Energy and GHG Reductions in the Chemical Industry via Catalytic Processes:

ANNEXES

International
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COUNCIL OF
CHEMICAL
ASSOCIATIONS

DECHEMA

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Introductory Remark

The annexes to the roadmap "Energy and GHG Reductions in the Chemical Industry via Catalytic Processes" contain supplementary material and more detailed technical information and data not included in the core roadmap in order to keep the volume of the document reasonable. All annexes are referenced in the core roadmap. Main target audience for the annexes are the scientific-technical stakeholders interested in gaining a deeper understanding in the approaches, assumptions and basic data used for the DECHEMA or IEA modelling work.

Annex 1: Data Approach and Assumptions

Development of process-specific production volumes in the chemical and petrochemical sector

Data on process and country specific production volumes expressed in kt/yr covering 2010-2030 was supplied by SRI (IHS) and CMAI. Missing data was extrapolated from existing values. Linear extrapolation was applied to cover the period beyond 2030. Country-specific data was grouped into regional data.

The existing chemical plants will during their lifetime experience constant optimization efforts (incremental improvement) but may also reach a point where they are no longer competitive and are either decommissioned or substantially retrofitted to the then state-of-the-art. Additionally, new production volume might be commissioned. The lifecycle of a chemical plant was modelled as a function of improvement, decommissioning rate and implementation rate of best practice technology.

Energy consumption and GHG emissions

Current state-of-the-art and best practice energy consumption and GHG emission values were derived by critical evaluation of publically available data sources, process-specific values supplied by SRI and licensors and verified by discussions with industrial experts. The energy intensity of a process is expressed as GJ per t of product and excludes the respective energy contents of feedstock and products unless otherwise stated[1]. For a given process, the average energy intensity of currently existing plants is expressed as specific energy consumption (SEC) and its current best practice technology (BPT). Both values are subject to incremental improvement due to ongoing optimization efforts. Energy intensity of new and retrofitted production is expressed as linear combination of SEC and BPT values.

GHG emissions are reported as CO_2 equivalents per ton of product. In this study, the CO_2-eq includes carbon dioxide, methane, and nitrous oxide. The fluorinated gases (sulphur hexafluoride, HFCs, and PFCs) are not included because they do not occur as emissions of the processes regarded here.
As for energy intensity, GHG emissions are subject to incremental improvements and best practise technologies exist, that represent the current benchmark. However, some of the chemical processes

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[1] Please note the different definitions of SEC for comparing existing processes with emerging or game changer routes. This is explained in the section "Boundary conditions for the DECHEMA model" of Annex 1.

regarded in this study co-produce a greenhouse gas in conjunction with the intended product. These emissions cannot be avoided as long as the process is based on this specific chemical reaction. The following section provides a more detailed discussion on the different types of GHG emissions and their relative impact.

Greenhouse gas emission intensity

The chemical sector is one of the most prominent industrial emitters of greenhouse gases. In contrast to the energy sector however, greenhouse gas emissions do not only occur due to the burning of fossil fuels. There are different reasons for GHG emissions which have been taken into account in the modelling. They are outlined below:

1.   Some chemical processes emit greenhouse gases by the very nature of the chemical reaction they are based on. These processes co-produce a greenhouse gas together with the intended product. These emissions cannot be avoided as long as the process is based on this specific chemical reaction. The most prominent process in this category is the production of ammonia used as a precursor for fertilizer production. The hydrogen used in the ammonia production is most efficiently generated by steam reforming of natural gas complemented with a water gas shift reaction. This process chain releases a certain stoichiometric amount of CO_2 as a co-product of the amount of H_2 produced. This stoichiometrically produced CO_2 amounts to more than half of the overall CO_2 emissions of the ammonia production. The actual amount only depends on the feedstock used for the hydrogen generation. Natural gas is the favoured feedstock with about 1 t CO_2 per t NH_3 produced, while coal based ammonia produces nearly 2 t CO_2 per t NH_3. It is worth noting that switching all coal-based ammonia production to gas-based production would have a major impact on the overall GHG balance. However, unless hydrogen is supplied by renewable carbon neutral sources, the amount of CO_2 produced by this process chain based on natural gas represents an absolute lower limit for the GHG emissions from ammonia production, independent on any improvement made in the area of energy efficiency. In case of ammonia, some of the CO_2 emitted is captured and subsequently used for the production of urea. It is eventually released into the atmosphere when used as fertilizer. However, these considerations are beyond the battery limits of the current study.

