins (MTO) process is a process in which olefins are produced from methanol. In this study, the so-called MTO UOP process of the company UOP LLC (cf. Johansson 2013; Ren et al. 2008) is assumed in this respect. Another process configuration is investigated in Hannula et al. (2015). The MTO UOP process can be divided into three main steps.

First, methanol is fed into a fluidized bed reactor. In the fluidized bed reactor a catalyst is used to produce a gas that is particularly rich in ethylene and propylene. The percentage yield of ethylene and propylene is determined, among other things, by the choice of catalyst and the control of the temperature and pressure in the reactor. The reactions inside the reactor are exothermic, i.e. heat is provided. In order to achieve the highest possible yield of ethylene, the reactor is operated at a temperature between 500 and 520 °C and a pressure between 1 and 3 bar. The gas stream leaving the fluidized bed reactor contains light olefins (ethylene, propylene, butadiene and butylene) as well as carbon monoxide (CO) and carbon dioxide (CO_2). Second, the gas stream exiting the reactor is cooled down to about 95–115 °C. This is done by quenching. This also removes water and dust from the gas stream. Dimethyl ether and methanol remaining in the gas stream is returned to the reactor. Third, the individual gas fractions are fractionated. This is analogous to the fractionation during production via the route with steam crackers.

Data and Method

DATA

To prepare the mass balances, the incoming and outgoing mass flows are calculated and assigned to the respective subsystems. Different data are used to prepare mass balances for the individual processes. These are presented in the following.

The mass balances for the production process of the **steam cracking** process were prepared based on the data in Falcke et al. (2017)/BREF LVOC. Table 3 14 shows the relative product yield with the steam cracking process when using naphtha for the production of olefins according to Falcke et al. (2017)/BREF LVOC as well as the allocation of the products manufactured from the starting material to the respective partial streams. It should be noted that these production quantities reflect a typical one-off production yield and that not all of the listed products occur in every steam cracking furnace.

For the **WTM** process we use the process description and data from Iaquaniello et al. (2017). The composition of the waste is given in Iaquaniello et al. (2017) as follows: 3 % wood, 29 % paper, 31 % plastics, 7 % textiles, 12 % organic substances, 18 % inert substances. The waste used in Iaquaniello et al. (2017) is a refuse-derived fuel (RdF). The relevant composition assumptions were obtained for the contribution from an Italian waste treatment company. Assumptions for the first step (high-temperature gasifier) were made in Iaquaniello et al. (2017) using a real existing plant in Italy (Malagrotta). The further steps and the entire WTM process were simulated in a process simulation program (process simulator PROII). This resulted in energy and mass balances for the entire process, which are summarized in the article (p. 613 in Iaquaniello et al. (2017)). There, the input flows resulting from the simulation (substitute fuel, electricity and distilled water) are compared with the output flows (CO_2 , inert substances, sulphur, salts and methanol). This comparison refers to a production quantity of 300 tonnes per day. These figures were used to determine material flows and energy balances. The daily electricity requirement is 16 MWh. The previous data were used to prepare the mass balances in this paper using the daily production volume.

For the production process **methanol from CO_2 and H_2** , all data regarding mass balances are taken from Pérez-Fortes et al. (2016). In this thesis a model for a possible plant configuration was created and analysed both materially and energetically. The individual steps of the process were simulated in the process simulation software CHEMCAD. In addition, a pinch analysis was carried out to model the possible heat exchangers and the energy demand. The size of the plant corresponds to that of a conventional plant with an annual production capacity of 440 kt methanol (CH_3OH) and a production time of 8,000 hours per year. To derive the material flows from Pérez-Fortes et al. (2016) the following procedure was followed: In Pérez-Fortes et al. (2016) the process was modeled using the process simulation software CHEMCAD. The mass of the entire flow and the percentage composition of the flow are given for each flow entering or leaving the process. From this, the masses of the respective substances can be calculated for each stream. Based on this, an overall balance for the process is drawn up by adding the individual substances in the streams.

