

OPTISOCHEM

“OPTimized conversion of residual wheat straw
to bio-ISObutene for bio based CHEMicals”

Grant Agreement n° 744330 –
Innovation Action-Demonstration Project

Deliverable D7.1

**Full Life Cycle Assessment report of fossil isobutene reference
process according to ISO 14040/14044**

Start date of the project: 1st June 2017

Duration: 48 months

Project Coordinator: Bernard Chaud – Global Bioenergies (P1 - GBE)

Contact: Bernard Chaud – Global Bioenergies (P1 - GBE)

Bernard.Chaud@global-bioenergies.com

Document Classification

Title	Full Life Cycle Assessment report of fossil isobutene reference process according to ISO 14040/14044
Deliverable	D7.1
Reporting Period:	RP1
Date of Delivery foreseen in DoA	M12 30.05.2018
Actual Date of Delivery to JU	M14 31.07.2018
Authors	Simon Lassacher, Karin Fazeni-Fraisl, Johannes Lindorfer P5-JKU
Work package	WP7 biomass supply, LCA, environmental & socio-economic performances
Dissemination	PU = Public, fully open, e.g. web
Nature	R: Document, report
Version	V1.1
Doc ID Code	D7.1 _OPTISOCEM_P5_JKU_190311
Keywords	LCA, fossil isobutene, benchmark, report

Document History

Partner	Remark	Version	Date
P5_JKU	Final version	1	31.07.2018
P5_JKU	Final version	1.1	11 03 2019

Document Validation

Partner	Approval (Signature or e-mail reference)
P5_JKU	lindorfer@energieinstitut-linz.at

Document Abstract

Deliverable 7.1 documents Life Cycle Assessment (LCA) for fossil isobutene. The report contains the results of literature research, which is conducted to specify the examined fossil isobutene routes. Based on literature research and expert consultation three routes are chosen for further investigation: MTBE decomposition, TBA decomposition and isobutene dehydrogenation. After defining the system boundaries for these processes, the Life Cycle Inventory is compiled based on LCA databases such as thinkstep GaBi 8 Professional database, ecoinvent 3.0 database, literature data as well as expert consultation. The fossil isobutene routes are implemented in the thinkstep GaBi 8 software and the LCA results are derived using CML 2001 impact categorization method.

The LCA results for fossil isobutene are not definite. From a greenhouse gas perspective, MTBE decomposition or isobutene dehydrogenation are the preferable process routes. From a primary energy demand perspective TBA dehydration would be the preferable process routes. As greenhouse gas emissions do not fully correspond with primary energy demand for all process options, a decision for one or another process route requires specific weighing. The result for fossil isobutene production presented in this deliverable is the basis for comparison with LCA results for 1st generation sugar isobutene LCA and 2nd generation sugar isobutene LCA in the upcoming Deliverable reports of the OPTISOChem project

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Abbreviations

Bio-IBN

GWP

IBN

LCA

LCI

MTBE

TBA

biobased isobutene

Global Warming Potential

isobutene

Life Cycle Assessment

Life Cycle Inventory

Methyl-tert-butylether

t-butyl alcohol

1 Introduction

This Deliverable report (D7.1 Full Life Cycle Assessment report of fossil isobutene reference process according to ISO 14040/14044) is part of WP 7 of the OPTISOCEM project (H2020, GA No. 744330). The goal of the H2020 funded project OPTISOCEM is to demonstrate the performances, reliability as well as environmental and socio-economic sustainability of the entire value chains, for the transformation of excess wheat straw via fermentation into biobased isobutene (bio-IBN) derivatives. These compounds, oligomers (DIB, TIB, TeIB) and polyisobutylenes (PIBs) are currently used in a wide range of applications such as lubricants, adhesives, sealants, flavors & fragrances and substituted phenols. Beside the development & up-scaling of bio-IBN production from wheat straw hydrolysate, another part of the project is an environmental product performance profile for the bio-IBN, which is benchmarked with conventional fossil production route and different feedstocks for the fermentation process (first generation sugar).

The aim of the current Deliverable report is to document the Life Cycle Assessment (LCA) methodology and results for three fossil isobutene routes, which are chosen based on an extensive literature review, LCA data-set screening and expert consultation. At the end the three most common fossil isobutene production reference processes -isobutane dehydrogenation, MTBE decomposition and TBA decomposition – are examined via LCA methodology. After defining the system boundary for these fossil isobutene routes a full life cycle inventory was compiled and set-up in the LCA software program GaBi ts 8. The environmental impacts were characterised via the CML-method (2001 - Jan. 2016). The environmental impacts for fossil isobutene are the benchmarks for bio-IBN from 1st and 2nd generation sugar.

2 Fossil Isobutene Production

2.1 Characteristics of fossil isobutene production

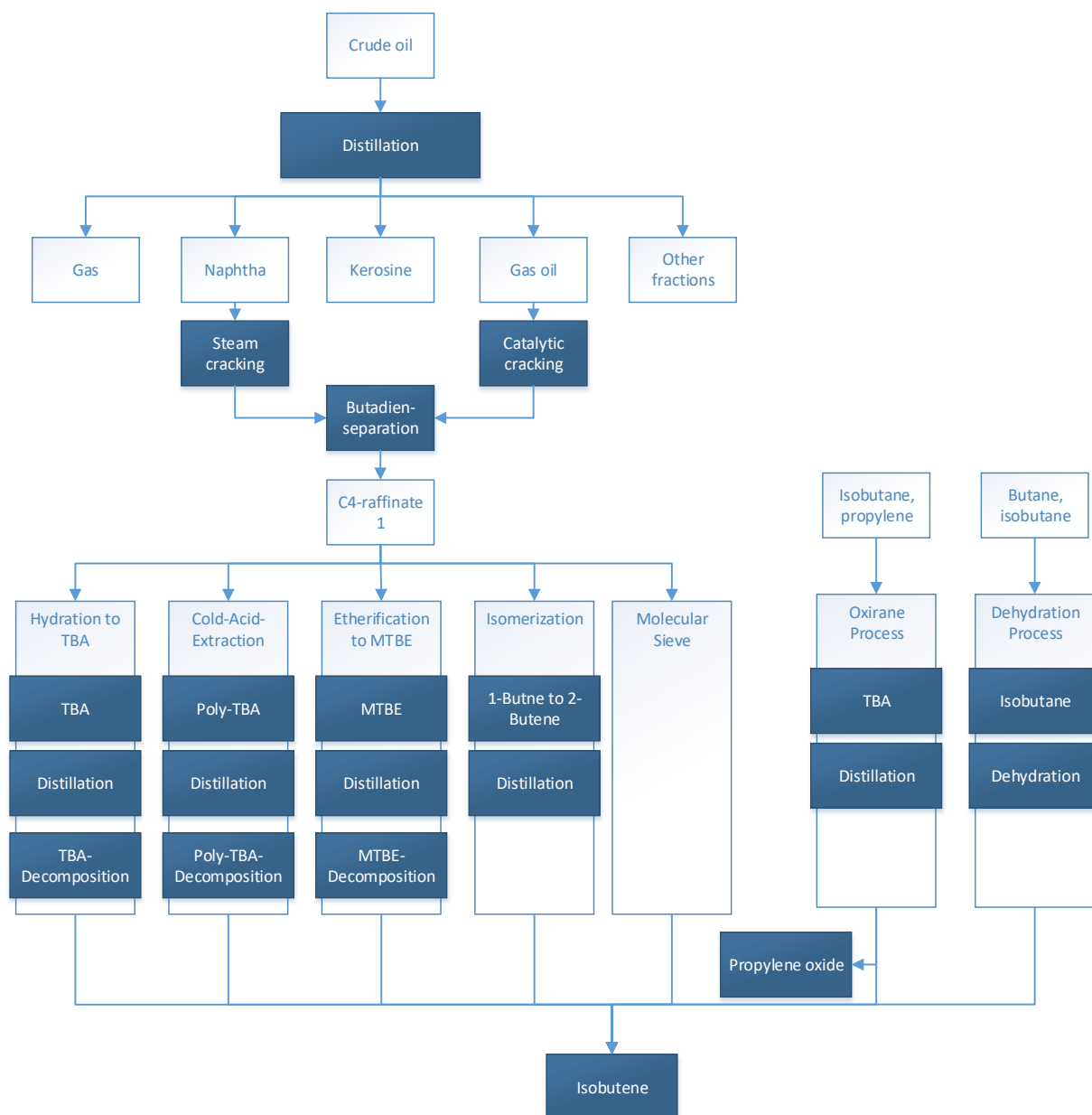
Isobutene, or Isobutylene is the most important isomer of the four isomers of butene (George A. Olah et al. 2003). This is because Isobutene has the highest reactivity in respect to addition and polymerization reactions, which are widely required in the chemical industry. Butenes are unsaturated olefinic hydrocarbons, thus, no natural products and are known for more than 100 years, but were of minor importance in the petrochemical industry for a long time due to their scarce availability. Since the growth in application of cracking processes in crude oil refining and for ethylene production, butenes could be obtained as coproduct in huge quantities. Isobutene is contained in the C4 stream from the cracking processes, beside the isomers of butene and butane and multiple unsaturated C4 hydrocarbons. The complex nature (rather similar physical properties as seen in Table 2-1) of this fraction prevents the applicability of conventional distillation and was the main barrier for specific use of butene. The sensitive increase in prizes of hydrocarbons especially from 1980 onwards accelerated the development of economic separation processes, which are further described in section 0. (Fritz Obenaus et al. 2005)

Table 2-1: Boiling points of C4-fraction components (Streich et al. 2016)

Component	Boiling Point [°C]
Isobutane	-11,7
Isobutene	-6,9
1-Butene	-6,3
1,3-Butadien	-4,4
N-Butane	-0,5
2-trans-Butene	0,9
2-cis-Butene	3,7

2.2 Processes for fossil isobutene production

As mentioned before, Isobutene is contained in the C4 stream of cracking processes, and cannot be separated by conventional distillation. Before further processing, the butadien in the C4 fraction is removed by extractive distillation (George A. Olah et al. 2003). The new stream is then called raffinate 1. Due to the higher reactivity of isobutene, all separation processes (as seen in Figure 1) are based on selective reactions with isobutene, where the formed derivatives can easily be separated and then be split back during subsequent steps to produce pure isobutene. Another possibility to produce isobutene is the dehydrogenation of isobutane from natural gas or gas from the crude oil production. Furthermore propylene oxide plants produce high amounts of tert-butyl alcohol (TBA), which is another source of isobutene. It can easily be converted back to isobutene (George A. Olah et al. 2003). Alternative separation methods are physical separation by molecular sieves (Weissermel und Arpe 2003). Subsequent, the different processes are described in more detail.



TBA ... tert-butanol; MTBE ... Methyl-tert-butylether

Figure 1: Overview of isobutene production processes (Energy Institute at the Johannes Kepler University)

2.3 Feedstock for fossil isobutene

As crude oil does not contain olefins like butenes (unsaturated linear hydrocarbons) it has to be further processed to obtain valuable olefins. After the distillation the fractions of crude oil consist of long chain hydrocarbons, so they have to be cracked into smaller parts. Figure 2 shows the routes, how the butene-containing C4-fraction is produced.

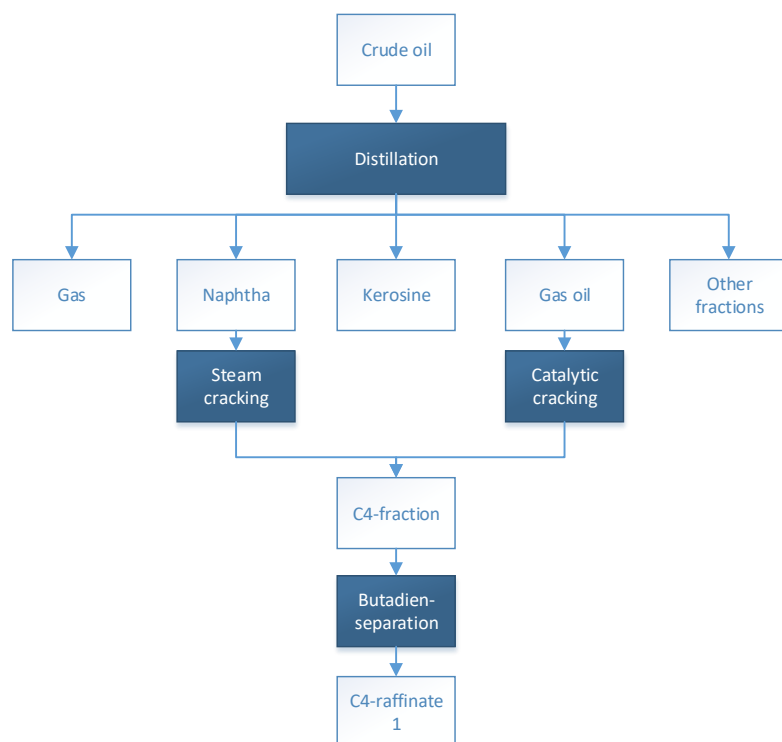


Figure 2: routes for the C4-fraction (Energy Institute at the Johannes Kepler University)

To obtain the C4-fraction naphtha or gas oil from the crude oil distillation has to be cracked. This means that the bonds of the long chain hydrocarbons have to be cracked, to form short chain hydrocarbons like butenes. For naphtha, steam cracking is preferred, for heavier hydrocarbons like gas oil, catalytic cracking is applied. Actually crackers were introduced to get an additional source for gasoline, which was primarily produced by the distillation of crude oil. Steam cracking uses lighter educts like naphtha (boiling points around 25-180°C) and is a non-catalytic, thermal cracking process in presence of water steam, to avoid the polymerization of the products. Catalytic cracking is used for heavy crude fractions (boiling points around 340-560°C). The long chains are cracked at high temperatures, moderate pressure and in presence of a catalyst. Products of both technologies are more valuable chemicals, like olefins, different kinds of fuel, etc. (Weissermel und Arpe 2003) Finally the composition of the C4-fraction is strongly affected by three factors:

1. Type of cracking process
2. Severity of cracking conditions
3. Feedstock

As shown in Table 0-1, steam cracking of naphtha produces a significantly higher fraction of butenes than catalytic cracking of gas oil. When the severity of the cracking conditions (higher temperatures) is increased, the production of butenes decreases, while the proportion of butadiene increases due to its higher stability. (Weissermel und Arpe 2003)

Table 0-1: composition of C4 fractions from steam cracking of naphtha and catalytic cracking of gas oil (in wt%), (Weissermel und Arpe 2003)

Cracked products	SC-Low severity	SC-High severity	CC
1,3-Butadien	26	47	0,5
Isobutene	32	22	15
1-Butene	20	14	12
Trans-2-Butene	7	6	12
Cis-2-Butene	7	5	11
Butane	4	3	13
Isobutane	2	1	37
Vinylacetylene	2	2	-
Ethylacetylene	2	2	-
1,2-Butadiene	2	2	-

Steam-cracked naphtha would be the preferred feedstock for the C4 production. But its availability depends on the applied refining process which is differing for geographical location. As shown in Figure 3 there are significant differences in feedstocks for steam cracking. While in Europe (Figure 4) and Asia naphtha is used as a main source, in America, Africa and Middle East it is Ethane.