2.   Another source of GHG emissions unique to the chemical sector are GHGs caused by non-selectivity of chemical reactions. Most prominently, non-selectivity occurs in partial oxidation processes, which are notoriously difficult to control to an extend that avoids further oxidation of the intended product. Examples are the production of CO_2 in ethylene oxide plants or HCN as an unintended by-product in the production of acrylonitrile. The extent of non-selectivity strongly depends strongly on specific process conditions. Catalysis steers the chemical reaction towards a specific outcome and generally allows for less drastic and easier controllable process conditions. It has therefore a significant impact on the amount of GHGs emitted by processes suffering from competing reactions. GHG-emissions caused by non-selectivity are also independent to any improvements in the area of energy efficiency. However, they are subject to improvements in the area of process design and catalysis. While GHG emissions based on non-selectivity might be reduced, they might not always be completely avoidable. Other examples caused by imperfect

reaction control are: N_2O emissions by nitric acid plants or by adipic acid plants (unlike CO_2, N_2O can be decomposed catalytically to nitrogen and oxygen).

Both GHG produced by the chemical reaction and by non-selectivity are localized and relatively pure streams of the respective gas. In case of CO_2 these processes represent an opportunity for CCU or CCS.

3.   As in other sectors, GHGs are emitted in the chemical sector as function of the energy requirements for heat and power. In both cases, fossil fuels are generally burned, sometimes within the chemical reactor. These emissions can be reduced by minimizing the energy requirements for a given process. Chemical reactions are subject to absolute thermodynamic energy limitations that may cause a minimum energy required for a given process. This minimum energy is beyond optimization and energy efficiency efforts. It is the minimum energetic price to be paid in order to obtain a certain product. That said the chemical industry has strongly been optimizing its energy use. Large potentials are accessed by efficient heat integration with exchange of heat between several processes at a given site. Consideration of integrated sites is beyond the scope of this study; however it significantly reduces the overall energy requirement and accordingly GHG emissions of the chemical sector compared to the single process perspective assumed in this roadmap.

4.   Finally, the chemical sector is also the producer of some of the most potent GHGs, notably refrigerants. These GHG as chemical products are outside the battery limit of this study since they are not emitted by the chemical industry. Generally, they form part of a product sold to the consumer (e.g. a fridge) and are released at the end of the lifetime if proper recycling procedures are not adhered to. Strictly speaking, urea also falls into this category, since its CO_2 is released when used as fertilizer in the agricultural sector. These effects are not taken into account in this study.
Figure 1 visualizes the relative impact of the different sources of GHG emissions (unavoidable stoichiometric formation, non-selectivity and energy/fuels).

Figure 1: Contribution of the different sources of GHG emissions to the overall emission level of the chemical industry
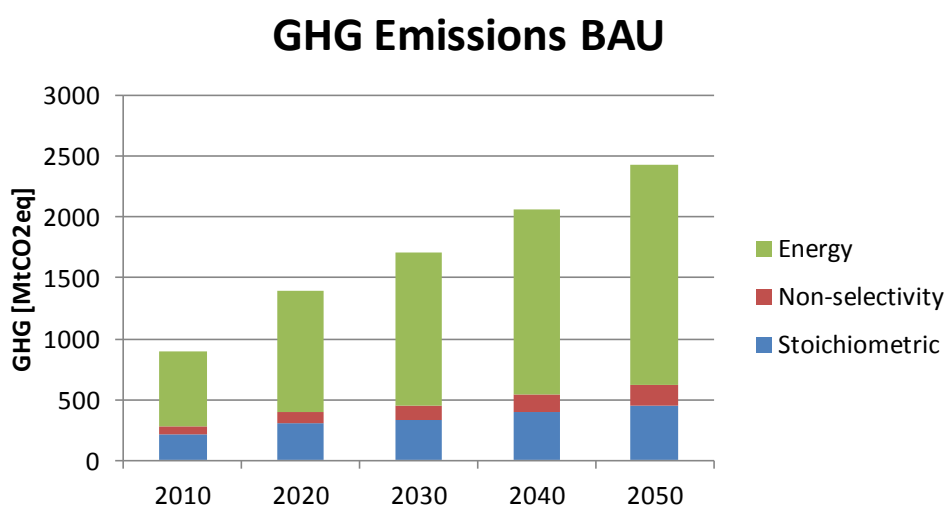
Boundary conditions for the DECHEMA model

The **process system boundaries** for energy consumption and GHG emissions in this roadmap strictly follow a fence to fence approach from precursor feedstock to product unless stated otherwise. For instance, ethylene oxide (EO) production starts from ethylene as feedstock, the ethylene production is not included in the EO process. This way double counting of energy consumptions is avoided.