In Johansson (2013) a model of an **MTO** plant was created using the process simulation software Aspen Plus, which was integrated into an existing plant. Additionally, the MTO plant is considered as a single process. Two different process conditions for operating the reactor were investigated. One is a “high propylene” model in which the conditions are strongly designed to increase the yield of propylene. On the other hand, a “high ethylene” model in which the conditions are designed to increase the ethylene yield. Since in our investigations the mass balances

are based on ethylene, the “high ethylene” model is used in this case. The modelled plant has a production of 200 kt ethylene per year. The operating time of the plant is given as 8,000 h per year. To determine the energy demand of the MTO process, the publications Ren et al. (2008) and Ortiz-Espinoza (2017) were also evaluated.

METHOD

Our methodology for calculating the exergetic efficiency of the production processes consists of four steps:

1. Preparation of mass balances
2. Calculation of the exergies of the substances
3. Preparation of exergy balances
4. Comparison of the exergy balances of the different processes

In the first step, we prepare the mass balances of the production processes based on a detailed literature research. For each of the three production processes, we define the system boundaries and prepare a mass balance for the incoming and outgoing material flows. Further information on the literature used can be found in the chapter Data.

In the second step, the exergies of the individual entering and exiting substances are calculated. The calculation of these exergies is mainly based on Riedl (2006) and Radgen (1996). For the calculation of the exergy, a distinction is made between substance-free (work and heat) and substance-flow-bound exergy. Work W is free of entropy and thus represents pure exergy (exergy of work E_W):

$$E_W = W \quad (1)$$

In contrast, the exergy of heat E_Q depends on the temperature level, the exergy of heat is calculated using the Carnot efficiency η_c according formula 2:

$$E_Q = \frac{T - T_U}{T} * Q = \eta_c * Q \quad (2)$$

The Exergie E_s , which is linked to the material flow, consists of several components. These are mainly the physical exergy E_{PH} (or thermomechanical exergy), the chemical exergy E_{CH} and the potential E_{POT} and kinetic exergy E_{KIN} and is calculated according formula 3. More details can be found in Riedl (2006) and Radgen (1996). The physical exergy is based on pressure and heat of the respective substances. To calculate the physical exergy of heat, the Carnot factor must be taken into account. The chemical exergy depends on the chemical composition of the material flows. Our chemical exergy calculations are based on Szargut (1987).

$$E_s = E_{PH} + E_{CH} + E_{POT} + E_{KIN} \quad (3)$$

E_{POT} and E_{KIN} are so small in our analyzed processes that they are neglected in the course of further consideration.

The sum of all these exergies represents the total exergy of a substance within the production process. The exergetic analysis is carried out with the help of these calculation bases. A distinction is made between the usable exergy flows E_{USE} , the external exergy losses E_L and the exergy destruction (e.g. irreversibility

and process-related exergy destruction according to the definition of external exergy losses) E_D .

$$\sum E_{IN} = \sum E_{USE} + \sum E_L + \sum E_D \quad (4)$$

The usable exergy flows represent the targeted products of a production process (here e.g. ethylene or propylene). The external losses contain the exergy stored in the unused material flows (e.g. flue gas). They show the theoretical potential of using the by-products (e.g. excess heat recovery from flue gases) of a process. Analogous to Bühler et al. (2016), the exergy destruction is calculated by subtracting the usable exergy as well as the external exergy losses from the exergy input. Thus the exergy destruction includes both the destruction by irreversibility in the process and the process-related exergy destruction. Consequently, the internal degree of loss is not to be interpreted as a theoretical minimum. The allocation of the individual exergy flows to the categories expenditure, benefit, losses and destruction is carried out individually for each production process. We calculate the following exergetic evaluation indicators:

- Exergy efficiency
- External loss
- Internal loss

In the third step, we supplement the mass balances with the exergies of the individual substances and prepare exergy balances for the production processes.

In the fourth step, we compare the results of the exergy balances of the three investigated production processes. It is analysed which process has the highest efficiency from an exergetic point of view and for what reasons.