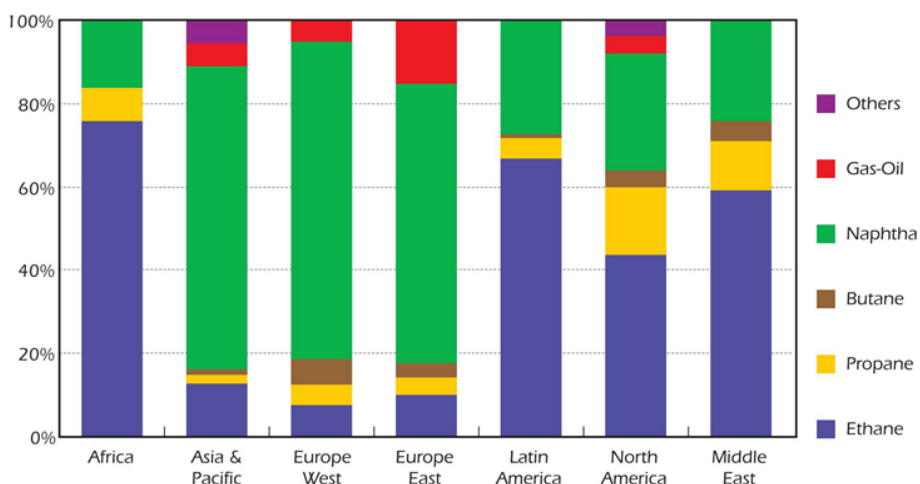


Figure 3: Shares of Feedstocks for steam cracking (IEA 2007)

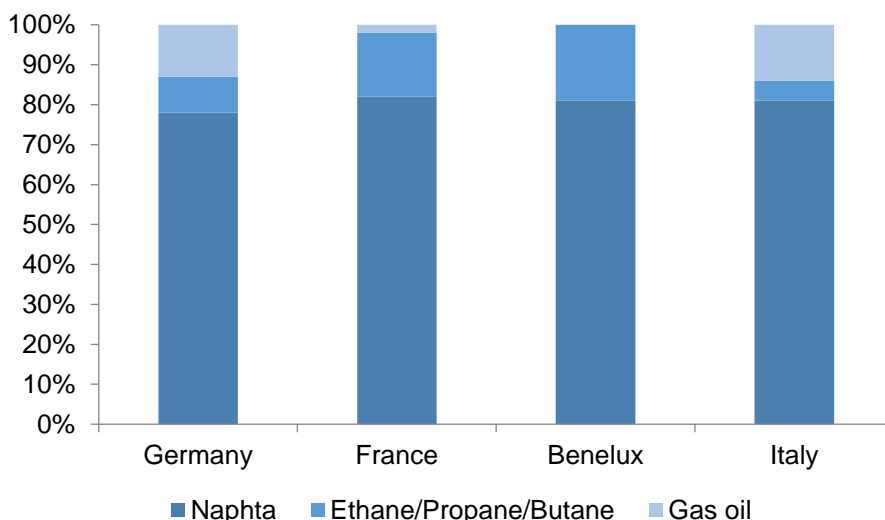


Figure 4: Share of feedstocks for steam cracking in Germany, France, Benelux and Italy (IEA 2009)

The C4 mixture still contains butadiene, which is recovered in almost all cases by extractive distillation. After the removal the butene-rich stream is also known as raffinate 1. (Fritz Obenaus et al. 2005). Table 0-2 lists the typical composition of raffinate 1.

Table 0-2: typical composition of C4-fraction / raffinate 1 (Weissermel und Arpe 2003)

Components	Vol %
Isobutene	44-49
1-Butene	24-28
2-Butene (cis and trans)	19-21
n-Butane	6-8
Isobutane	2-3

2.4 Separation of isobutene from the C4-stream

These separation processes are based on the differences in activity of the C4 fraction due to the different electron densities, polarities and steric effects. Isobutene is the chemically most reactive component, followed by 1-butene and 2-butenes (cis/trans). (Fritz Obenaus et al. 2005)

2.4.1 Cold Acid Extraction

In this early stage process isobutene is extracted in cold sulfuric acid, which subsequently polymerizes it to tert-butanol (TBA) and it's dimer and trimer, depending on the acid concentration and type of acid regeneration (Fritz Obenaus et al. 2005). The sulfuric acid has a concentration between 45 to 70 wt % and a temperature between 10 and 20°C (Weissermel und Arpe 2003). After dilution with H₂O, TBA is vacuum-distilled from the acidic solution and then cleaved to regenerate isobutene or to be used as an intermediate (Matar und Hatch 2000). This process is still widely used to reduce the concentration of isobutene to <0.2 wt % in the spent C4 mixture (Fritz Obenaus et al. 2005). The costly reconcentration of sulfuric acid recovered after hydrolysis and it's corrosive nature led to the search for more economic alternatives (George A. Olah et al. 2003).

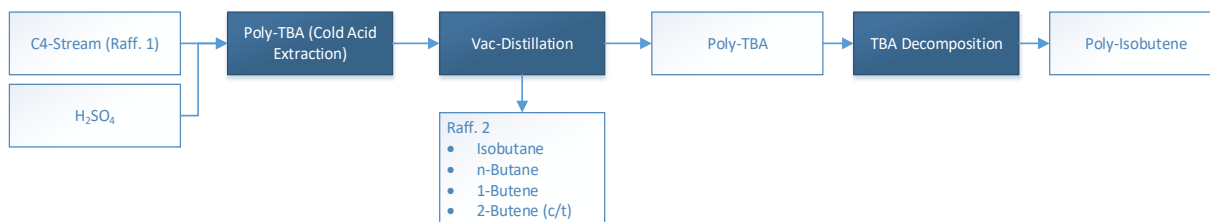
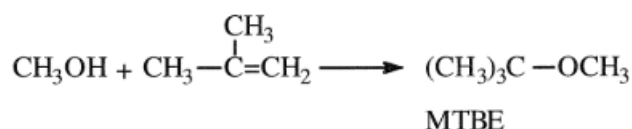


Figure 5: schematic representation of the cold acid extraction process (Energy Institute at the Johannes Kepler University)

2.4.2 Etherification of Isobutene to MTBE

This process is designed for the production of methyl tert-butyl ether (MTBE) out of the raffinate 1 of the C4 stream.



The produced MTBE can subsequently be converted to isobutene. This very selective etherification reaction takes place when isobutene from the C4 fraction is mixed with methanol, between 30 and 100°C in presence of a macroporous cation exchange resin as a catalyst (Weissermel und Arpe 2003). In 1978 Hüls was the first to modify its raffinate 1 based MTBE production to achieve more than 99,9% isobutene conversion. Because of the pressure-dependent azeotrope formed from methanol and MTBE, preparation of pure MTBE requires a multistep pressure distillation (Weissermel und Arpe 2003).

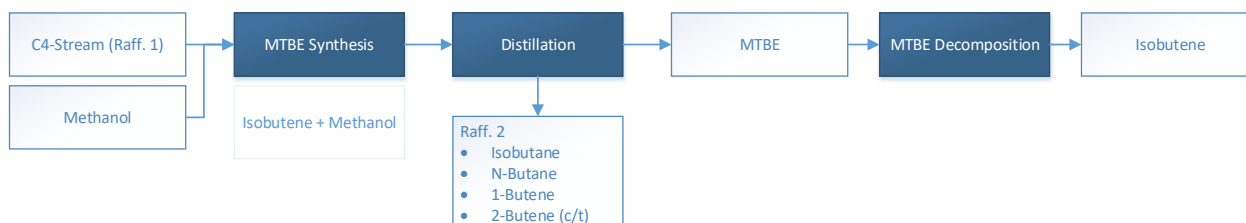


Figure 6: schematic representation of the etherification process of isobutene to MTBE (Energy Institute at the Johannes Kepler University)

As the reaction takes place in liquid phase and in presence of water, there is a side reaction from isobutene to TBA. There are several patents which try to solve the recovery of the lost share of isobutene in TBA. Figure 7 represents a flowchart of a typical MTBE plant.

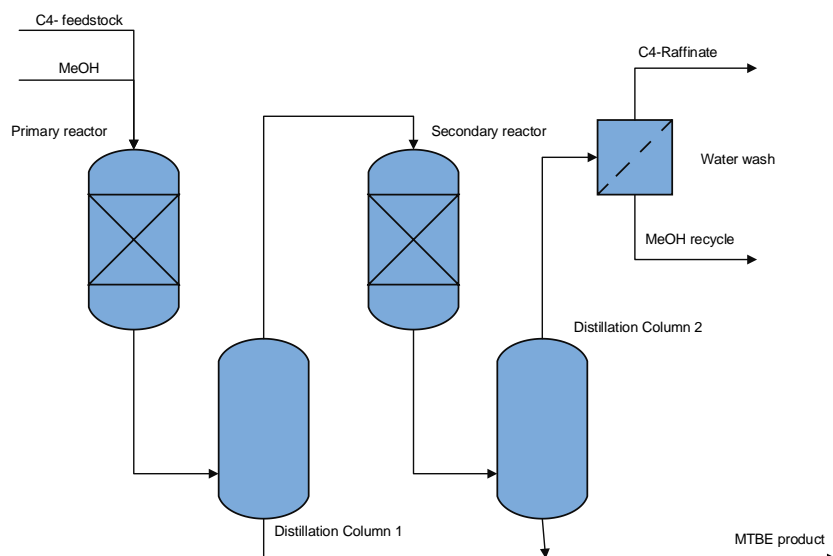
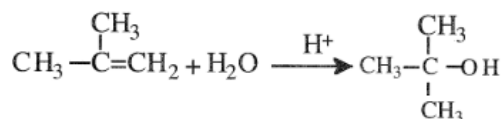


Figure 7: process scheme of the MTBE production (Energy Institute at the Johannes Kepler University)

2.4.3 Hydration of Isobutene to TBA

There is another process introduced by Hüls which selectively hydrates isobutene from raffinate 1 to tert-butanol (TBA) under non corrosive liquid-phase conditions.



Similar to the MTBE process a cation exchanger is used as catalyst. The conversion to TBA is limited by equilibrium and incomplete phase miscibility to about 90%. However the decomposition of TBA is more favoured than of MTBE due to the different equilibria. In the Hüls process in a second step, TBA is catalysed heterogeneously to high-purity isobutene. (Fritz Obenaus et al. 2005)

Isomerization of 1-butenes

As the boiling point of 1-butene in the raffinate 1 is similar to isobutene, it can be isomerized to 2-butene. Alternative sources can be raffinate 2, e.g. after MTBE production. As cis and trans 2-butene boil at sufficiently different temperatures than isobutene it subsequently can be separated by distillation. (George A. Olah et al. 2003) The industrial reactions involving cis and trans 2-butene are the same and produce the same products, as it yields to higher quantities of 2-butene in the product stream, hence a higher feasibility of the isomerization reaction (Weissermel und Arpe 2003). After distillation each stream is obtained at a purity of 80-90% (Matar und Hatch 2000). In the process of Snamprogetti a A1203 catalyst with a surface modification via SiO₂ is used. At 450-490°C, 2-butenes isomerize with a conversion of 35% and selectivity to isobutene of 81%. An analogous process was also developed by, e.g., Kellogg (Weissermel und Arpe 2003).

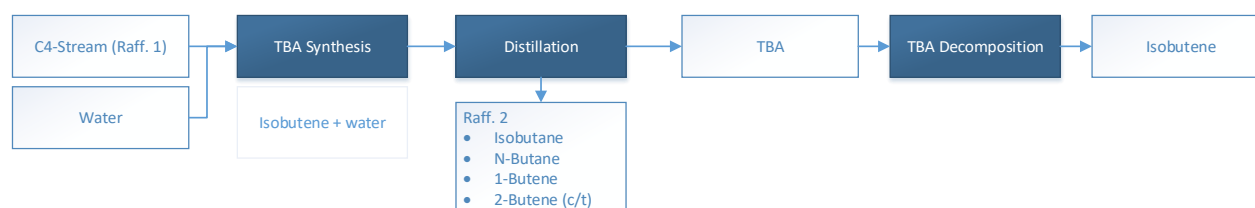


Figure 8: Hydration process of isobutene to TBA (*Energy Institute at the Johannes Kepler University*)

2.5 Separation of isobutene from other sources

2.5.1 Catalytic dehydrogenation of isobutane

The high demand of isobutene for the production of MTBE couldn't be covered by C4 cuts (Maples 2000). This led to the development of alternative processes like the dehydrogenation of isobutane. There are several sources for isobutane, e.g. it is contained in the C4 cuts, in raffinate 2 or can be produced from butane isomerization.

There are different commercial processes; most of them use noble-metal-based catalyst or chromia on alumina. Although also thermal, non-catalytic process configurations can be used, the catalytic processes are favoured due to their higher selectivity (Kaiser et al. 2007).

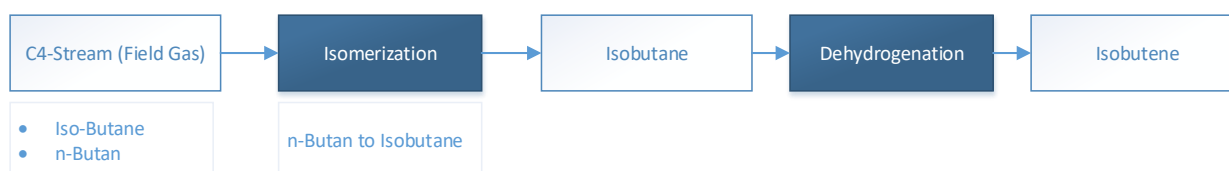


Figure 9: catalytic dehydration processes of isobutane (*Energy Institute at the Johannes Kepler University*)

The most important processes are characterised shortly in the next paragraph (George A. Olah et al. 2003):

CATOFIN process, (Kaiser et al. 2007):

The CATOFIN process originally derives from the Catadiene process developed by Houdry and is now owned by United Catalysts Inc. and licensed by ABB Lummus Crest (now CB&I Lummus). In the process at least three horizontal reactors with fixed bed of catalyst are used. The catalyst are alumina pellets with chromic oxide. The parallel reactor operation work in offset time cycles, like following:

1. On-stream dehydrogenation of isobutane
2. Steam purge
3. Reheat catalyst with preheated air and simultaneous combustion of coke formed during step 1
4. Evacuation of residual air
5. Return to on-stream operation

To guarantee a continuous overall process, the switching times of the individual reactors are run offset. The size of the reactors and the required feed rate determine the overall cycle time. Per hour the total cycle can be repeated on each reactor about two or three times. The sequencing and switching of valves is fully automated with appropriate safety interlocks. Figure 10 shows a schematic representation of an individual CATOFIN reactor and its main components.