The **energy consumption of a process** reported as **Specific Energy Consumption (SEC)** includes direct energy use (fuel, steam) and indirect energy use (electricity) for the process. Unless stated otherwise, the energy equivalent of feedstock transformed to the target product is not included in the SEC. Hence the SEC is defined as energy required in the process to transform the feedstock to the product without taking the energy content of the feed into account. This energy difference contains the thermodynamic difference between feedstock and product as well as any energy required for downstream separation and purification or any energy requirements imposed by the imperfections of the overall process (which is the main target of the model). The implicit assumption for this SEC definition is, that the main process technology does not change dramatically, especially with respect to feedstock applied. A given processes which use gas as a feedstock might gain importance relative to one that use naphtha for example; however a given individual plant built for a specific process is not expected to undergo a change to a different feedstock. This SEC definition therefore applies to the numbers given for the current status of the 18 products investigated, as well as for all calculations referring to incremental improvement, conservative and optimistic BPT scenarios relative to the BAU scenario.

It is important to state that the situation changes, if an existing process is replaced by an alternative process scheme. The notion of improvement of existing technologies with "constant" feed is no longer valid for the scenarios dealing with emerging technologies and gamechangers (hydrogen and biomass). New synthetic pathways add a perturbation into the existing value chains of the chemical industry by requiring e.g. the production of a new feedstock compared to the existing reference process. The aim of the scenarios was to quantify the energy and GHG differences by essentially replacing the existing process with a new one, including its specific different feed preparation. As a consequence, a different definition of SEC was used for comparing current processes with emerging technologies and game changer processes and feedstock production has been included in the SEC to allow for a fair comparison of the energy consumption of such alternative process routes. The specific implications are explained in the section on Emerging Technologies in Annex 4 as well as in Annex 5 and Annex 6.

The SECs for different processes originate from different sources. SRI (IHS) provided data from their Process Economic Reports, based on representative flow sheets and typical plant designs and equipment. The SECs were then confirmed by literature sources, where available. Another source were the responses to the questionnaires on the top 40 energy consuming catalytically relevant industrial processes sent to chemical manufacturers. 92 reports on individual processes were received from 28 companies; 73 of those reports included energy data for defined processes. The reported SECs usually reflected the specific circumstances (feedstocks, regional distribution of production sites etc.) of plants operated by the process owners providing the report. The reports were therefore used for validation only, unless several reports for the same process were available. Finally estimates on average energy consumptions and BPT levels for various processes have been provided by licensors.

GHG emissions include direct process emissions as CO_2 equivalents, direct utilities emissions (fuel) and indirect emissions from the production of the amount of electricity required for the process (MWh/t -> tCO_2/t). The latter is based on regional energy mix used for electricity generation (IEA). Emissions were again provided by SRI, chemical manufacturers and licensors, and supported by available publications, such as Weiss et. al. (Weiss, 2008).

For **multi-product processes**, the ISO 90040 weight allocation to high value chemicals (HVC) has been used to avoid double counting of energy use or the allocation of the total energy consumption to one product only. For example, it would be biased to allocate all energy consumption of ethylene production from Naphtha Cracking to ethylene, as Naphtha cracking also results in a number of other products. Typically, Naptha cracking results in 29-34 wt.% ethylene, 13-16 wt.% propylene, 4-5 wt.% butadiene, 10-16% aromatics and C4+. Per ton ethylene 0.887 tons of other HVC are produced. Accordingly, the SEC for Naphtha cracking is expressed as GJ/tHVC and GHG emissions as tCO_2-eq /tHVC.