Results

PREPARATION OF MASS BALANCES

The first step of our methodology is the preparation of process-specific mass balances. For this purpose, existing literature is evaluated. In addition, we define the system boundaries in order to decide which substances are fed into the process from outside and which are produced on site. This is relevant, for example, for the production of methanol by CO_2 and H_2 . Here we assume that the required hydrogen is produced on site. This means that we include the effort required to produce the hydrogen in the balance. The definition of the system boundary for the steam cracking process is analogous to the classification in the BREF LVOC (Falcke et al. 2017/BREF LVOC). The system boundary of the future production processes contains the two process steps presented (for the CO_2 and H_2 to methanol process, additionally the process step of electrolysis). The mass balances prepared then contain a large number of substances, which are evaluated. Table 1 shows the summarized mass balances of the analysed production processes for producing one tonne of Ethylene. Our analyses do not simulate an existing plant. Our analyses are based on literature data and, in the case of the steam cracking furnace, on the European average of the BREF document. For this reason, it is possible that processes are represented which do not exist in reality.

Table 1. Mass balances of the production processes (Falcke et al. 2017; Iaquaniello et al (2017); Pérez-Fortes et al (2016); Johansson 2013; Ren et al. 2008).

	Input [t/t _{Ethylene}]			Output [t/t _{Ethylene}]		
	Steam Cracker	WTM and MTO	CO ₂ and H ₂ to Methanol and MTO	Steam Cracker	WTM and MTO	CO ₂ and H ₂ to Methanol and MTO
Naphtha energetic	0.6	–	–	–	–	–
Naphtha material	3.3	–	–	–	–	–
Air	22.7	–	–	–	–	–
Flue Gas (incl. CO ₂)	–	–	–	24.4	5.7	3.8
Ethylene	–	–	–	1.0	1.0	1.0
Other HVC	–	–	–	1.3	1.0	1.0
Other (Ash, Inert etc.)	–	–	–	–	2.3	0.1
CO ₂	–	–	6.8	–	–	–
Water	–	1.7	8.3	–	2.6	5.7
Air	–	31.1	3.8	–	–	–
Refuse derived Fuel	–	11.1	–	–	–	–
O ₂	–	–	–	–	–	7.3
N ₂	–	–	–	–	23.5	–
Ar	–	–	–	–	0.4	–

PREPARATION OF THE EXERGY BALANCES

Exergy balances are drawn based on the mass balances prepared. We calculate the specific exergies of the individual input and output materials. The method for calculating the exergies is essentially based on Riedl (2006), Radgen (1996) and Szargut (1987). More details can be found in the chapter Method. The specific exergies of the substances are multiplied with the mass balances and the resulting exergy balances are calculated.

For the exergetic evaluation we assign the exergy flows leaving the material to the categories usage, internal and external losses. The usage corresponds to the sum of physical and chemical exergy of the product produced in each case, i.e. in the case of olefin production, the quantity of olefins produced (ethylene, propylene, butadiene) External losses are classified as all output exergy flows that do not represent a product (in this case the olefins). These are, for example, waste gases, water, ashes, etc. The internal losses are determined in the balance sheet according to formula 5:

$$\sum E_{extloss} = \sum E_{Input} - \sum E_{usage} - \sum E_{intloss} \quad (5)$$

The internal losses therefore represent the exergy destruction, which cannot be detected in other substances.

Figure 1 shows the so calculated exergy balance of the steam cracking process. In this exergetic view, only those material flows are shown which enter or leave the system boundary. Therefore the products which are circulating within the process are not shown. It becomes clear that the largest source of exergy is the entering naphtha. The entering air has a comparatively

small share in the entering exergy flows. Approx. 56 % of the exergetic output is in the products (ethylene, propylene, etc.). This means that the exergetic efficiency of the process is about 56 %. The external losses are approx. 2 %. The external losses in this production process are mainly exhaust gases. Accordingly, the internal loss of the production process is 41.4 %.

Figure 2 shows the calculated exergy balance of the Waste to Methanol and Methanol to Olefin process. Similar to the steam cracker process, the largest exergetic input is the refuse derived fuel (both materially and energetically used). Other input materials are air and electricity, with a lower exergetic share. The exergetic output of the process is similar to the steam cracking process. Approx. 54 % of the exergetic output is in the products (ethylene, propylene, etc.). Like in the steam cracking process, the remaining output streams only have a low exergy amount of 2.4 %. These substances are mainly flue gas and ash. The internal exergy loss (exergy destruction) in this case is approx. 43 %.