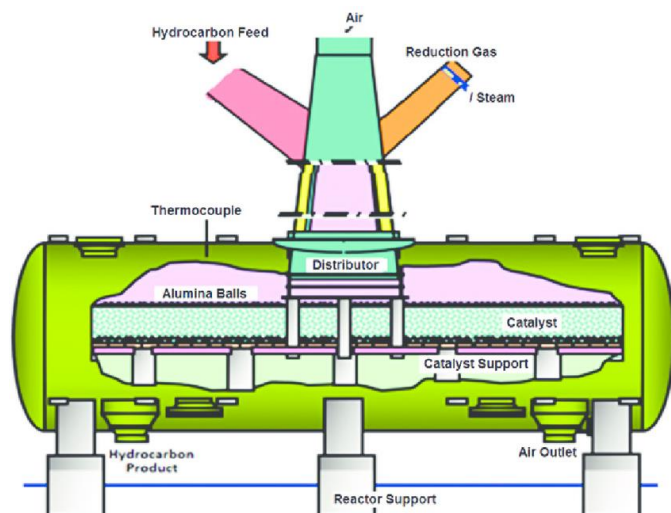


Figure 10: cross-sectional view of an individual CATOFIN reactor (Zeeshan Nawaz 2015)

The CATOFIN technology is characterized by the following points (Sanfilippo et al.):

- Due to the high selectivity ensured by the catalyst only a low amount of reagent is needed.
- Heat of reaction is supplied by the combustion of coke and by the catalyst's surface reduction using natural gas and potentially by co-feeding a fuel during the regeneration phase.
- The reaction is carried out below atmospheric pressure due a high yield per pass.
- The catalyst shows a high level of thermal stability which results in resistance to friction and tolerance to a potential poisoning via e.g. heavy metals.

The Oleflex process, (Kaiser et al. 2007)

The Oleflex process was developed and licensed by UOP and consists of two UOP LLC technologies:

1. UOP LLC trademarked Pacol process for producing monoolefins from kerosine range paraffins
2. UOP LLC trademarked CCR Platforming process

The platinum containing catalyst is fixed on a unique spherical alumina support. The reaction section consists of three reactors in series. There is a preheater before the first reactor and respectively a reheater before the second and third reactor for the reaction's heat demand. Reactants as well as hydrogen recycle gas flow radially through the very slowly downward moving beds of catalyst. Coke formation on the catalyst is less than 0.02 wt% of the hydrocarbon feed due to the sufficient hydrogen partial pressure maintained. As a result catalyst regeneration requirements are reduced and necessary in a period of about 3 to 10 days. As catalyst regeneration can be completely discontinued for several days, a continuous olefin production is guaranteed for maintenance. In contrast to that normal operation involves the continuous transfer of catalyst from reactor 1 to reactor 2 to reactor 3 for regeneration and then return to reactor 1.

Philips STAR (STeam Active Reforming) process, (Sanfilippo et al.) (Kaiser et al. 2007):

In the Philips STAR process (now commercialized by Krupp-Uhde), pelleted catalyst on an alumina base containing a noble metal are utilized and contained as a fixed bed in externally fired tubes. The external heating provides the heat for the reaction and allows the reaction to be conducted essentially in isothermal conditions, which reduces unwanted thermal cracking reactions. To lower the partial pressure and allowing higher conversion at a given temperature, steam is fed through the catalyst with the hydrocarbon. Furthermore coke formation is reduced and a stable reaction temperature is guaranteed. The use of steam as a partial pressure diluent instead of gases, such as nitrogen, reduces the cost of downstream separation and recovery facilities, because the steam can

easily be condensed from the reactor effluent. The catalyst has to be periodically regenerated, due to the coke deposition. The process can be operated continuously, because just a small portion of the tubes of the multiple passes in the reactor are in the regeneration step at any time. The regeneration is executed as follows:

1. Stop hydrocarbon feed while continuing steam flow long enough to purge the reactants
2. Add air to the steam flow
3. Stop air and continue steam flow to purge air
4. Restart hydrocarbon feed

An economically sizing of process equipment ensures that a given number of catalyst tubes can be regenerated in about 1 hr. Regeneration of each such bank occurs only two or three times in a 24-hr period (Kaiser et al. 2007).

SNAMPROGETTI YARSINTEZ PROCESS, (Kaiser et al. 2007):

The Snamprogetti Yarsintez process was developed in the former Soviet Union and is similar to a fluid-bed catalytic cracker, where a chromium oxide powder catalyst is utilized. The latter is fluidized in the dehydrogenation reactor by the isobutane feed vapor and superheated steam. The used catalyst is removed continuously from the reactor and transported to the regenerator. In the regenerator coke is burned off the catalyst and additional fuel is used to raise the catalyst temperature before returning it to the reactor.

Table 0-3 shows an overview to the different dehydration processes and their process parameters. For further information about dehydration technologies, the papers of (Nawaz 2015) and (Sanfilippo et al.) are recommended, as they provide a good overview to the state-of-the-art and future dehydration processes.

Table 0-3: overview to the different dehydration processes (Maples 2000)

	Catofin/Hourdry	UOP	Snamprogetti	Phillips
Pressure [bar]	0,3-1,0	1,4-2,5	1,2-1,5	steam thinner
Temperature [°C]	593-635	555-654	549-599	482-621
Conversion [%]	60	49	48	55
Selectivity [%]	89	88	88	91
Reactor type	Fixed bed	Moving bed	Fluidized ned	Tubular
No. reactors	2 min., usually 4 or 5	3	1	8
No. regenerators	Regen. In situ	1	1	Regen. In situ
Catalyst type	Chromic oxide on alumina	Platinum on alumina	Chromia-alumina	Noble metal
Catalyst life	1,5 years	2-2,5 years	3 years	1 year
Cycle time	7-15 minutes	Continuous	Continuous	7 h process, 1 h regeneration
Reaction heat source	Coke on catalyst plus fuel	Reheat furnaces	Coke on catalyst plus fuel	Fire outside tubes

2.5.2 Conversion of TBA from propylene oxide production

There are two commercial processes to produce propylene oxide (PO); the chlorine method, and the organic peroxide method. The latter was developed by Halcon Corp. and Atlantic Richfield Oil Corp in the 1970s and produces, beside propylene oxide, TBA as a coproduct, which further can be dehydrated to isobutene. For each ton of PO there are 3-4 tons of TBA coproduced. (Tsuji et al. 2006) About 50% of the current worldwide propylene oxide capacity is based on this process.

The first process step is the liquid-phase air oxidation of isobutane to tert-butyl hydroperoxide (TBHP) in presence of 10-30 wt % TBA, at about 95-105°C and a pressure of 20-55 bar, resulting in a conversion of 20-30% of isobutane and a selectivity for TBHP of 60-80% and for TBA of 20-40%. Increasing the temperature and reaction time increases the expense of selectivity of TBHP. (Trent 1999)



Then, in the epoxidation step, TBHP is mixed with a catalyst solution to react with propylene. The soluble catalyst typically is organometal and is used in concentrations of 200-500 ppm in a solution of 55% TBHP and 45% TBA. The water content is less than 0,5 wt %. To maximize the conversion of hydroperoxide an excess of 2-10 mol propylene is used. In this step temperatures of 100-130°C, pressures of 14,8-35,5 bar and a residence time of about 2h yield to a conversion of more than 95% of hydroperoxide. (Trent 1999)



After the epoxidation step, a distillation is performed to remove propylene, propylene oxide, and a portion of the TBHP and TBA overhead. The TBA coproduct is further purified and dehydrated to isobutene (Trent 1999). In this process with each ton of propylene oxide, about 2.1 tons of isobutene are coproduced (Trent 1999).

2.5.3 Physical separation (molecular sieves)

Molecular sieves use the bulkiness of the methyl branching of isobutene, which is not absorbed by the very uniform 3-10 Å pores of the molecular sieve. Only n-butenes and butane are absorbed, and then desorbed using a higher boiling hydrocarbon. An example for such a process is the Olefin-Siv process of UCC. Isobutene with 99% purity can be achieved from the C4 fraction. (Weissermel und Arpe 2003)

2.6 Energy intensity of chemical production processes

For benchmarking energy consumptions from various literature sources for the production of different chemicals and gate-to-gate processes are investigated, as seen in Table 0-4 and Table 0-5. For the isobutene production very scarce data is available. In literature research, there was just one value found for the isobutene production (from TBA). Apart from that, some data was given for the C4-fraction and other hydrocarbons and chemicals. It is to notice, that the majority of the data, its confirmability (boundary conditions, process data) is not provided.

Table 0-4 lists the total energy consumption for the production of specific chemicals as a black box, without considering the production processes. Table 0-5 shows the energy consumption of individual process steps, e.g. the steam cracking from naphtha to high value chemicals (HVC). With these two tables one should be able to roughly estimate the energy consumption of the isobutene production process.

In the current case, the most important values are the ones for the C4-fraction, like butene and butadiene. The energy consumption for their production ranges between 47,30 GJ/t and 63,83 GJ/t. As the C4-fraction consists of butenes and also butadiene, the extraction of butadiene from the C4-fraction should be more energy intensive. The latter is confirmed, if we compare the values from butene and butadiene from the same literature sources. The range of the C4-fraction is a first reference point for the energy consumption of the isobutene production. The subsequent process steps, such as MTBE or TBA formation, separation and decomposition to isobutene must further be considered. But as the allocation and synergy effects within the whole production process are unknown, it is problematic to estimate the actual energy consumption for the isobutene production.

Table 0-4: Energy consumption of chemical production processes

Chemical	[GJ/t]	source
Butadiene	63,83	(IEA 2007)
Butadiene (C4 separation)	53,80	(IEA 2009)
Butene	59,11	(IEA 2007)
Butene	47,30	(IEA 2009)
MTBE onsite	45,8	(GREET 2017)
MTBE offsite	50,0	(GREET 2017)
MTBE	69,3	(IFEU)
Propylene	59,72	(IEA 2007)
Propylene (FCC)	47,20	(IEA 2009)
Propylene (steam cracking)	56,60	(IEA 2009)
Propylene oxide	15,80	(IEA 2009)
Ethylene	60,02	(IEA 2007)
Ethylene	56,60	(IEA 2009)
Ethylene from gas oil	64,00	(PATEL 2003)
Ethylene from light hydrocarbons	62,20	(PATEL 2003)
Ethylene from naphtha	60,40	(PATEL 2003)
Gas oil	42,70	(PATEL 2003)
HVC - High Value Chemical max	24,90	(Unido 2010)
HVC - High Value Chemical min	16,90	(Unido 2010)
Isobutylene from TBA	53,35	(U.S. DOE 2006)
Olefins (Ethylene, Propylene)	21,23	(Ministry of Energy Thailand 2006)
Polyethylene	64,60	(PATEL 2003)

Table 0-5 lists various energy consumptions of gate-to-gate processes from steam cracking and different production processes. For some processes also the theoretical energy consumption is given, which is the minimum theoretical reaction energy without any losses. For the MTBE process the available numbers differ significantly from the energy consumption of the real processes. This is related to the losses for the recovery of MTBE in the distillation column and its high condensing load.

Table 0-5 energy consumption for steam cracking

Process: Gate to Gate	GJ/t	Source
Naphtha Steamcracking to:		
HVC _{theoretical}	5,0	(REN et al. 2006)
HVC	15,6	(REN et al. 2006)
HVC	14,0-17,0	(REN et al. 2006)
HVC	16,9-24,9	(Unido 2010)
HVC (EU-average)	14-22	(IEA 2009)
Commercial Steam Crackers:		
Cracker - Technip-Coflexipa	18,8-20,0	(PATEL 2003)
Cracker - ABB Lummus (now CB&I Lummus)	18,0	(PATEL 2003)
Cracker - Linde AG	21,0	(PATEL 2003)
Cracker - Stone and Webster	20,0-25,0	(PATEL 2003)
Production Processes:		
MTBE etherification with Methanol theoretical	0,3	(U.S. DOE 2006)
MTBE etherification with Methanol	20,6	(U.S. DOE 2006)
MTBE to Isobutene	12,5	(Nexus Report)
TBA to Isobutene	14,4	(Nexus Report)
TBA to Isobutene theoretical	0,13	(U.S. DOE 2006)
TBA to Isobutene	5,34	(U.S. DOE 2006)
Dehydrogenation of isobutane (Catofin)	12,2	(Mikhailov et al. 1988)

2.7 Use of isobutene and production volume

Isobutene is mainly used for the production of MTBE as an octane booster/combustion promotor in gasoline. Further it is applied in the chemical industry for the production of polybutenes, butyl rubber, polyisobutene or substituted phenols. (Riegel 2007) Figure 11 shows an overview on the applications of isobutene.

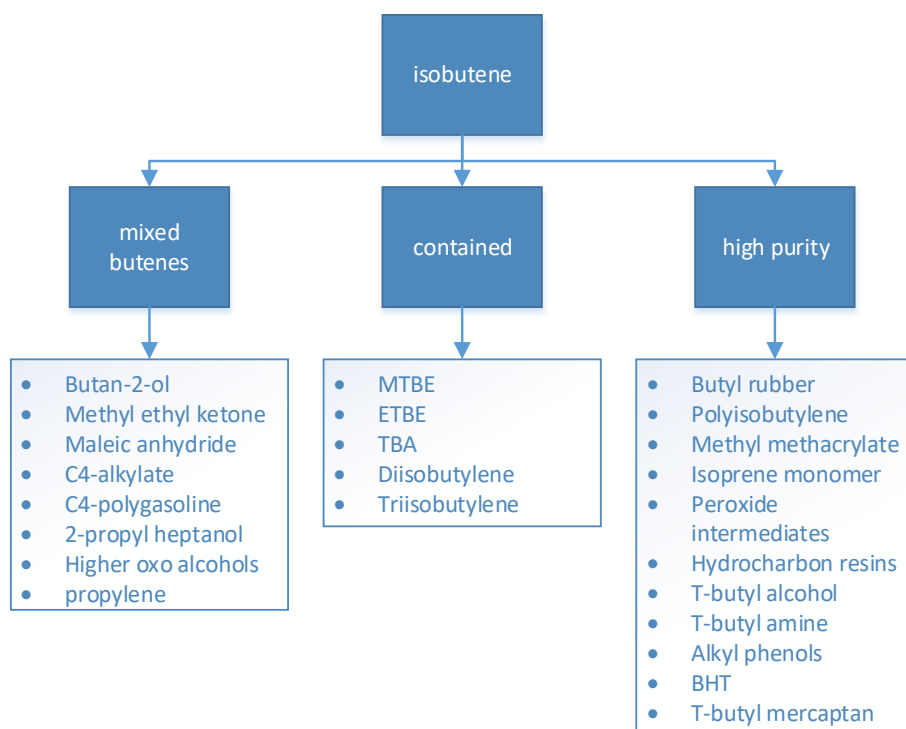


Figure 11: Applications of isobutene, in the style of (Nexant 2007)

The world capacity of MTBE grew from 8 million tons in 1990 to 25 million tons by 2000. The increases were mainly caused by the gasoline oxygenate requirements regulated by the 1990 Clean Air Act Amendments in the US. The increase in capacity was focused on production from isobutane (from low cost gas) but there was also a growth in production in refineries. Approximately 70% of the world's MTBE supply is originating from refinery based production and 20 % from the raffinate of butadiene extraction. Nearly all of the rest is produced by TBA dehydration, the co-product of propylene oxide production. (Hamid und Ali 2004)

There are only limited sources on the isobutene production volumes available. In 2004 4,05 million tons of isobutene were produced in the US (U.S. DOE 2006). World-wide, isobutylene production from all sources is estimated between 10 Mt per year (OECD 2003; van Leeuwen et al. 2012) and 15 Mt per year (David Gogerty 2014). More production volumes, but older data, was found in (Fritz Obenaus et al. 2005) for the year 1984, as seen in Table 3-3. In that year worldwide 9,9 Mt per year of isobutene were produced, where 5,3 million tons were produced in North America and 1,7 million tons in Western Europe. In the US the production of isobutene declined due to restrictions around MTBE. The worldwide share of the isobutene production in 1984 is represented in Figure 12.