Table 1. Model Assumptions DECHEMA and IEA

Unit	DECHEMA			IEA		
	Sources	Assumptions	Comments	Sources	Assumptions	Comments
Production (t) [t]	SRI (until 2020) CMIA (2020-2030) IFA data (until 2030) linear projection from 2030 to 2050.	Missing data of individual processes adjusted for by linear projections.	SRI-/ CMIA-data is country specific and summarized into regions. IFA data is regional.	SRI (for 2009 and 2010) for HVC and methanol; USGS (2009 and 2010) for ammonia Supplemented with IEA Oil Industry and Market data (regional disaggregation).	Missing data for some regions are estimated based on calibration procedure (so that sum of region is consistent with the source of data) and information on the web.	The production data are presented for 36 countries/regions.
Development of Production (t) [t]	SRI and licensors for lifetime of plants.	Exponential decay of existing production volume defined by lifetime. Half of decayed production is "refurbished", the other half replaced by "new" units, each expressed as linear combinations of SEC(t) and BPT(t). Additional production is considered to be "new".	Lifetime (process-specific) : 20-30 years. "Refurbished"(conservative)=30% BPT(t)+70%SEC(t) "New" (conservative) =50%BPT(t)+50%SEC(t) "Refurbished"(optimistic) and "New"(optimistic)=100%BPT(t)	Based on development of historical production/income (GDP/capita) and production to GDP elasticity. Short term development at the regional level adjusted to account for announced additional capacity	Production "age" is assumed to be equally distributed through time and is "aged" based on assumed lifespan. 25% of the production is retired after lifespan and replaced with new units; 75% is refurbished. Additional production is considered to be "new".	BTX and methanol = 60 years; ammonia = 50 years (in a 2DS, lifespan is reduced by 10 years). "Refurbished" about 20% better than the average ; with BPT as the lower constraint "New" is 5% to 10% better than the average in the baseline (BPT as the lower constraint) and close to BPT in the 2DS; "retired" about 20% to 5% less efficient than the average (from 2010 to 2050; declining)
SEC(t) [GJ/t] (increm. improve-ment)	SEC(0) based on SRI. Value x taken from historical data (questionnaire) or average of existing	Development as SEC(t)=SEC(0)*(1-x)^t	Specific Energy Consumption (process-specific) For (conservative) the historical data was used	Historical data from various published sources; IEA energy balance.	Development is a function of status of production (in place, new, retrofitted, retired) and the associated SEC for each time period (as	"Refurbished" about 20% better than the average ; with BPT as the lower constraint "New" is 5% to 10% better than the average in the

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	improvements.		(overall production weighted average: 0.55%), while for (optimistic) the improvement rate was doubled.		indicated above) In a baseline scenario, the SEC of the new production is between the "average" SEC and BPT. For 2DS, all new production comes in at BPT	baseline (BPT as the lower constraint) and close to BPT in the 2DS "retired" about 20% to 5% less efficient than the average (from 2010 to 2050; declining)
BPT(t) [GJ/t] (BPT deploy-ment)	Based on information from licensors or set to be 20% better than SEC.	Improvement as for SEC(t).	Best Practice Technology (process-specific)	Based on information from IEA indicators work.	Improvement of about 10% to 2050.	Best Practice Technology (process-specific)
Energy (t) [GJ]				IEA energy balance for total chemicals and petrochemicals sector in the base year. Energy consumption for HVC, ammonia and methanol sub category calculated from production and SEC values.	Calculation based on production and SEC development	Product specific, weighted sum over all processes contributing to a given product.
Energy Intensity(t) [GJ/t]	Product specific amount of energy [GJ] needed to produce 1 ton of product.		Product specific, weighted sum over all processes contributing to a given product.	Product specific amount of energy [GJ] needed to produce 1 ton of product.		Product specific, weighted sum over all processes contributing to a given product.
CO_2 (t) [CO_2]				IEA CO_2 emission factors for combustion	Energy consumption by fuel times associated CO_2 emission factor	Total emission is the sum of fuel-specific emission
GHG	3 different sources	GHG Intensity caused by	Product specific,			

Intensity (t) [CO_2-eq/t]	(process-specific): Chemical Reaction (Stoichiometry) Overoxidation (industrial sources) Energy Intensity (SRI, adjusted for IEA regional factors)	chemical reaction can't be improved. Overoxidation is subject to improvement (historical rate) Energy Intensity is defined by portfolio of processes, age and production.				
CO_2 Intensity (t) [CO_2/t]				calculated	Calculation based on production and SEC development	Product specific, weighted sum over all processes contributing to a given product.
Bio	Ren, T., Petrochemicals from Oil, Natural Gas, Coal and Biomass: Energy Use, Economics and Innovation, Utrecht University, 2009	Dried biomass used as feed, CO_2-neutral, same SEC as coal. Double improvement rate assumed for bio-based processes. SEC includes feedstock production to compare biomass with fossil routes	Only applied for NH_3 (coal), MeOH (coal), Ethylene (EtOH), BTX (coal). Slow introduction of bioprocesses (10% for refurbished, 20% new production). Overall max. biomass per process: 15% (2050)			
Hydrogen	Licensors	Syngas-based processes only. SEC includes electrolysis and compression. Double improvement rate assumed for hydrogen-based processes.	NH_3, MeOH (not natural gas)			
Feedstock Change	As above	Substituting Coal for Gas				

Annex 2: Process routes for propylene oxide

Table 2: Process routes for propylene oxide

Process	Feedstock	By-product	Licensors or Process Owners
Hydrochlorination: chlorohydrin process	Propylene, chlorine	Calcium chloride	Various
Hydroperoxidation	Isobutane	t-butyl alcohol	Lyondell, Huntsman
	Ethylbenzene	Styrene	Lyondell, Shell, Repsol
	Cumene		Sumitomo
HPPO	Propylene and hydrogen peroxide	Only water	BASF/Dow, Evonik/Uhde