Figure 3 shows the exergy balance of the CO₂ and H₂ to methanol and MTO process. In this production process, the largest exergetic input is the required electricity. This is mainly needed for the electrolysis to produce hydrogen. The remaining input materials (CO₂, water and air) have only a small exergetic share. The exergetic output is similar to the two processes described above. About 50 % of the outgoing exergy is contained in the products. This means that the process has an exergetic efficiency of about 52 %. The external losses are about 0.9 %. These are mainly exhaust gases and wastewater. The internal exergy loss (exergy destruction) in this case is approx. 49 %.

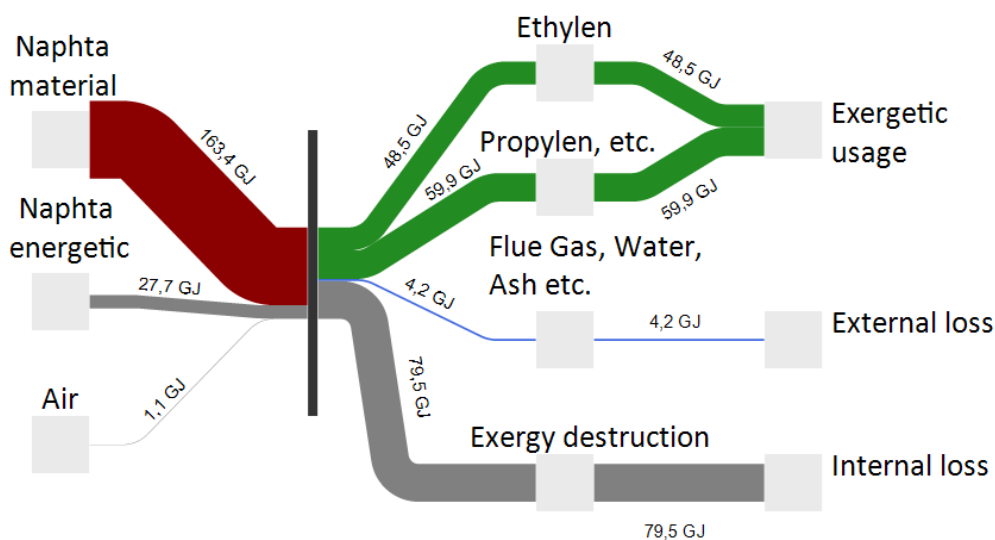


Figure 1. Exergetic balance steam cracking for producing one tonne of ethylene.