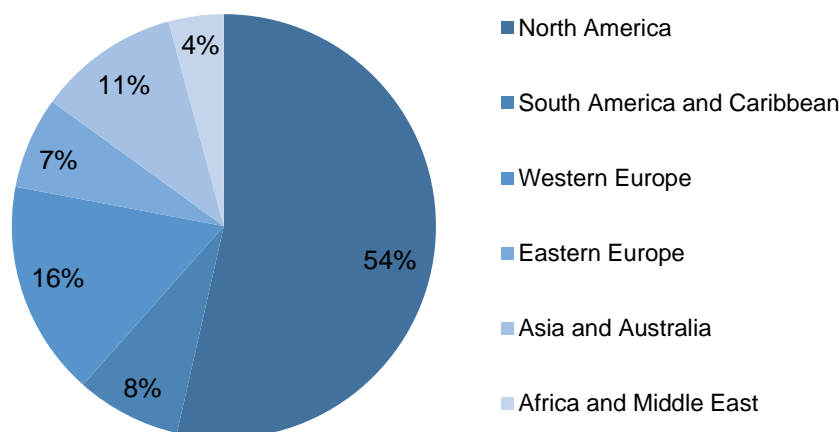


Figure 12: Isobutene consumption by region in 1984

Table 0-6: Isobutene Production Volume from different sources in 1984 (10³t) (Fritz Obenaus et al. 2005)

Source	Western Europe	North America	World
Steam Cracker	920	590	2540
Refinery	730	4420	7100
Dehydrogenation	-	-	50
TBA	50	250	300
Total	1700	5260	9990

2.8 Types of isobutene/MTBE plants

(Lidderdale 2000) provides an overview to the different types of isobutene or MTBE production plants:

Refinery/Petrochemical plants

Isobutylene is a by-product in refinery catalytic crackers and in petrochemical ethylene plants. In order to produce MTBE isobutylene is reacted with methanol. This process is primarily used in smaller MTBE plants which are the least expensive ones to build – \$6,000 to \$10,000 per daily barrel of capacity. A typical plant with a capacity of 2,500 barrel per day would need investments of about \$15 to \$25 million.

Merchant plants

Merchant plants use a different process to obtain MTBE: Butane is isomerized to isobutane, and then isobutene is dehydrogenated to isobutylene. In a next step isobutylene is reacted with methanol to the final product MTBE. These plants are the most expensive to build at investment costs of \$20,000 to \$28,000 per daily barrel of capacity. A typical 12,000 barrel per day merchant plant would need investments of about \$240 million to \$336 million to build.

TBA plants

Tertiary butyl alcohol (TBA) is a by-product of the propylene oxide production process. TBA is reacted with methanol to produce MTBE. It is assumed the capital replacement cost of the existing

TBA-MTBE capacity is equivalent to that of refinery/petrochemical plants. Patents related to isobutene production technologies

2.9 Patents for isobutene productions

A research on different patents about the production technologies of isobutene is done in order to get a market overview of existing technologies. Following, the patents are sorted by year and company:

Cold Acid Extraction isobutene in C4

- Standard Oil Dev Co 1947 - Sulfuric acid extraction of isobutylene from hydrocarbon mixtures
- Polymer Corp 1960 - Olefin extraction process using vacuum reconcentrated sulfuric acid
- Raffinage Cie Francaise 1961 - Process for the separation of isobutylene from mixtures of hydrocarbons

Etherification of isobutene in C4 (MTBE)

- Basf Aktiengesellschaft 1981 - Process for obtaining isobutene from C4 -hydrocarbon mixtures containing isobutene
- Basf Aktiengesellschaft 1982 - Process for conjointly preparing methyl tert.-butyl ether and obtaining isobutene
- Snamprogetti S.P.A. 1985 - Integrated process for producing tert.butyl alkyl ethers and butene-1
- Petro-Tex Chemical Corporation 1986 - Production of isobutene from methyl tertiary butyl ether
- Evonik Oxeno Gmbh 2011 - Preparation of isobutene by cleavage of MTBE
- Evonik Oxeno Gmbh 2011 - Producing isobutene by cracking mtbe

Hydration of isobutene in C4 (TBA)

- Nippon Oil Co Ltd 1970 - Process for producing high-purity isobutylene
- Hüls AG 1983 - Verfahren zur Herstellung von hochreinem Isobuten durch Dehydratisierung von tertiär-Butanol
- Uop 1983 - Process employing sequential isobutylene hydration and etherification
- Cities Service Company 1979 - Continuous process for dehydration of tertiary butyl alcohol
- ARCO 1996 - Liquid phase dehydration of tertiary butyl alcohol
- Huntsman International Llc 2003 - Process for producing isobutylene from tertiary butyl alcohol

Isobutene dehydration

- Sinclair Research Inc 1969 - Dehydrogenation process
- Uop Inc. 1984 - Dehydrogenation process using a catalytic composition
- Petro Tex Chem Corp 1969 - Production of isobutylene from isobutane
- Petro Tex Chem Corp 1973 - Production of isobutylene
- Arco Chemical Company 1988 - Dehydrogenation of isobutane

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Isobutene through molecular sieve

- Exxon Research Engineering Co 1962 - Isobutylene purification process using a pre-treated zeolitic molecular sieve
- Petro Tex Chem Corp 1970 - Isobutene separation with a molecular sieve
- Chemical Research And Licensing Company 1980 - Catalyst system for separating isobutene from C4 streams

Butene isomerization

- Exxon Research & Engineering Co. 1984 - Isomerization of butene-1 to butene-2 in isobutylene
- Chemical Research & Licensing Company 1984 - Isomerization of C4 alkenes
- Uop 1992 - Butene isomerization process
- Texaco Inc. 1996 - Skeletal isomerization of n-butylenes to isobutylene on zeolites
- Institut Francais Du Petrole 2001 - Method for producing high purity isobutylene from a butane plus fraction containing isobutylene and butylene-1
- Catalytic Distillation Technologies 2001 - Process for the separation of isobutene from normal butenes
- Catalytic Distillation Technologies 2002 - Process for the separation of isobutene from normal butenes

3 LCA Modelling of fossil isobutene

In a discursive process (e.g. telephone conference 16th Oct. 2017) with the project's coordinator Global Bioenergies (GBE) it was agreed to focus on three routes for the fossil isobutene reference process within the Life Cycle Assessment of fossil isobutene in Task 7.2:

- Isobutene from tert butyl alcohol (TBA) dehydration where TBA is a co-product of propylene oxide production (Oxirane process)
- Isobutene obtained from MTBE cracking
- Isobutene obtained from isobutene using catalytic dehydrogenation

These three routes are chosen to be the reference process for benchmarking biogenic isobutene production done by GBE as core activity within the project. The processes are investigated “cradle-to-gate”. Accordingly the processes encompass all life cycle stages (downstream processes) from resource depletion (e.g. crude oil mining) over refining until the product “isobutene”. The system boundaries exclude the use of isobutene in the use phase (e.g.: various industry applications). The geographical system boundary is defined as Europe or the EU-28 countries. Wherever it is possible European data is used, especially for energy mixes. The time horizon for the investigation is 2013 - 2017 – wherever it is possible the latest LCA data is used. A lot of data is used from the GaBi Professional database with its last update in 2017 where process data was updated (e.g.: country specific energy mixes).

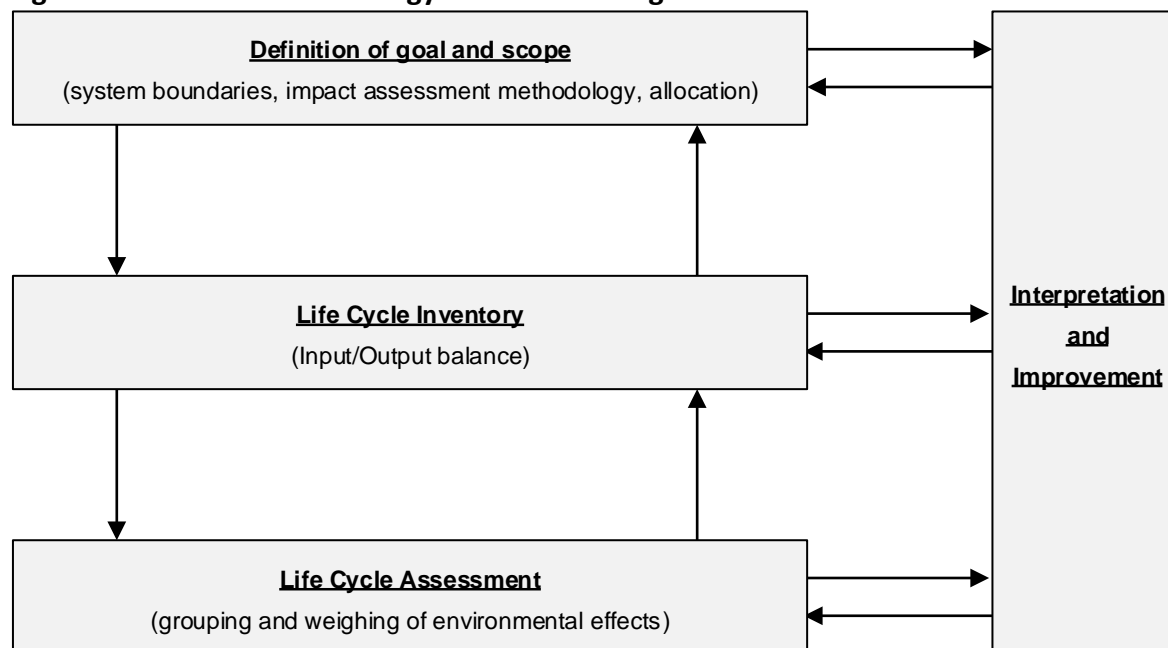
The detailed in-/output data and the preliminary GaBi results are listed in an additional excel file, which is added as a screenshot in Appendix 3. Furthermore, process descriptions and flowsheet diagrams can be found in Appendix 1 and Appendix 2.

3.1 Life Cycle Assessment methodology

The following chapter gives an overview of applied LCA methodology. In general the applied LCA methodology has been described extensively in literature (Kloepffer 1997; Guinee 2002; Guinee, J. B. et al 1993; Rebitzer; Reap 2008; Finnveden 2009) and therefore the upcoming chapter just aims to give an overview of the most important methodological issues for conducting the LCA within the framework of the OPTISOCHEM project. Life Cycle Assessment is a powerful decision support tool, complementing other methods, which are equally necessary to help effectively and efficiently make consumption and production more sustainable. The ISO 14040 and 14044 standards provide the indispensable framework for Life Cycle Assessment, as summarized in Figure 13. Its individual steps and iterative approach are briefly introduced in the following paragraphs.

Conducting an LCA is an iterative process. Goal and scope settings define the requirements for the subsequent work. During the life cycle inventory phase of data collection and during the subsequent impact assessment and interpretation more and more information on the process is gathered, which may lead to a revision of scope settings. System boundaries may be refined or assumptions overworked. In general, it is recommended to collect data and select external data sources in an iterative manner. The four methodological steps of LCA are described briefly in the following section.

Figure 13: General methodology of LCA according to ISO 14040 and 14044



Source: Energy Institute at the Johannes Kepler University based on ISO 14044

3.1.1 Definition of goal and scope

The system boundaries determine which unit processes are included in the LCA of the isobutene production processes. In general there are three different kinds of system boundaries. First the boundaries between the technical system (isobutene production process) and nature is determined. Usually a life cycle starts with the extraction of raw materials and energy carriers and ends with waste generation, energy recovery or disposal. Second the geographical system boundaries play an important role in a life cycle assessment as they determine for example the mix of electricity generation, energy supply structure, transport distances and also ecosystem sensitivity. The third system boundary which is to determine is the time horizon (Finnveden 2009; Kloeppfer und Grahl 2009; ISO 14044; European Environment Agency 1997). Another important step of defining the goal and scope as well as the system boundaries is to determine the function of the system as well as the functional unit. This secures comparability of the investigated system with reference processes (European Commission 2010). The system boundaries for fossil isobutene production is set “cradle-to-gate” – from raw material extraction to the final product isobutene. Details on the system boundaries for fossil isobutene production are shown in the following chapters.

3.1.2 Life Cycle Inventory analysis

The inventory analysis is done on the basis of unit processes. It is a quantitative assessment of the inputs going in the unit process and outputs of unit processes in terms of material and energy flows. Inputs are for instance raw materials and outputs are besides products, emissions and waste materials.

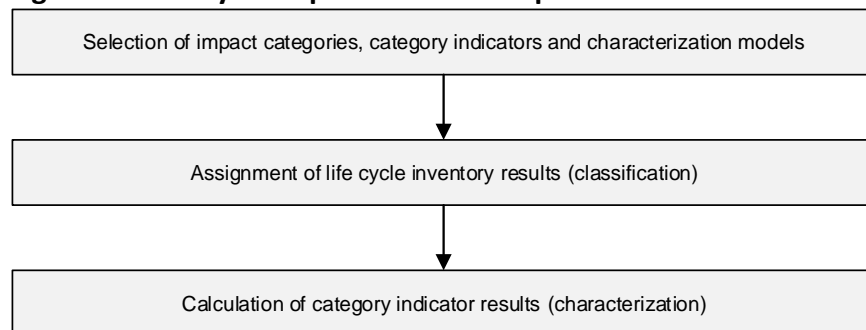
A major issue in life cycle inventory (LCI) compilation is data collection and generation. For every unit process within the process system the inputs and outputs have to be quantified (European Commission 2010) and (Azapagic A. 1999). The mass and energy balances are performed to quantify all material and energy inputs as well as wastes and emissions as outputs. These are related to the functional unit (Pieragostini). Data collection and generation is the core of LCI. According to (Curran

2012) data is the driving force behind Life Cycle Assessment. This indicates that the quality and significance of LCA crucially depends on the data behind. Of course there are numerous potential data sources, ranging from specialized LCA databases encompassed in LCA modeling software such as GaBi, over laboratory test results and industry data reports to data in literature (Curran 2012), though data collection and generation still is often a challenge and connected to making assumptions. The LCI (mass and energy balance) for fossil isobutene production is compiled based on literature data. Unit processes for the generation of materials and energy used within the process are taken from the GaBi ts 6.5 professional database.

3.1.3 Life Cycle Impact Assessment

On the basis of inventory analysis resulting environmental burdens are aggregated to a defined number of impact categories. Life cycle impact assessment is the stage during life cycle assessment where results of inventory analysis are interpreted in terms of environmental impact and societal preferences. The material and energy flows of the life cycle inventory are matched to impact categories in a step called classification and in the following step of characterization category indicator results are calculated (Koch 2009). These steps require the choice of impact categories, category indicators and characterization models (Khoo 2009). For example the amount of CO₂ and CH₄ emitted during a process are the life cycle inventory results which are attributed to impact category of climate change. The following category indicator is the quantification of the intensification of infrared radiation oriented on a reference substance. As a result the impact of CO₂ and CH₄ on environment is subsumed as kg CO₂-equivalents which is the measure for the Global Warming Potential (GWP) (Kloepffer und Grahl 2009).