Annex 3: Theoretical potential

Figure 2 depicts the cumulated theoretical energy loss for 20 processes (calculated based on 2010 production and reflect the difference of BPT energy consumption and the theoretical minimum). This difference includes an "excess energy use" which is lost as waste heat and "losses due to non-selectivity" corresponding to the formation of undesired by-products. The theoretical numbers **do not** necessarily reflect real improvement potentials as there may be large technical hurdles, they rather merely indicate how far processes are from the optimum. For many of the large volume processes the question will be whether relatively small improvements can make a big impact considering the volume of chemicals made, while for smaller processes whether larger improvements vs. theoretical will add up significant impacts. Step change to a new process path could have a potentially lower theoretical minimum, but such improvements require large R&D efforts over many years and typically require significant investment.

Figure 2: Cumulated theoretical total energy loss for major chemical processes based on 2010 production volumes
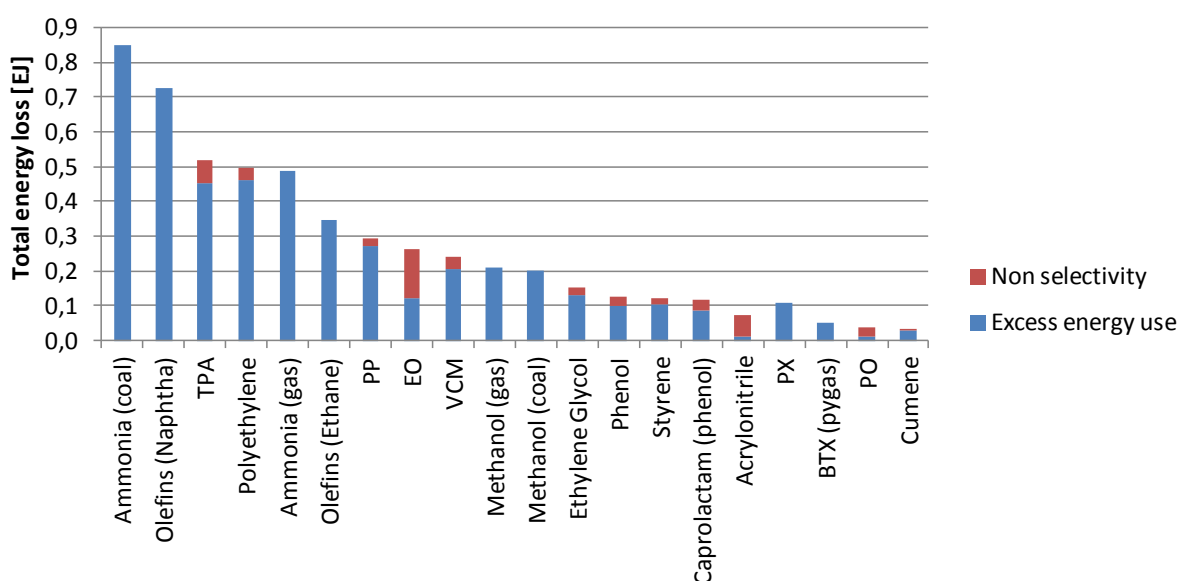
(Neelis, 2007) et al. have investigated the theoretical energy saving potential of various petrochemical processes by analysing the energy inputs into the respective process and comparing this cumulated process energy use with the theoretical energy use given by the heat of the stoichiometric reaction. The difference represents the "excess energy use" which is lost as waste heat in their model. A second type of loss is referred to as "losses due to non-selectivity", i.e. the conversion of raw material not into the desired product but into low-value by-products or CO_2 (in case of total oxidation). The very simple model of Neelis adopted here only includes the reactor section of the process, which results in even negative theoretical energy consumption for exothermic processes (net energy providing reactions). Product separation and purification steps are disregarded, but these downstream operations always consume large amounts of energy. In addition, the model disregards the re-use of waste heat, which is common practise in the usually highly heat-integrated large petrochemical plants. Nevertheless this analysis provides general directions for potential energy savings. Losses due to non-selectivity are generally observed for oxidation processes (acrylonitrile, ethylene oxide, propylene oxide, terephthalic acid). Non-selectivity losses are a direct measure of catalyst selectivity and can be overcome by more selective catalysts. For example, according to (Neelis, 2007) 18 mass% of the ethylene fed into the EO production is still burned rather than converted to EO, despite long term catalyst development work. This example shows that these processes still allow for substantial improvements enabled by catalysis. For the excess energy use the impact of catalysis is difficult to determine[2], other process improvements and improved heat integration can dominate.