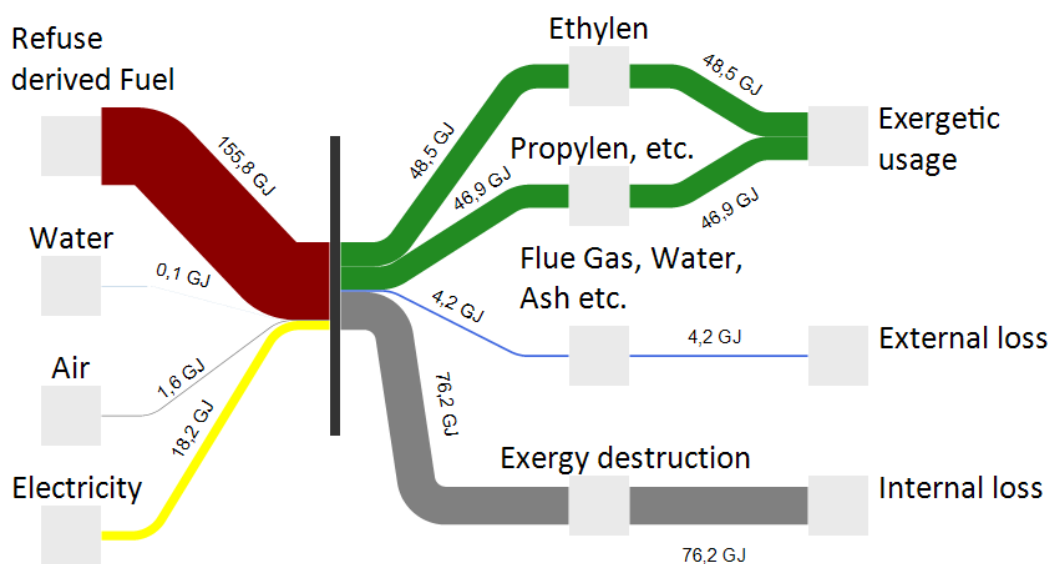


Figure 2. Exergetic balance WTM and MTO for producing one tonne of ethylene.

EXERGETIC COMPARISON OF THE PRODUCTION PROCESSES

For the production of olefins, we consider one current and two possible future production processes. In contrast to the current production process, these future production processes differ mainly in the production of methanol. Table 2 shows the results of the exergetic evaluation indicators for all three production processes considered.

In the first alternative production process studied (olefin production with waste-to-methanol (WTM) and methanol-to-olefins (MTO)), waste is used as raw material for the production of methanol. For this purpose, waste is gasified and then the synthesis gas obtained is used to produce methanol (methanol synthesis).

In the second alternative production process investigated (olefin production with methanol synthesis (CO_2 & H_2) and

methanol-to-olefins (MTO)), methanol is produced by the synthesis of carbon dioxide (CO_2) and hydrogen (H_2). For this purpose, the necessary CO_2 must be provided by means of CO_2 deposition processes. In addition, hydrogen is produced by electrolysis and synthesized with CO_2 to methanol.

From an exergetic point of view, the process olefins from waste is slightly better compared to the process olefins from CO_2 & H_2 , as it has an efficiency that is about 4 % points higher. It should be noted, however, that both future production processes investigated have exergetic efficiencies that are about two to six percentage points lower compared to the current production process (production of olefins by the steam cracking process). Overall, the exergetic efficiencies of all the production processes under consideration are at a comparable level.

From an energetic point of view, the evaluation of the possible future production processes investigated depends in particular on the balance limits set for the raw materials used. For the production of olefins, the current system generally reports the proportion of raw materials used for energy and materials separately. For example, in the production of olefins using the steam cracking process, naphtha used as a material is usually not taken into account when considering the specific final energy consumption (cf. inter alia (Fleiter et al. 2013)). If this approach is transferred to the future production processes investigated, the proportion of waste used as energy and material in the olefins from waste process would have to be determined using a thermodynamic model. Our approach is to assign the waste used completely to material use. In both possible future production processes considered, electricity is the only energy source used. In this case, the production process olefins from waste and MTO requires significantly less energy (electricity) compared to the process olefins from CO_2 & H_2 (about 18 GJ/t versus about 183 GJ/t ethylene). This is mainly due to electrolysis, which is responsible for over 80 % of the energy consumption. However, electrolysis is used to produce hydrogen, which in turn is used to produce olefins (source of the H molecules). For a more detailed consideration of the consumption it is therefore advisable to consider the consumption of exergetically high-grade substances in all three processes cumulatively.

In addition to electricity, naphtha is then also taken into account for the production of olefins using the steam cracking process and the waste used for olefin production from waste and MTO. In this case, the high differences in energy consumption for all three production processes considered are equalized. The production of olefins using the steam cracking process then totals about $176 \text{ GJ/t}_{\text{Ethylene}}$, the process olefins from waste about $174 \text{ GJ/t}_{\text{Ethylene}}$ and the process olefins from CO_2 & H_2 about $186 \text{ GJ/t}_{\text{Ethylene}}$. The energy inputs are then equivalent to the exergetic efficiencies at a comparable level. However, it should be noted that this approach does not only consider “the energetic use of raw materials”, but the “use of raw materials with potentially high energetic benefits” as a whole.

In terms of greenhouse gas emissions, the production process olefins from CO_2 & H_2 represents a CO_2 sink. This means that no CO_2 emissions are produced, but CO_2 from other processes in this process can be used to produce olefins. However, in order to use this process across the board, a very large amount of CO_2 must be available.