Figure 14: Life cycle impact assessment procedure



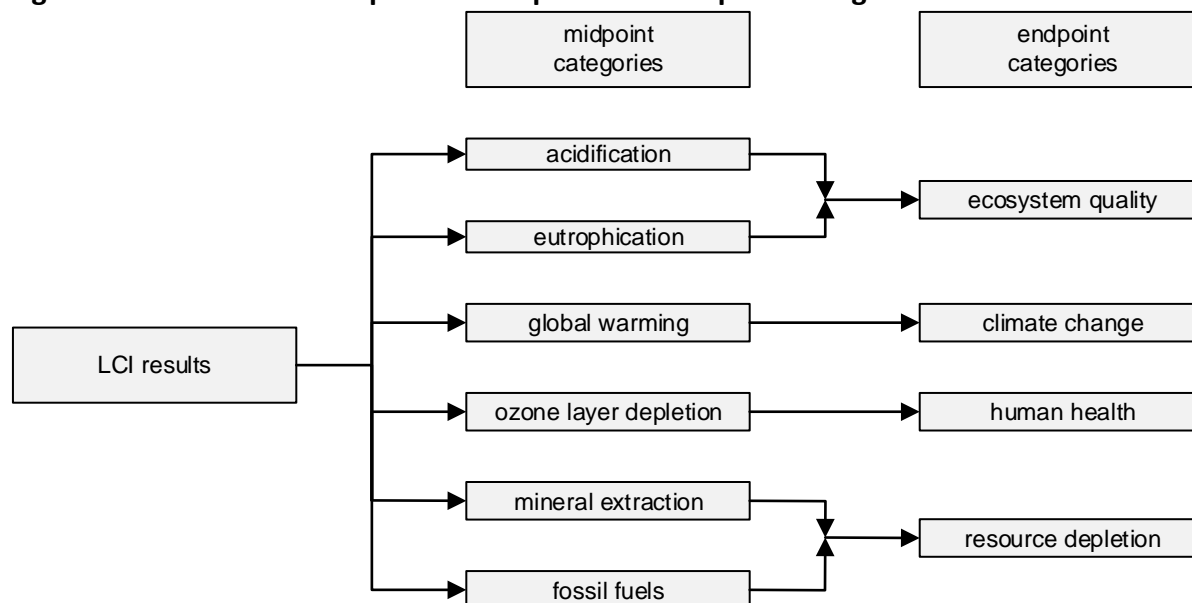
Source: Energy Institute at the Johannes Kepler University based on (Kloepffer und Grahl 2009)

The CML 2013 impact assessment method developed Institute of Environmental Sciences, Leiden University, The Netherlands covers goal and scope definition, life cycle inventory and the impact assessment and therefore confirms the norm ISO 14040. In general the CML method is a problem oriented classification of material and energy flows for impact assessment and categorizes results in so-called midpoint categories (Guinée und Lindeijer 2002). As the CML method is an internationally approved method for life cycle impact assessment, it is used within the OPTISOICHEM project.

Figure 14 shows the impact categories which are used for life cycle impact assessment within the CML method. CML method uses IPCC factors for the quantification of global warming potential and ozone layer depletion (Charoenvuttitham et al. 2006). The impact categories shown in the table are so-called midpoint categories. These midpoint categories can be aggregated to endpoint categories which describe the damage brought about the environment (Jolliet et al 2003). The estimation of

such endpoint categories is not an issue of the CML method and therefore an endpoint category estimation is not subject of the LCA conducted in the OPTISOCEM project. Nevertheless it should be schematically described what the difference between midpoint and endpoint categories is. Figure 15 shows a schematic description of midpoint and endpoint categories. The figure only gives examples of midpoint categories and the attributable endpoint categories. It was already mentioned that the CML method does not take into account endpoint categories. This method stops at calculating midpoint categories. The endpoint categories describe the final impact of the life cycle inventory results and midpoint categories have on environment (Jolliet et al 2003).

Figure 15: Schematic description of midpoint and endpoint categories



Source: Energy Institute at the Johannes Kepler University based on ISO 14044

Table 3-1 shows the impact categories within the CML method. As already described above, these categories are classified as mid-point categories. Mid-point categories do not evaluate which effects for example the monitored eutrophication potential has on ecosystem quality. It follows that there is no quantification of how many species cease because of that environmental effect. All impact categories shown in Table 3-1 are calculated within the LCA of the OPTISOICHEM process (Jolliet et al 2003) in line with the proposed approach in the description of work.

Table 3-1: Impact categories and units within the CML method

Impact categories within the CML method	Unit
Global warming potential (GWP 100 years)	[kg CO ₂ -Equiv.]
Ozone layer depletion potential (ODP, steady state)	[kg R11-Equiv.]
Acidification potential (AP)	[kg SO ₂ -Equiv.]
Eutrophication potential (EP)	[kg Phosphate-Equiv.]
Photochemical ozone creation potential (POCP)	[kg Ethene-Equiv.]
Human toxicity potential (HTTP inf.), Terrestrial ecotoxicity potential (TETP inf.)	[kg DCB-Equiv.]
Freshwater aquatic ecotoxicity potential (FAETP inf.), Marine aquatic ecotoxicity potential (MAETP inf.)	[kg DCB-Equiv.]
Abiotic depletion (ADP)	[kg Sb-Equiv.]

Source: own table based on (PE International 2010)

Every substance monitored in the life cycle inventory is attributed to one of the CML impact categories shown above. This is done by converting the substances of the life cycle inventory to the units which describe the particular impact categories by using characterization factors. The result is a complete life cycle impact assessment (PE International 2010).

3.1.4 Life Cycle Interpretation

Interpretation of LCA has to contain the identification of significant issues, an evaluation considering completeness, sensitivity and consistency checks, conclusions, limitations, and recommendations. Further the appropriateness of the definitions of the system functions, the functional unit and system boundary has to be checked and also limitations has to be identified as well as a sensitivity analysis conducted.

The final outcome of the interpretation should be conclusions or recommendations that respect the intentions and restrictions of the goal and scope definition of the LCA. The interpretation should present the results of the LCA in an understandable way and help the user to appraise the robustness of the conclusions and understand any potential limitations of the LCI/LCA. The interpretation proceeds in three stages:

- First, the significant issues (i.e. the key processes, parameters, assumptions and elementary flows) are identified.

- Then these issues are evaluated with regard to their sensitivity or influence on the overall results determined during the LCA. This includes an evaluation of the completeness and consistency how the significant issues have been handled during the LCI/LCA.
- Finally, the results of the evaluation are used to formulate conclusions and recommendations based on the LCA.

3.2 Isobutene from TBA decomposition

In this process isobutene is produced from TBA, which is the coproduct of the propylene oxide (PO) production process, the Oxirane process. The process flow chart is shown in Figure 16. The different process blocks and their modelling are presented in the following chapters. The flowsheet diagram and the used input values for the TBA dehydrogenation process in GaBi can be seen in Appendix 2 and Appendix 3.

For the whole process two allocations are made:

1. Oxirane process: two products
2. TBA decomposition: three products

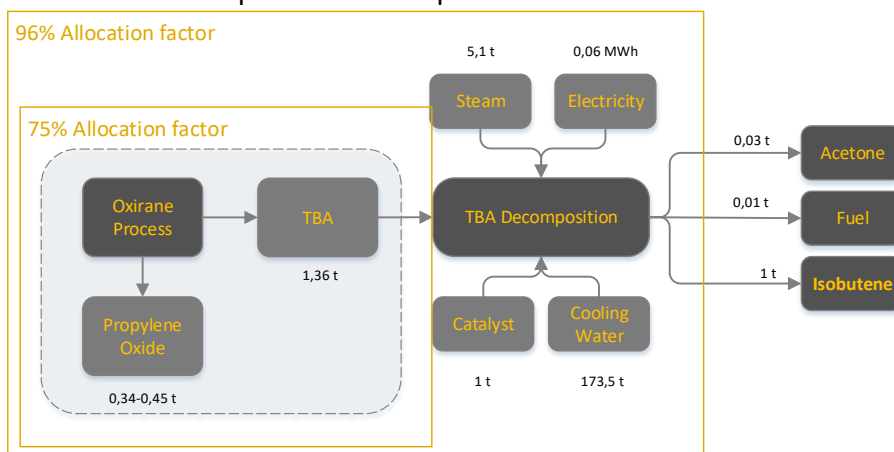


Figure 16: Flow chart - Isobutene from TBA dehydrogenation

3.2.1 Model description

Oxirane Process:

The first process block in Figure 16, the Oxirane process, is available in the GaBi database. According to (Tsuji et al. 2006) with every ton of propylene 3 to 4 tons of TBA are coproduced. For the simulations two scenarios are set up, the worst case with a production rate of 3 tons and the best with 4 tons of TBA.

TBA dehydrogenation process

The further process information required for the TBA decomposition is adopted from the Nexus Report 2007 and is listed in Table 3-2. For gathering additional information about the catalyst, a conference call (15.05.2018) with experts within the project consortium was held. According to the discussion, it was decided to define a catalyst with a carrier material made of zeolite with poly-phosphoric acid (as proposed in the Nexus report 2007) as a catalyst. Further the ratio for the zeolite/catalyst was set to 1:1.3.

As there is no process for poly-phosphoric acid in the GaBi database, phosphoric acid (from ecoinvent) is used in the simulations. This process describes the production of 70% phosphoric acid, in the Nexus report 2007 a dilute of 18% poly-phosphoric acid is used. To overcome this problem, two values for the acid consumption are supposed. First, for the worst case and the upper boundary, the ecoinvent process of phosphoric acid with a consumption of 565 kg per ton isobutene was applied. The lower boundary is described by the assumption to dilute the 70% acid to 18%, as

described in the Nexus report. To implement this in the Gabi Process, a 52% lower consumption of the acid (271 kg) was supposed. As poly-phosphoric acid is produced through dehydration of phosphoric acid at temperatures above 300°C it needs additional energy input and therefore should be in between the two values.

The impact of the zeolite support material is varied with a loss of material between 5% and 30% each cycle, which are in total 22 kg and 120 kg of zeolite per ton of isobutene.

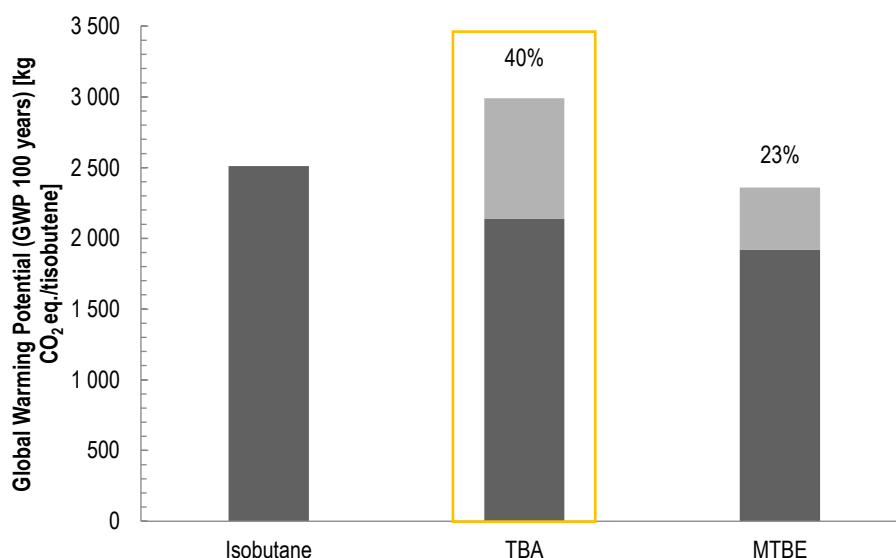
All the relevant input data for the model listed in Table 3-2, where the values for the best- and worst case scenario just differ in the catalyst input and in the different production rate of the Oxirane process (not shown in Table 3-2).

Table 3-2: In-/Outputs of the TBA dehydrogenation process

	Best case	Worst case	unit
Input			
TBA	1,362	1,362	t
Power	0,22	0,22	GJ
Cooling Water	173,5	173,5	t
Steam (13,79bar)	14,21	14,21	GJ
Catalysts & Chemicals	1	1	t
Zeolite	22 (95% regen.)	120 (70% regen.)	kg
Poly-phosphoric acid	271 (18% P.A.)	565 (70% P.A.)	kg
Output			
Isobutene	1	1	t
Fuel	0,0098	0,0098	t
Acetone	0,0317	0,0317	t

3.2.2 Results – Global Warming Potential

Figure 17 shows an overview of the results of the LCA-simulation in respect to the global warming potential. The bar in the orange frame indicates the range of the GWP of the TBA decomposition process. The bright grey bar indicates the interval between best and worst scenario GWP. Collectively the GWP for the production of isobutene from TBA lies between 2,140 and 2,990 kg per ton Isobutene, which means a variation of about 40%.


Figure 17: Global warming potential - TBA decomposition

To get further into detail and understand the variation in the results, Figure 17 shows the disaggregated TBA decomposition process. The highest impact on the balance has the production

of steam, followed by the Oxirane process. As already mentioned, the TBA product output of the Oxirane process can vary between 3 and 4 tons per ton propylene oxide. The higher conversion rate would decrease the GWP to 20%.

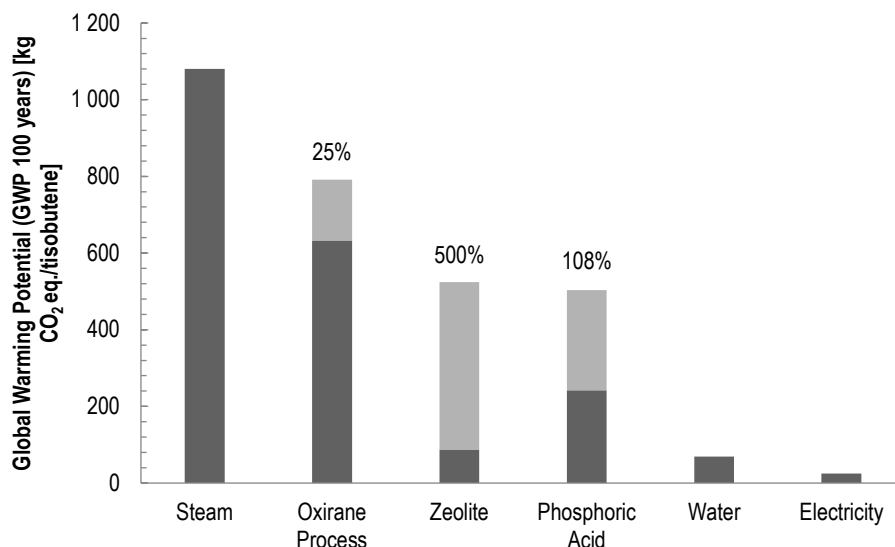


Figure 18: Global warming potential - disaggregated TBA decomposition

The impact of the catalyst provides the highest variance in the simulation based on the available data. It can be seen that the consumption of zeolite has a fundamental impact on the system. The same counts for the results of the phosphoric acid. The values of “reality” should be more close to the lower boundaries.

3.2.3 Results – Primary Energy Demand

Primary Energy is by the definition of (Watson et al.) “The energy that is embodied in resources as they exist in nature: the chemical energy embodied in fossil fuels or biomass, the potential energy of a water reservoir, the electromagnetic energy of solar radiation and the energy released in nuclear reactions”.