Table 3 shows the current SECs of average and best practise plants compared to the theoretical minimum for a number of selected processes

Table 3: Specific energy consumption of average plants, best practise technology plants and theoretical minimum

Process	Avrg. SEC [GJ/t]	BPT SEC [GJ/t]	Theor. Minimum [GJ/t]
Ammonia (from coal, partial oxidation)	27.92	22.00	8.1
Ammonia (from natural gas, steam ref.)	15.38	7.2-9.0	5.8
Ethylene (from naphtha)	16.5*	12.0	8 (5*)
Propylene (from naphtha)	16.5*	12.0	5*
MeOH (from methane via syngas)	13.9	9.0-10.0	5.12
Acrylonitrile (from propylene)	15.5	12.9	-10.3

* per t high value chemicals (HVC)

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[2] Effects are even contradictory: exergy-wise an exothermic reaction should be operated at high temperatures, whereas conversion is higher at low temperatures, and vice-versa for endothermic reactions.

Annex 4: Improvement options

Processes & Products

The chemical industry makes converts a number of raw materials (feedstocks) using a number of major processes into thousands of products that are used by a multitude of industries serving consumers. The distinction between process and product can be confusing. Catalysis can play a role across this entire value chain, but it has the largest direct influence in making the processes which do the primary conversion. The figure below illustrates the feedstocks, processes, and primary products (which can be further converted into finished consumer products).

Figure 3. Illustration of chemical industry conversion of feedstocks to products.
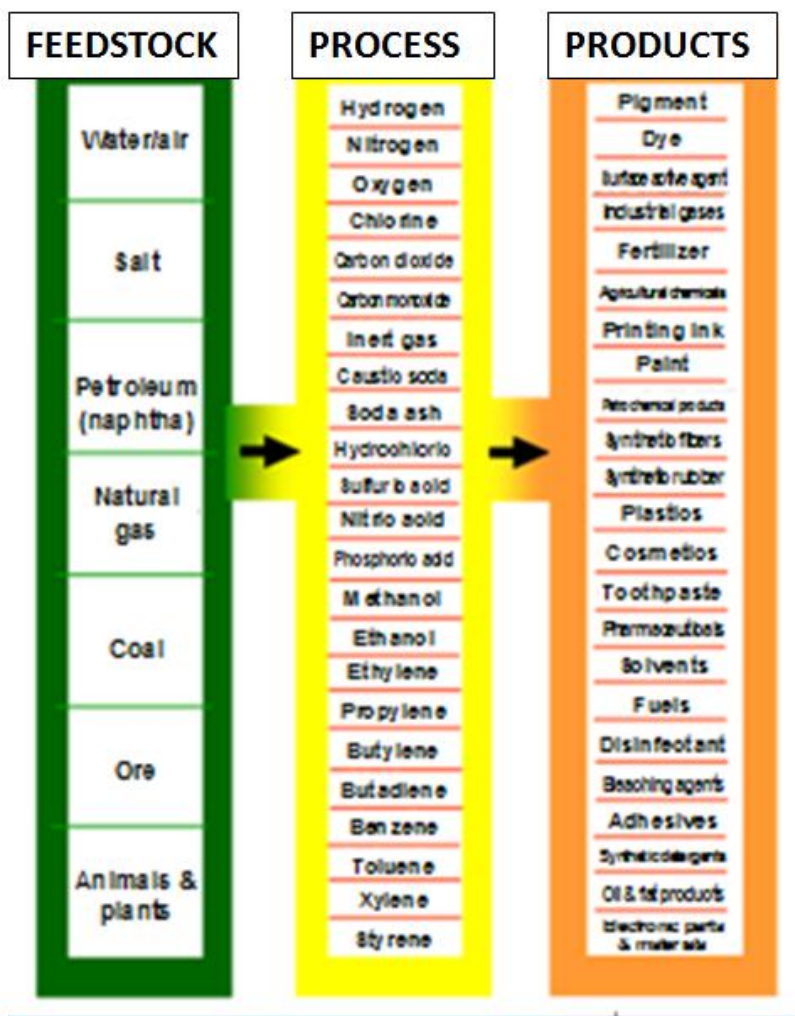
Incremental improvement

Higher catalyst selectivity means that more of the target product and less by-products are formed. For example, the selectivity of ethylene oxide catalysts increased from 70% in the 1960s, 80% in 2000 (Lange, 2001) to close to 90% today[3]. The ultimate goal for all chemical processes is to form the target product at 100% selectivity, but even if this is not achieved, higher selectivity means less energy demand for separation/purification operations, less recycle streams , less GHG and other process emissions, reduced waste treatment and hence improved overall energy efficiency and emission levels of the whole process. In most cases a new catalyst is implemented together with other process improvements and catalyst and reactor form an entity. It is therefore more meaningful to discuss improvements of catalytic processes rather than catalyst improvements only, as the isolated impact of a catalyst is difficult or even impossible to quantify. Hence, incremental improvements in this study include the combined impact of catalyst and other process technology advances.