Discussion and Conclusions

Our analyses are based on literature data. Especially the production process H_2 and CO_2 to methanol and MTO presented by us is found in the literature (Bazzanella 2017; VCI 2019). The data

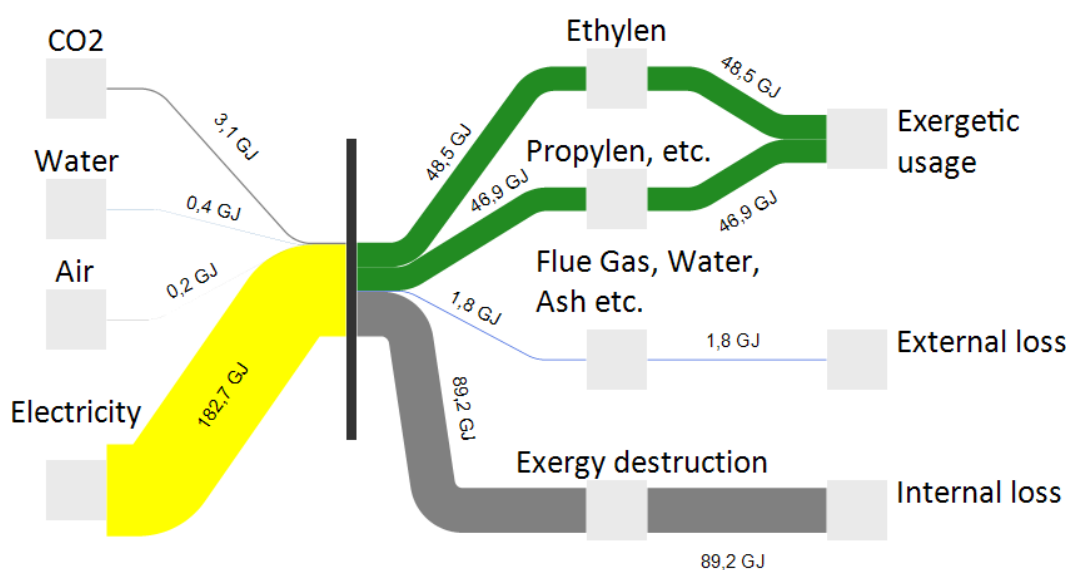


Figure 3. Exergetic balance CO_2 and H_2 to methanol and MTO for producing one tonne of ethylene.

Table 2. Comparison of exergetic evaluation indicators.

Indicator	Unit	Steam Cracking	Waste to Methanol and Methanol to Olefins	CO_2 and H_2 to Methanol and Methanol to Olefins
Exergy efficiency	%	56.4	54.3	50.3
External loss	%	2.2	2.4	0.9
Internal loss	%	41.4	43.4	48.8

we use are also consistent with the data of other literature sources. Based on the data of Pérez-Fortes et al. (2016) we assume an electricity demand of $39 \text{ GJ/t}_{\text{Methanol}}$ for the CO_2 and H_2 to methanol process. In VCI (2019) an electricity demand of $39.6 \text{ GJ/t}_{\text{Methanol}}$ is given. In Bazzanella (2017) an electricity demand of $39.7 \text{ GJ/t}_{\text{Methanol}}$ is given. For the MTO process, we assume based on Johansson (2013), Ren et al. (2008) and Ortiz-Espinoza (2017) an electricity demand of $4.9 \text{ GJ/t}_{\text{HVC}}$. In VCI (2017) an electricity demand of $5 \text{ GJ/t}_{\text{HVC}}$ is given for this process. However, since there is no information in the literature on the exergetic evaluation of the presented production processes, we cannot present a comparison of our exergetic results with the literature.

We analyze typical plants for the production process, but these do not have to exist as such. For a detailed analysis to select a production process for a real site, the real production data should be used for the analyses. Since our analyses show that the exergetic efficiency of all three considered production processes is very similar, even small changes for real plants can change the results.