As shown in Figure 19 the TBA decomposition provides with 49,500 and 67,600 MJ per ton of isobutene the lowest primary energy demand (PED), compared to the other two routes, although the global warming potential was determined to be the highest. The triangles in the diagram show the GWP/PED factor, which quantifies the CO₂ emissions per GJ of primary energy (calculated for the best case scenarios). In this case the GWP/PED factor is the highest compared to the others, which means that with a low primary energy demand more CO₂ is emitted. Probably this is due to a higher proportion of renewable energy carriers in the overall energy mix.

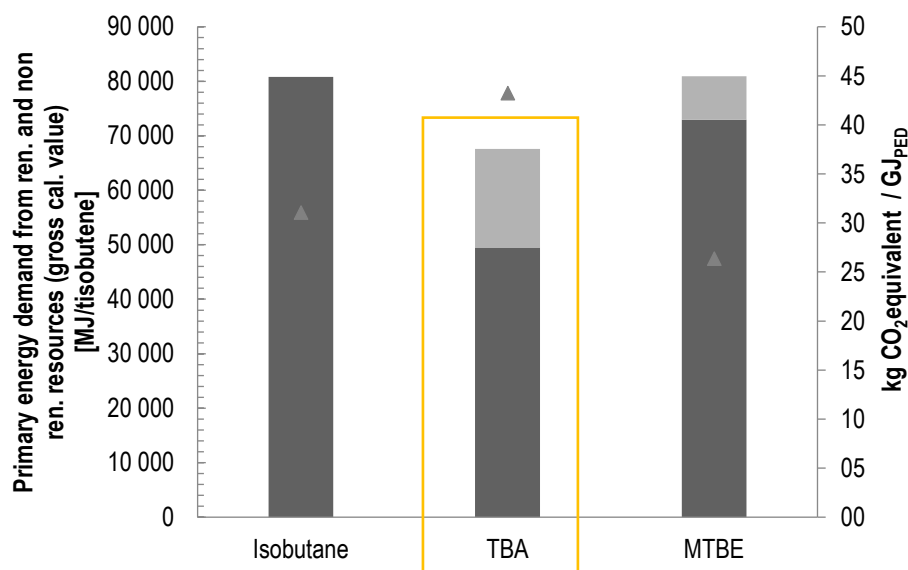


Figure 19: Primary Energy Demand - TBA decomposition

Comparing the disaggregated results of the PED to the global warming potential from the last chapter it stands out that there is no direct proportional correlation between the PED and the GWP. In Figure: 20 it can be seen that the order of the processes in respect of the highest values is different to the global warming potential. Here the Oxirane process has highest PED. Also the zeolite process has a lower impact than the phosphoric acid. This means that the factor of GWP per PED for every process is different, which is presented by the triangles in Figure: 20 (calculated for the best case scenarios). This factor for example is more than two times higher for zeolite than for the Oxirane process, which can be interpreted less primary energy used but more emissions. It might cohere with the specific process parameters and the energy carrier used. The process of tap water production shows high greenhouse gas emissions per GJ primary energy demand for water production. This is probably influenced by the high complexity of water purification background processes in GaBi database. Nevertheless the overall impact of water consumption for TBA decomposition is quite low although water consumption is relatively high (~168.000 kg/t_{isobutene}) in the model.

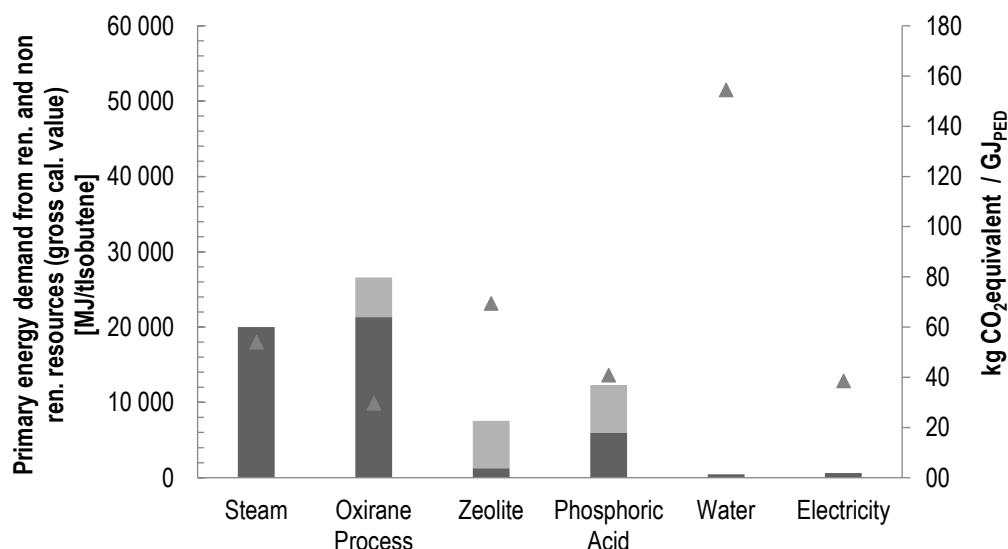


Figure 20 Primary Energy Demand - disaggregated TBA decomposition

3.3 Isobutene from MTBE decomposition

In this process isobutene is produced from MTBE via dehydrogenation. The whole process flow chart can be seen in Figure 21. The flowsheet diagram and the used input values for the MTBE dehydrogenation process in GaBi can be seen in Appendix 2 and Appendix 3.

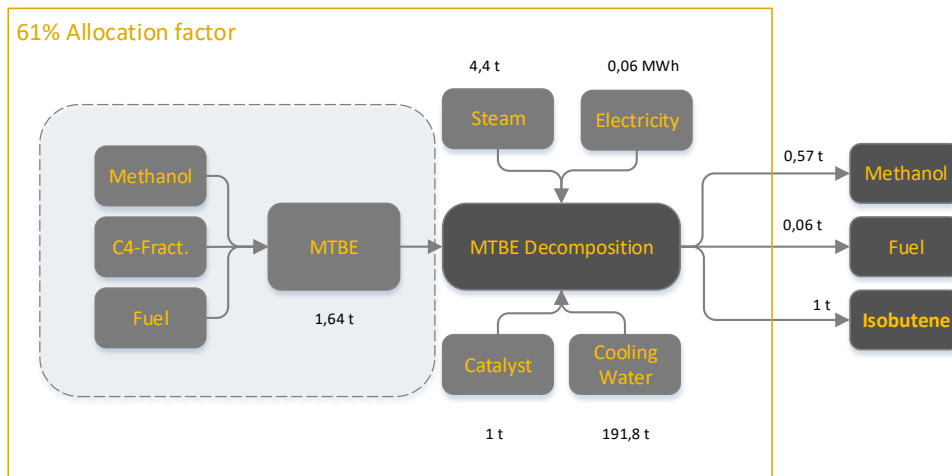


Figure 21: Flow chart – isobutene production process from MTBE

3.3.1 Model description

MTBE production

The first process step, the MTBE production, is a readymade lifecycle process pathway from Ecoinvent database and was imported to GaBi. All relevant information is included in this sealed process. Unfortunately there is no insight to the input- and process data. The process used is called “methyl tert-butyl ether production”, presents the conversion of MTBE from isobutene with methanol in presence of a catalyst and is valid for Europe.

MTBE decomposition modelling

The used input- and output parameters for the best and worst case scenarios (MTBE decomposition) are shown in Table 3-3. The data source is the Nexus report 2007. Inputs are first of all MTBE, followed by the required energy and materials for the decomposition (steam, electricity, cooling water, catalyst). The scenarios differ in the different inputs of the catalysts materials, which are the same assumptions as for the decomposition of TBA.

The outputs are isobutene, methanol and traces of dimethyl ether. For the output, as seen in Figure 12, a mass allocation was applied.

Table 3-3: In-/Outputs of the MTBE decomposition process

	Best case	Worst case	unit
Input			
MTBE	1,64	1,64	t
Steam (HPS, 14bar)	12,26	12,26	GJ
Electricity	0,06	0,06	t
Cooling water	191,8	191,8	GJ
Catalysts & Chemicals	1	1	t
Zeolite	22 (95% regen.)	120 (70% regen.)	kg
Poly-phosphoric acid	271 (18% P.A.)	565 (70% P.A.)	kg
Output			
Isobutene	1	1	t
Methanol	0,574	0,574	t
Fuel	0,064	0,064	t

3.3.2 Results – Global Warming Potential

Figure 22 shows an overview of the results of the LCA-simulation in respect to the global warming potential. The bar in the orange frame indicates the range of the GWP of the MTBE decomposition process. The bright grey bar indicates the interval between minimum and maximum GWP and is given as the share of the maximum value.

It can be seen that the MTBE decomposition resulted the lowest GWP (1,990-2,360 kg CO₂ equivalent per ton isobutene) compared to the other processes.

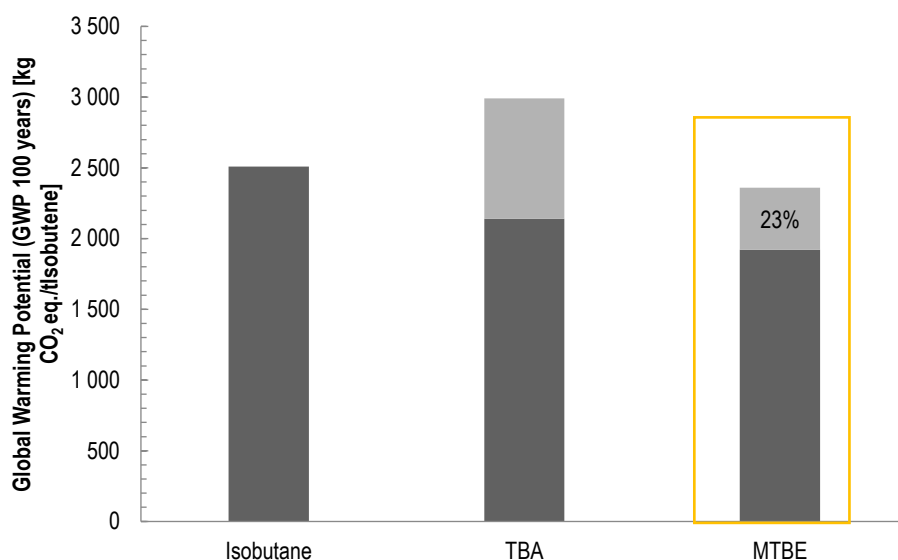


Figure 22: Global warming potential - MTBE decomposition

To get further into detail and understand the variation in the results, Figure 23 shows the disaggregated MTBE decomposition process. The MTBE production shows the highest impact in the process chain, followed by process steam and the phosphoric acid. The composition of the catalyst is identical to the TBA-decomposition. The difference in the values originates from the high allocation of 61% (61% of the impact is accounted to isobutene). If the byproduct Methanol would be neglected, the impact of all processes would increase by a factor of 1.54, which means an allocation factor of 95% to isobutene. This would increase the total GWP to 3,065-3,634 kg CO₂ equivalent per ton isobutene.

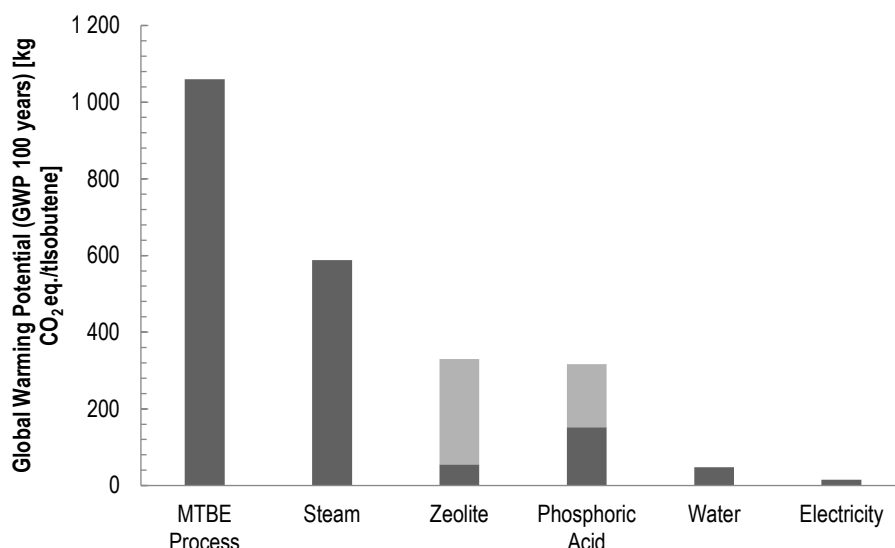


Figure 23: Global warming potential - disaggregated MTBE decomposition

3.3.3 Results – Primary Energy Demand

As shown in Figure 24, MTBE decomposition is with 72.9500 and 80.900 MJ per ton of isobutene in the same range like isobutane dehydrogenation with 80.800 MJ. The GWP/PED factor for this process is with 26 kg CO₂ equivalent per GJ primary energy the lowest compared to the others.

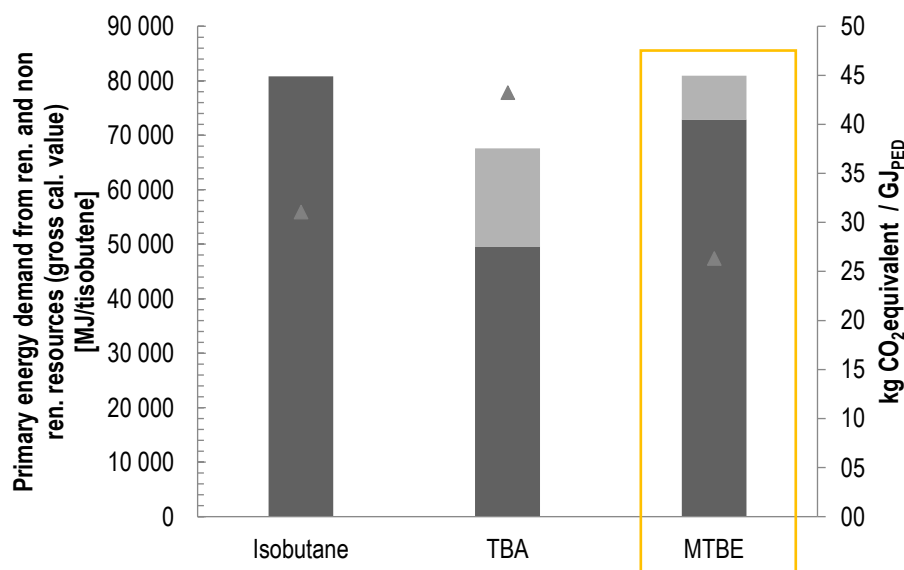


Figure 24: Primary Energy Demand- MTBE decomposition

Comparing the disaggregated results (Figure 25) of the PED to the GWP from the last chapter the order of the highest values just differs with zeolite, which again has (TBA decomposition) a higher PED than phosphoric acid. MTBE has by far the highest PED (56.8 GJ) with a relatively low GWP/PED factor of about 19 kg CO₂ equivalent / GJ.