BPT deployment

The following example shall illustrate what is meant by BPT. The average natural gas based ammonia plant performs at 15.4 GJ/t NH_3 (feedstock excluded). The 2009 benchmark report of the International Fertilizer Association (Association, December 2009), quantifies the top quartile of natural gas based ammonia plants in the year 2008 in the range of 28 to 33 GJ/t NH_3.Excluding feedstock the corresponding SEC for BPT ammonia plants is in the range of 7.5 to 12 GJ/t NH_3. Corresponding CO_2 emissions for BPT level plants are at 1.5 to 1.6 t/t NH_3. A BPT type ammonia plant is the SAFCO IV plant in Al Jubail, Saudi Arabia, based on the "Uhde Dual Pressure Process" with a single-train capacity of 3300 t. The SEC of this type of plants is in the range of 7.5 to 10 GJ/ t NH_3 depending on local conditions. This range already shows that it is difficult to attribute one fixed SEC for a given plant type. Moreover, a given process route can have various process configurations.

Ammonia synthesis from natural gas via syngas typically involves seven different catalytic reaction steps (eight including gas purification). It is therefore obvious that the BPT is not represented by a single type of technology, but by a range of process configurations belonging to the top 10% of plants performing at highest energy efficiency. As the highest efficiency is only achievable under optimal local circumstances and for the largest, highly energy-integrated installations, numbers on the BPT option in this report are based on the medium value of the SEC range, in the case of ammonia 11 GJ/t NH_3.

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[3] Several recent patents (e.g. US 6,368,998;WO 2006/102189; US 6,717,001; WO 2004/078736; WO 2007/123932; US 6,511,938; WO 2005/039757) report EO an initial selectivity in the range from 82 to 90%. Shell commercial catalyst S-882 (which contains rhenium promoter) is reported to have a theoretical initial EO selectivity of 93% (US 6,717,001).

Assumptions for BPT deployment in the DECHEMA model

- It is assumed that new plants are predominately erected using the best practice technology, i.e. having a SEC similar to the most energy efficient plant today. In the **BPT optimistic** scenario **all** new built plants are assumed to have an SEC at BPT level; for the **BPT conservative** scenario new plants are assumed to have an SEC, which corresponds to 50 % to the average SEC level and to 50 % to the BPT level.

- Both, the average SEC and the BPT improve over time. It is assumed that existing plants are steadily improved and that the best performing plants are also subject to incremental improvements. For both cases, the incremental improvement factors have been applied.

- At some point in time, plants reach their end of lifetime and are decommissioned. As the real age distribution and lifetime of production plants worldwide is unknown, a lifetime of 20 years (30 years for highly capital intensive plants such as crackers and refinery plants) has been assumed. For installed production capacities, an exponential decay has been assumed within the plant lifetime

- Half of the decommissioned plants get retrofitted while the other half gets replaced by new plants. For old capacities being replaced the same assumptions have been made as for new capacities (see above). Retrofitted plants have energy values assigned to them as linear combinations of current SEC and BPT values. In the **BPT optimistic** scenario retrofitted plants are assumed to have an SEC at BPT level, for the **BPT conservative** scenario retrofitted plants combine 70% average SEC with 30% BPT.

Emerging Technologies

Olefin production via methanol

The "methanol-to-olefin process" (MTO)[4] circumvents steam cracking of naphtha or ethane and allows producing olefins from gas or coal instead of oil. For a meaningful comparison of the SEC of this route with conventional naphtha steam cracking, it is necessary to include the production of the required methanol as feedstock for the MTO process in the battery limit for the olefin production[5]. The average SEC of naphtha steam cracking is in the range of 14 to 17 GJ/t HVC (Ren, 2009). For MTO technologies, the SEC is in the range of 5 to 8 GJ/t HVC (Ren, 2009). The methanol production for providing the feedstock of the MTO process requires additional 23 GJ/t HVC. Hence, methanol production clearly dominates the energy consumption for the gas based route via methanol and MTO, and nearly 200% of the energy for steam cracking is required for this process. This is shown in Figure 4, in which the entire process chain is depicted. More efficient methanol synthesis and more selective catalysts for the MTO process will improve the SEC of the entire process chain, but it is questionable if the SEC of naphtha cracking will be reached any time soon. However, if methanol is produced with renewable hydrogen, as described below, substantial GHG savings can be achieved.