In the production process Waste to Methanol, waste is used as input material. In this paper the term waste describes a refuse derived fuel which contains processed municipal waste and commercial waste. The production process is based on a certain waste composition. The exact composition is described in Iaquaniello et al (2017). Untreated waste cannot be recovered in the process presented. In Xiang et al. (2015) an exergetic analysis of the WTM and MTO process was also carried out. The results of Xiang et al. (2015) show an exergy efficiency of the process of approx. 48 %. Our analyses show an exergy efficiency of about 54 %. The results are in a similar range and the difference is due to the fact that in our analyses there is a waste heat recovery.

Our analyses are based on a methodology in which exergy balances for production processes are prepared using literature data. We have analysed literature data and thereby modelled three production processes for the production of olefins. We have shown the steam cracking process, the H_2 and CO_2 to methanol and methanol to olefins (MTO) process and the waste to methanol (WTM) and MTO process.

When calculating energy balances, materially and energetically used energy sources are often considered separately. This leads to the fact that the energy balance is not correct if used incorrectly. In the chemical industry, an energy balance, if carried out correctly, provides very similar results to the exergy balance, as the products here have high exergies and high calorific values. The exergy analysis shows up to which point the processes could theoretically be optimized. However, it does not take into account any technical restrictions and does not show any concrete potential for improvement. Our results show that the exergy efficiency cannot be increased with any of the possible future production processes we have investigated. The exergetic efficiency of all processes investigated is between 50 % and 56 %. This means that from an exergetic point of view, none of the processes considered has advantages over the other. For this reason none of the processes presented should be discarded. For the selection of future processes, therefore, the dialogue with industry and road mapping for the future production of olefins are essential.

Our results show that it is very important to consider both the material and the energetic components. If only the ener-

getic components were considered, the production process waste-to-methanol would be the best from an energetic point of view. In this case, however, the exergetic value of the waste is not taken into account.

Future research could look into the effort required to provide CO_2 . For the production process of CO_2 and H_2 to methanol, we have assumed that the hydrogen is produced on site. However, in this production process we assume that the CO_2 is supplied to the plant from outside. This means that in our analyses the CO_2 has only the exergy of the substance, but we do not take into account the energy required to produce the CO_2 . Currently, CO_2 can come from several sources, for example from flue gas streams, direct air capture or biomass. Since it is currently not yet certain which CO_2 sources will prevail, we have assumed in our analyses that the CO_2 is supplied to the production process from outside. For analyses for real locations, the effort required to provide the CO_2 should also be taken into account.

References

- Brunke, J. C. U. (2017). Energieeinsparpotenziale von energieintensiven Produktionsprozessen in Deutschland: eine Analyse mit Hilfe von Energieeinsparkostenkurven.
- Bazzanella, A., & Ausfelder, F. (2017). Low carbon energy and feedstock for the European chemical industry. DECHEMA, Gesellschaft für Chemische Technik und Biotechnologie eV.
- Falcke, H.; Holbrook, S.; Clenahan, I.; Sanalan, T.; Brinkmann, T.; Roth, J. et al. (2017): Best Available Techniques (BAT) reference document for the production of large volume organic chemicals. Hg. v. Joint Research Centre der Europäischen Kommission. Luxembourg (EUR, Scientific and technical research series).
- Fleiter, T.; Schlomann, B.; Eichhammer, W. (2013): Energieverbrauch und CO_2 -Emissionen industrieller Prozesstechnologien – Einsparpotentiale, Hemmnisse und Instrumente. Stuttgart: Fraunhofer Verlag.
- Hajjaji, N., Pons, M. N., Houas, A., & Renaudin, V. (2012). Exergy analysis: An efficient tool for understanding and improving hydrogen production via the steam methane reforming process. *Energy Policy*, 42, 392–399.
- Hannula, I., & Arpiainen, V. (2015). Light olefins and transport fuels from biomass residues via synthetic methanol: performance and cost analysis. *Biomass Conversion and Biorefinery*, 5 (1), 63–74.
- Hernandez, A. G., & Cullen, J. M. (2016). Unlocking plant-level resource efficiency options: a unified exergy measure. *Procedia CIRP*, 48, 122–127.
- Hernandez, A. G., & Cullen, J. M. (2019). Exergy: A universal metric for measuring resource efficiency to address industrial decarbonisation. *Sustainable Production and Consumption*, 20, 151–164.
- Iaquaniello, G., Centi, G., Salladini, A., Palo, E., Perathoner, S., & Spadaccini, L. (2017). Waste-to-methanol: Process and economics assessment. *Bioresource technology*, 243, 611–619.
- IEA, ICCA. DECHEMA (2013) Technology roadmap: Energy and GHG reductions in the chemical industry via catalytic processes. International Energy Agency (IEA), The