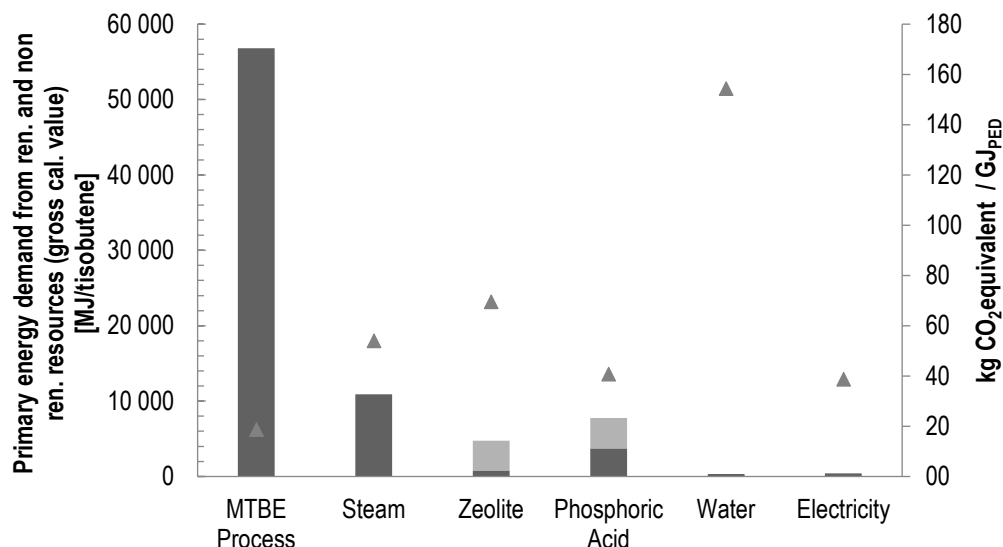


Figure 25: Primary Energy Demand- disaggregated MTBE decomposition

Again the process of tap water production shows high greenhouse gas emissions per GJ of PED. As already mentioned this is due to a relatively high complexity of water purification processes as background processes in the GaBi LCA database. The overall influence of tap water consumption on the MTBE decomposition is relatively low.

3.4 Isobutene from isobutane dehydrogenation

3.4.1 Model description

The dehydrogenation process (Figure 26) of butane to isobutene is a standard process in GaBi ts 6.5 Professional database. It is the simplest implementation of a process, with the disadvantage of no insight to the exact assumptions. The process description, the flowsheet diagram and the used input values for the TBA dehydrogenation process in GaBi can be seen in Appendix 1, Appendix 2 and Appendix 3.

The dehydration of isobutane is valid for Germany and comprises the following process steps:

1. Isomerization: N-butane is mixed with hydrogen in presence of a catalyst and converted to isobutene
2. Dehydrogenation: Isobutane is dehydrated to isobutene on a platinum catalyst in the feed heaters

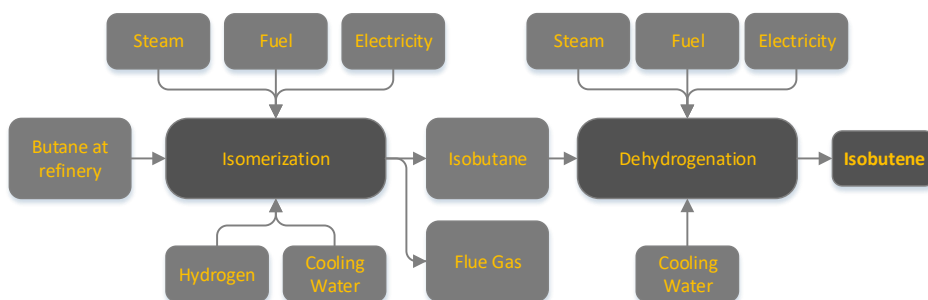


Figure 26: Flow chart – isobutene from dehydration of isobutene

3.4.2 Results – Global Warming Potential

As seen in Figure 27 (orange frame) the process of isobutane dehydrogenation results in the second highest GWP (2,510 kg CO₂ equivalent per ton isobutene) of all assessed variants.

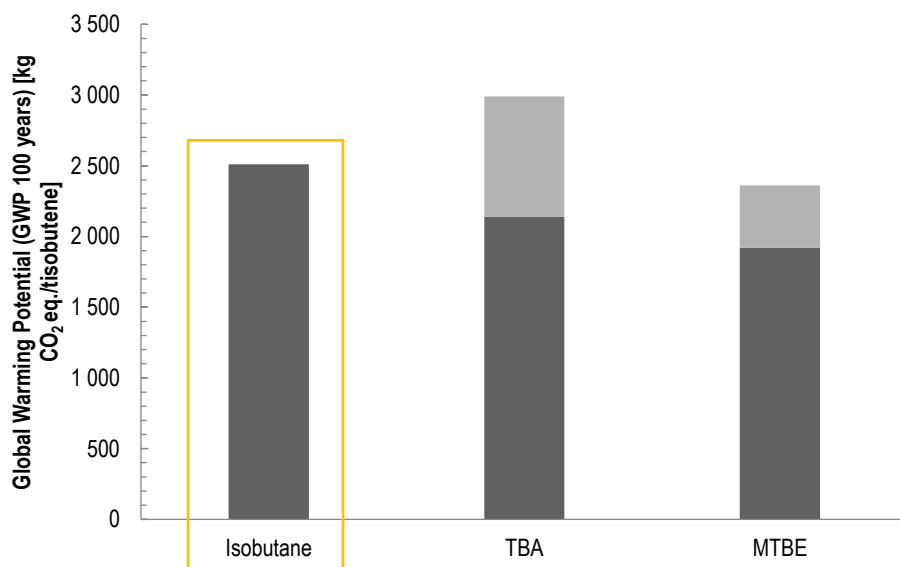


Figure 27: Global warming potential – isobutane dehydrogenation

3.4.3 Results – Primary Energy Demand

As seen in Figure 28 the isobutane dehydrogenation process result with 80.8 GJ in the highest primary energy demand. The ratio of GWP to PED is with 31 kg CO₂ equivalent per GJ primary energy in between the two other processes.

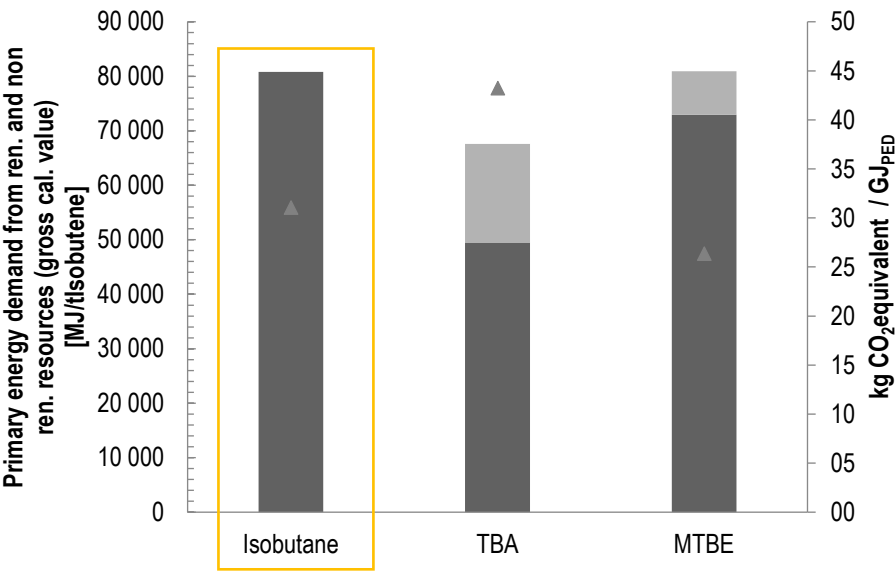


Figure 28: Primary Energy Demand– isobutane dehydrogenation

4 Discussion / Summary

Literature research on fossil isobutene production showed that there is a high variety of processes available. The complexity of those processes is significant as these are refinery integrated cracking processes. As a result the composition of product streams (e.g.: C4 stream) and the downstream processing in order to obtain isobutene very much depends on the specific process parameters such as severity of cracking processes. Another challenging aspect for conducting the LCA for fossil isobutene is to overcome the lack of literature data due to data secrecy of industry and patent rights. In order to simplify LCA of fossil isobutene in a first step three fossil isobutene processes are defined together with the project partners:

- Isobutene from tert butyl alcohol (TBA) dehydration where TBA is a co-product of propylene oxide production (Oxirane process)
- Isobutene obtained from MTBE cracking
- Isobutene obtained from isobutene using catalytic dehydrogenation

These three process routes are investigated by a full Life Cycle Assessment conducted in the LCA software GaBi. The LCA results for fossil isobutene are not definite. From a greenhouse gas perspective, MTBE decomposition or isobutene dehydrogenation are the preferable process routes. From a primary energy demand perspective TBA dehydration would be the preferable process routes. Details on the results are presented in chapter 2 of the current report. As greenhouse gas emissions do not correspond with primary energy demand for all process options, a decision for one or another process route without weighing is not possible. In case of MTBE decomposition process steam demand, zeolites and phosphoric acid used as catalysts are the main contributors to GWP and PED. In the case of TBA dehydration process steam, the Oxirane process for supplying TBA as a by-product and phosphoric acid are the main contributors to GWP and PED. The full LCA results – all CML 2001 associated impact categories are summarized in the Annex of this Deliverable Report. The result for fossil isobutene production presented in this deliverable is the basis for comparison with LCA results for 1st generation sugar isobutene LCA and 2nd generation sugar isobutene LCA in the upcoming Deliverable reports of the OPTISOICHEM project.

A discussion point for fossil isobutene LCA is data accuracy as the inputs and outputs for the life cycle inventory are based on literature data and own estimations based on literature values. Insecurities for example occur in the use of zeolites and catalysts. Regeneration rates are assumed for zeolites. In contrast, there is hardly any regeneration for the catalyst assumed. As a result there may be a slight overestimation of environmental impacts for catalyst consumption. Another point is that there is no cycle for cooling water assumed due to a lack of data on this topic. This probably leads to an overestimation of the impact of using tap water in the processes. Despite this obstacles in the life cycle inventory it can be assumed that the results deliver a valid insight to the environmental burden caused by fossil isobutene production. Therefore the results are classified valid to be used as benchmarks for comparing isobutene production based on 1st and 2nd generation sugars.

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8 Appendix

Appendix 1: GaBi Process description

Isobutene (from Isobutane) , production mix, at plant, catalytic dehydrogenation of isobutane (Germany)

<https://nexus.openlca.org/search/query=isobutene!Database=GaBi>

The data set covers all relevant process steps / technologies over the supply chain of the represented cradle to gate inventory with a good overall data quality. The inventory is mainly based on industry data and is completed, where necessary, by secondary data. This dataset is based on primary data from internationally adopted production processes, connected with regional precursor chains.

Foreground system:

n-Butane is mixed with hydrogen in the presence of catalyst and converted to isobutane. Isobutane is dehydrogenated to isobutylene on platinum catalyst in feed heaters.

Background system:

Electricity: Electricity is modelled according to the individual country-specific situations. The country-specific modelling is achieved on multiple levels. Firstly, individual energy carrier specific power plants and plants for renewable energy sources are modelled according to the current national electricity grid mix. Modelling the electricity consumption mix includes transmission / distribution losses and the own use by energy producers (own consumption of power plants and "other" own consumption e.g. due to pumped storage hydro power etc.), as well as imported electricity. Secondly, the national emission and efficiency standards of the power plants are modelled as well as the share of electricity plants and combined heat and power plants (CHP). Thirdly, the country-specific energy carrier supply (share of imports and / or domestic supply) including the country-specific energy carrier properties (e.g. element and energy content) are accounted for. Fourthly, the exploration, mining/production, processing and transport processes of the energy carrier supply chains are modelled according to the specific situation of each electricity producing country. The different production and processing techniques (emissions and efficiencies) in the different energy producing countries are considered, e.g. different crude oil production technologies or different flaring rates at the oil platforms.

Thermal energy, process steam: The thermal energy and process steam supply is modelled according to the individual country-specific situation with regard to emission standards and considered energy carriers. The thermal energy and process steam are produced at heat plants. Efficiencies for thermal energy production are by definition 100% in relation to the corresponding energy carrier input. For process steam the efficiency ranges from 85%, 90% to 95%. The energy carriers used for the generation of thermal energy and process steam are modelled according to the specific import situation (see electricity above).

Transports: All relevant and known transport processes are included. Ocean-going and inland ship transport as well as rail, truck and pipeline transport of bulk commodities are considered.

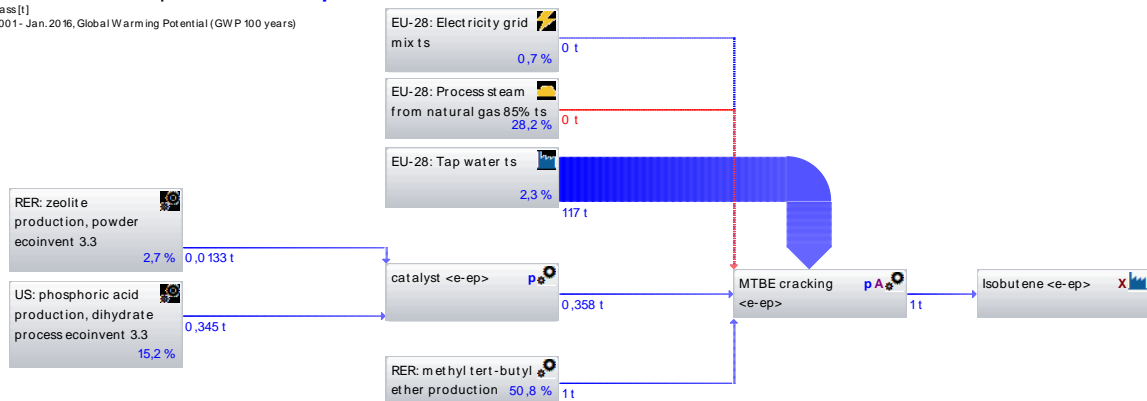
Energy carriers: The energy carriers are modelled according to the specific supply situation (see electricity above).

Refinery products: Diesel fuel, gasoline, technical gases, fuel oils, lubricants and residues such as bitumen are modelled with a parameterised country-specific refinery model. The refinery model represents the current national standard in refining techniques (e.g. emission level, internal energy consumption, etc.) as well as the individual country-specific product output spectrum, which can be quite different from country to country. The supply of crude oil is modelled, again, according to the country-specific situation with the respective properties of the resources.

Appendix 2: Flowcharts in GaBi MTBE Decomposition Flowcharts

Task 7.2.1 - MTBE Decomposition final

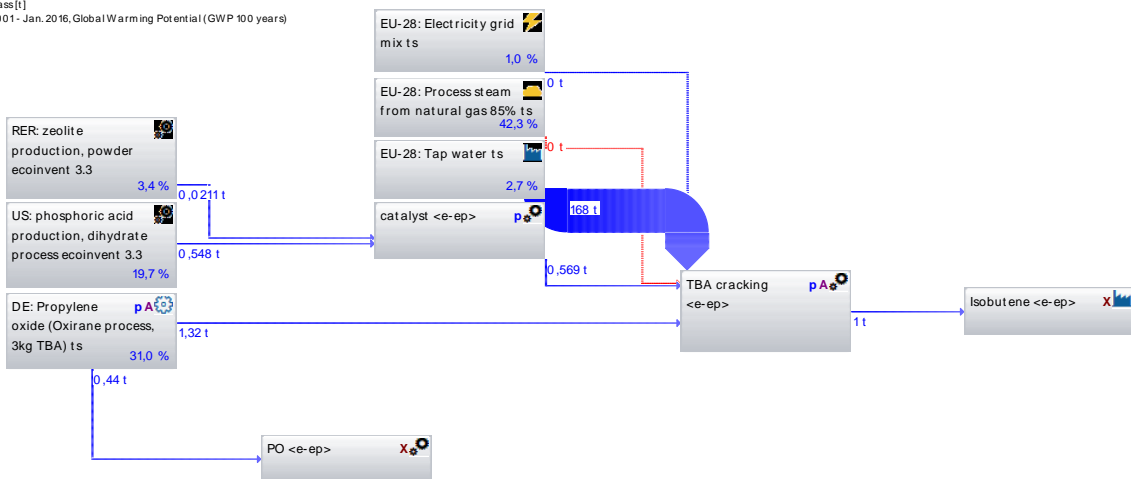
GaBi Prozess-Plan: Mass [t]
LCIA Vorschau: CML2001 - Jan. 2016, Global Warming Potential (GWP 100 years)



TBA Decomposition Flowcharts


Task 7.2.1 - TBA Ecoinvent (TBA all no cat (3kg TBA))

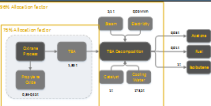
GaBi Prozess-Plan: Mass [t]
LCIA Vorschau: CML2001 - Jan. 2016, Global Warming Potential (GWP 100 years)



Appendix 3: Input/Output-data for GaBi

1. Isobutene from TBA decomposition





Completed by: SL

Date of completion:

Unit process 1

Reporting location: AT, Linz

Time period: Year 2017/2018

Starting month:

Ending month:

Description of scenarios:

Isobutene from TBA-Decomposition (1.2) TBA produced as a byproduct from the Oxirane Process (1.1). Allocations made in GaBi for the Oxirane Process (TBA, PO) and for the decomposition of TBA (Isobutene, Acetone, Fuel). In literature the share of TBA from the oxirane varies between 3 and 4 t per 1 t Propyleneoxide

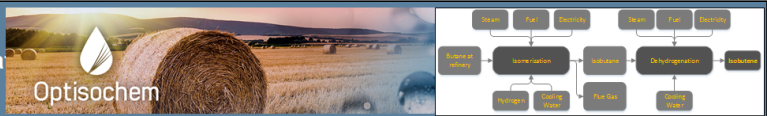
	parameter	value	unit	GaBi 6.5 dataset	notes
1.1 Oxirane Process					
inputs	input data included in GaBi Oxirane Process			DE: Propyleneoxide (Oxirane Process) TBA PE	Thinkstep, GaBi
outputs	TBA	3-4	t		Tsuiji, Junpei; Yamamoto, Jun; Ishino, Masaru; Oiku, Noriaki (2006): Development of New Propylene Oxide Process
	Propylene Oxide	100	t		Tsuiji, Junpei; Yamamoto, Jun; Ishino, Masaru; Oiku, Noriaki (2006): Development of New Propylene Oxide Process
decomposition					
inputs	TBA	1,36	t		Data out of Nexus Report
	Steam (High Pressure steam, 14bar)	14,21	GJ	EU-28: Process steam from natural gas 85% efficiency; technology mix	Data out of Nexus Report
	Electricity	0,06	MWh	EU-28: Electricity grid mix; technology mix; production mix (region specific plants)	Data out of Nexus Report
	Cooling water	173,50	t	Tap Water ts	Data out of Nexus Report
	Catalyst	100	t	not defined, no specification about catalyst in Nexus Report	Data out of Nexus Report
	Zeolite	22-120	kg	RER: zeolite production, powder	assumptions, imported from Ecoinvent 3.3
	Poly-phosphoric acid	271-565	kg	US: phosphoric acid production, dihydrate process	assumptions, imported from Ecoinvent 3.3
outputs	Isobutene	100	t		Data out of Nexus Report
	Acetone	0,03	t	Acetone [organic intermediate products]	Data out of Nexus Report
	Fuel	0,08	t	not defined, no specific details	Data out of Nexus Report

2. Isobutene from MTBE decomposition



Completed by: SL	Date of completion:				
Unit process 2:	Reporting location: AT, Linz				
Time period: Year 2017/2018	Starting month:	Ending month:			
Description of scenarios:					
Isobutene from MTBE-Decomposition (2.2). Allocations have been made for the MTBE decomposition (Isobutene, Methanol, Dimethylether).					
2.1 MTBE Production	parameter	value	unit	GaBi 6.5 dataset	notes
inputs	input data included in Ecoinvent Process			ecoinvent process: RER: methyl tert-butyl ether production	
outputs	MTBE	100	t		
Decomposition					
inputs	MTBE	164	t		Data out of Nexus Report
	Steam (High Pressure steam, 14bar)	12.26	GJ	EU-28: Process steam from natural gas 85% efficiency, technology mix	Thinkstep, GaBi
	Electricity	0.06	MWh	EU-28: Electricity grid mix, technology mix, production mix (region specific plants)	Thinkstep, GaBi
	Cooling water	191.80	t	EU-28: Water (deionised) from surface water, reverse osmosis	Thinkstep, GaBi
	Catalyst	1.00	t	not defined, no specification about catalyst in Nexus Report	Data out of Nexus Report
	Zeolite	22.120	kg	RER: zeolite production, powder	imported from Ecoinvent 3.3
	Poly-phosphoric acid	271.565	kg	US: phosphoric acid production, dehydrate process	imported from Ecoinvent 3.3
outputs	Isobutene	100	t		Data out of Nexus Report
	Methanol	0.57	t	Methanol [organic intermediate products]	Data out of Nexus Report
	Fuel	0.06	t	Dimethyl ether [organic intermediate products]	Data out of Nexus Report

3. Isobutene from Isobutane dehydrogenation



Completed by: SL	Date of completion:				
Unit process 3:	Reporting location: AT, Linz				
Time period: Year 2017/2018	Starting month:		Ending month:		
Description of scenarios:					
Catalytic dehydrogenation of isobutane to isobutene, GaBi Process used.					
	parameter	value	unit	GaBi 6.5 dataset	notes
3. Dehydrogenation Process					
inputs	input data included in GaBi Dehydrogenation Process				
				DE: Isobutene (from Isobutane) to	Thinkstep, GaBi
outputs	Isobutene	100	t		Thinkstep, GaBi

Appendix 3: Full LCA results

Appendix 3 shows the full LCA results for fossil isobutene production. The full LCA result encompasses the quantitative results for all CML 2001 impact categories as well as the primary energy demand split into renewable and non-renewable resources.

Full LCA results for TBA dehydration, best case

TBA dehydration, best case	
impact categories	
Abiotic Depletion (ADP elements) [kg Sb eq.]	0,0182
Abiotic Depletion (ADP fossil) [MJ]	4,36E+04
Acidification Potential (AP) [kg SO ₂ eq.]	7,48
Eutrophication Potential (EP) [kg Phosphate eq.]	1,27
Freshwater Aquatic Ecotoxicity Pot. (FAETP inf.) [kg DCB eq.]	253
Global Warming Potential (GWP 100 years) [kg CO ₂ eq.]	2,14E+03
Global Warming Potential (GWP 100 years), excl biogenic carbon [kg CO ₂ eq.]	2,10E+03
Human Toxicity Potential (HTP inf.) [kg DCB eq.]	5,33E+02
Marine Aquatic Ecotoxicity Pot. (MAETP inf.) [kg DCB eq.]	1,25E+06
Ozone Layer Depletion Potential (ODP, steady state) [kg R11 eq.]	0,0000729
Photochem. Ozone Creation Potential (POCP) [kg Ethene eq.]	0,987
Terrestrial Ecotoxicity Potential (TETP inf.) [kg DCB eq.]	5,86
primary energy demand	
Primary energy demand from ren. and non ren. resources (gross cal. value) [MJ]	49500
Primary energy demand from ren. and non ren. resources (net cal. value) [MJ]	4,56E+04
Primary energy from non renewable resources (gross cal. value) [MJ]	48500
Primary energy from non renewable resources (net cal. value) [MJ]	44500
Primary energy from renewable resources (gross cal. value) [MJ]	1030
Primary energy from renewable resources (net cal. value) [MJ]	1,02E+03

Source: *Energieinstitut an der JKU based on GaBi 8*

Full LCA results for TBA dehydration, worst case

TBA dehydration, worst case	
impact categories	
Abiotic Depletion (ADP elements) [kg Sb eq.]	0,0414
Abiotic Depletion (ADP fossil) [MJ]	5,88E+04
Acidification Potential (AP) [kg SO ₂ eq.]	15,9
Eutrophication Potential (EP) [kg Phosphate eq.]	3,16

Freshwater Aquatic Ecotoxicity Pot. (FAETP inf.) [kg DCB eq.]	887
Global Warming Potential (GWP 100 years) [kg CO ₂ eq.]	2,99E+03
Global Warming Potential (GWP 100 years), excl biogenic carbon [kg CO ₂ eq.]	2,96E+03
Human Toxicity Potential (HTP inf.) [kg DCB eq.]	1,42E+03
Marine Aquatic Ecotoxicity Pot. (MAETP inf.) [kg DCB eq.]	3,29E+06
Ozone Layer Depletion Potential (ODP, steady state) [kg R11 eq.]	0,000248
Photochem. Ozone Creation Potential (POCP) [kg Ethene eq.]	1,59
Terrestrial Ecotoxicity Potential (TETP inf.) [kg DCB eq.]	16,3
primary energy demand	
Primary energy demand from ren. and non ren. resources (gross cal. value) [MJ]	67600
Primary energy demand from ren. and non ren. resources (net cal. value) [MJ]	6,24E+04
Primary energy from non renewable resources (gross cal. value) [MJ]	65700
Primary energy from non renewable resources (net cal. value) [MJ]	60600
Primary energy from renewable resources (gross cal. value) [MJ]	1870
Primary energy from renewable resources (net cal. value) [MJ]	1,83E+03

Source: Energieinstitut an der JKU based on GaBi 8

Full LCA results for MTBE decomposition best case

MTBE decomposition, best case	
impact categories	
Abiotic Depletion (ADP elements) [kg Sb eq.]	0,0164
Abiotic Depletion (ADP fossil) [MJ]	6,55E+04
Acidification Potential (AP) [kg SO ₂ eq.]	9,44
Eutrophication Potential (EP) [kg Phosphate eq.]	1,56
Freshwater Aquatic Ecotoxicity Pot. (FAETP inf.) [kg DCB eq.]	358
Global Warming Potential (GWP 100 years) [kg CO ₂ eq.]	1,92E+03
Global Warming Potential (GWP 100 years), excl biogenic carbon [kg CO ₂ eq.]	1,89E+03
Human Toxicity Potential (HTP inf.) [kg DCB eq.]	8,18E+02
Marine Aquatic Ecotoxicity Pot. (MAETP inf.) [kg DCB eq.]	1,47E+06
Ozone Layer Depletion Potential (ODP, steady state) [kg R11 eq.]	0,000113
Photochem. Ozone Creation Potential (POCP) [kg Ethene eq.]	0,868
Terrestrial Ecotoxicity Potential (TETP inf.) [kg DCB eq.]	8,88

primary energy demand	
Primary energy demand from ren. and non ren. resources (gross cal. value) [MJ]	72900
Primary energy demand from ren. and non ren. resources (net cal. value) [MJ]	6,75E+04
Primary energy from non renewable resources (gross cal. value) [MJ]	72200
Primary energy from non renewable resources (net cal. value) [MJ]	66900
Primary energy from renewable resources (gross cal. value) [MJ]	696
Primary energy from renewable resources (net cal. value) [MJ]	6,75E+02

Source: Energieinstitut an der JKU based on GaBi 8

Full LCA results for MTBE decomposition worst case

MTBE decomposition, worst case	
impact categories	
Abiotic Depletion (ADP elements) [kg Sb eq.]	0,031
Abiotic Depletion (ADP fossil) [MJ]	7,20E+04
Acidification Potential (AP) [kg SO ₂ eq.]	14,6
Eutrophication Potential (EP) [kg Phosphate eq.]	2,73
Freshwater Aquatic Ecotoxicity Pot. (FAETP inf.) [kg DCB eq.]	756
Global Warming Potential (GWP 100 years) [kg CO ₂ eq.]	2,36E+03
Global Warming Potential (GWP 100 years), excl biogenic carbon [kg CO ₂ eq.]	2,34E+03
Human Toxicity Potential (HTP inf.) [kg DCB eq.]	1,37E+03
Marine Aquatic Ecotoxicity Pot. (MAETP inf.) [kg DCB eq.]	2,75E+06
Ozone Layer Depletion Potential (ODP, steady state) [kg R11 eq.]	0,000223
Photochem. Ozone Creation Potential (POCP) [kg Ethene eq.]	1,15
Terrestrial Ecotoxicity Potential (TETP inf.) [kg DCB eq.]	15,4
primary energy demand	
Primary energy demand from ren. and non ren. resources (gross cal. value) [MJ]	8,09E+04
Primary energy demand from ren. and non ren. resources (net cal. value) [MJ]	7,51E+04
Primary energy from non renewable resources (gross cal. value) [MJ]	7,97E+04
Primary energy from non renewable resources (net cal. value) [MJ]	7,40E+04
Primary energy from renewable resources (gross cal. value) [MJ]	1,15E+03

Primary energy from renewable resources (net cal. value) [MJ]	1,11E+03
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Source: Energieinstitut an der JKU based on GaBi 8

Full LCA results for isobutene dehydration

Isobutane dehydration	
impact categories	
Abiotic Depletion (ADP elements) [kg Sb eq.]	0,00039
Abiotic Depletion (ADP fossil) [MJ]	7,38E+04
Acidification Potential (AP) [kg SO ₂ eq.]	3,8
Eutrophication Potential (EP) [kg Phosphate eq.]	0,367
Freshwater Aquatic Ecotoxicity Pot. (FAETP inf.) [kg DCB eq.]	23,6
Global Warming Potential (GWP 100 years) [kg CO ₂ eq.]	2,51E+03
Global Warming Potential (GWP 100 years), excl biogenic carbon [kg CO ₂ eq.]	2,50E+03
Human Toxicity Potential (HTP inf.) [kg DCB eq.]	1,83E+02
Marine Aquatic Ecotoxicity Pot. (MAETP inf.) [kg DCB eq.]	8,23E+04
Ozone Layer Depletion Potential (ODP, steady state) [kg R11 eq.]	1,69E-10
Photochem. Ozone Creation Potential (POCP) [kg Ethene eq.]	2,11
Terrestrial Ecotoxicity Potential (TETP inf.) [kg DCB eq.]	1,58
primary energy demand	
Primary energy demand from ren. and non ren. resources (gross cal. value) [MJ]	80800
Primary energy demand from ren. and non ren. resources (net cal. value) [MJ]	7,49E+04
Primary energy from non renewable resources (gross cal. value) [MJ]	80100
Primary energy from non renewable resources (net cal. value) [MJ]	74200
Primary energy from renewable resources (gross cal. value) [MJ]	734
Primary energy from renewable resources (net cal. value) [MJ]	7,34E+02

Source: Energieinstitut an der JKU based on GaBi 8