- International Council of Chemical Associations (ICCA), DECHEMA Gesellschaft für Chemische Technik und Biotechnologie eV (Society for Chemical Engineering and Biotechnology): Paris, France, 2014.
- Johansson, E. (2013). Process integration study of biomass-to-methanol (via gasification) and methanol-to-olefins (MTO) processes in an existing steam cracker plant.
- Luis, P., & Van der Bruggen, B. (2014). Exergy analysis of energy-intensive production processes: advancing towards a sustainable chemical industry. *Journal of Chemical Technology & Biotechnology*, 89 (9), 1288–1303.
- Material Economics (2019). Industrial Transformation 2050 – Pathways to Net- Zero Emissions from EU Heavy Industry.
- Michalakakis, C., Cullen, J. M., Hernandez, A. G., & Hallmark, B. (2019). Exergy and network analysis of chemical sites. *Sustainable Production and Consumption*, 19, 270–288.
- Ortiz-Espinoza, A. P., Noureldin, M. M., El-Halwagi, M. M., & Jiménez-Gutiérrez, A. (2017). Design, simulation and techno-economic analysis of two processes for the conversion of shale gas to ethylene. *Computers & Chemical Engineering*, 107, 237–246.
- Pérez-Fortes, M., Schöneberger, J. C., Boulamanti, A., & Tzimas, E. (2016). Methanol synthesis using captured CO₂ as raw material: Techno-economic and environmental assessment. *Applied Energy*, 161, 718–732.
- Radgen, Peter (1996): Energiesystemanalyse eines Düngemittelkomplexes. Dissertation. Gerhard-Mercator-Universität – Gesamthochschule Duisburg, Duisburg. *Forschr.-Ber. VDI Reihe 6 Nr.* 342.
- Ren, T., Patel, M. K., & Blok, K. (2008). Steam cracking and methane to olefins: Energy use, CO₂ emissions and production costs. *Energy*, 33 (5), 817–833.
- Riedl, Karsten (2006): Exergetische und Exergoökonomische Bewertung von Verfahren der Energie- und Stoffwandlung. Dissertation. Martin-Luther-Universität, Halle-Wittenberg.
- Romero, J. C., & Linares, P. (2014). Exergy as a global energy sustainability indicator. A review of the state of the art. *Renewable and Sustainable Energy Reviews*, 33, 427–442.
- Skelton, A. C., & Allwood, J. M. (2013). The incentives for supply chain collaboration to improve material efficiency in the use of steel: an analysis using input output techniques. *Ecological economics*, 89, 33–42.
- Szargut, J., Morris, D. R., & Steward, F. R. (1987). Exergy analysis of thermal, chemical, and metallurgical processes.
- VCI (2019): Roadmap Chemie 2050. Auf dem Weg zu einer treibhausgasneutralen chemischen Industrie in Deutschland. Material Economics, VUB Institute for European Studies & Wuppertal Institute for Climate, Environment and Energy.
- Wilson, C., Grubler, A., Gallagher, K. S., & Nemet, G. F. (2012). Marginalization of end-use technologies in energy innovation for climate protection. *Nature Climate Change*, 2 (11), 780–788.
- Xiang, Y., Zhou, J., Lin, B., Xue, X., Tian, X., & Luo, Z. (2015). Exergetic evaluation of renewable light olefins production from biomass via synthetic methanol. *Applied Energy*, 157, 499–507.
- Zimmermann, Heinz; Walzl, Roland (2012): Ullmann's Encyclopedia of Industrial Chemistry. Weinheim, Germany: WILEY-VCH Verlag GmbH & Co. KGaA.