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[4] The MTO process includes the dehydration of methanol to first dimethylether and then further via shape selective transformation to olefins using ZSM or SAPO catalysts (see for example (Yuen et al. 1994). Usually the process is combined with an olefin cracking process of higher olefins produced.
[5] See discussion of SEC definition in Annex 1, section on Boundary conditions for the DECHEMA model.

Figure 4: Comparison of olefin production via MTO vs. naphtha steam cracking; the entire process chain including feedstock production (methanol for MTO) and olefin production (MTO or cracking) are considered.
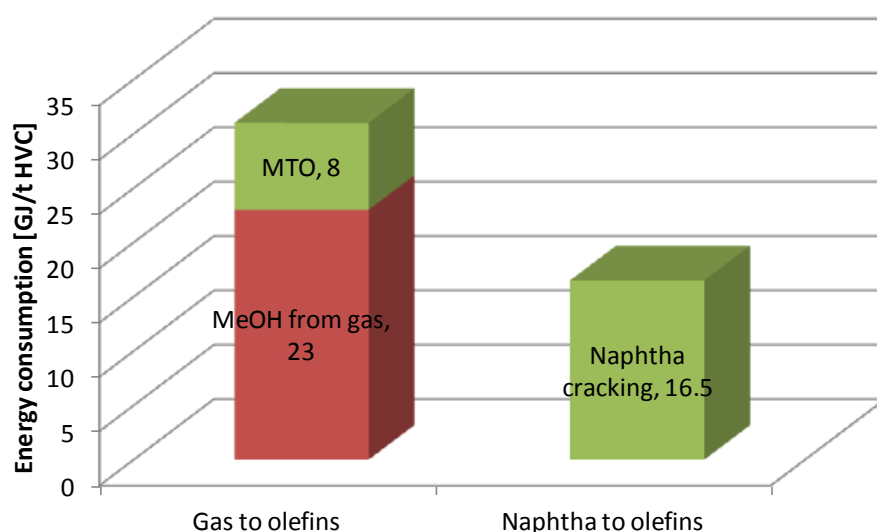
Key point: Naphtha cracking still provides the most energetically efficient way to produce olefins. A comparison with the MTO process needs to consider the energy required to produce methanol.

Gamechangers

Table 4 shows some examples for processes, which are subject to intense fundamental research activities. Naturally, this type of gamechangers requires long term developments with a high level of uncertainty. No attempt has been made to quantify the potential impact of these processes as both commercial entry and energy consumption of a real process based on these routes are unclear.

Table 4: Novel process routes for large volume chemicals

Target product	Feedstock	Process route
Aromatics	Lignin	Catalytic hydrocracking or catalytic pyrolysis over zeolite (ZSM-5) catalyst
Aromatics	Ethanol	Conversion over a zeolite catalyst to aromatics
Ethylene	Methane	Alkane activation and carbon linking reactions
Methanol	Methane	Alkane activation and partial oxidation to methanol Direct methane to methanol
Methanol	CO_2	Hydrogenation of CO_2
Propylene oxide	Propylene	Direct epoxidation with oxygen

SECs, GHG emissions and improvement factors

Table 5: Average specific energy consumption, BPT specific energy consumption, GHG emissions of processes and improvement factors[6]; the corresponding 18 large volume products are highlighted in bold[7].

Process	Average SEC [GJ/t]	BPT SEC [GJ/t]	Avg. GHG [tCO_2/t]	Incremental improvment factor	Potential for BPT deployment
Acrylonitrile from propylene	15.50	12.90	2.391	1.26%	17%
Ammonia from coal (partial oxidation)	27.92	22.00	4.910	0.55%	21%
Ammonia from natural gas (steam reforming)	15.38	7.2-9.0	2.518	0.55%	28%
Benzene from catalytic reformate	4.12	2.20	0.280	0.50%	47%
Benzene from coal tar	4.12	2.43	0.138	0.50%	41%
Benzene from coke oven light oil	4.12	2.43	0.138	0.50%	41%
Benzene from mixed xylenes via toluene disproportionation (MSTDP)	5.57	3.10	0.550	0.50%	44%
Benzene from mixed xylenes via toluene disproportionation (MTPX)	5.57	3.10	0.550	0.50%	44%
Benzene from propane/butanes (Cyclar)	4.12	2.20	0.550	0.50%	47%
Benzene from pyrolysis gasoline	5.50	2.20	0.000	0.50%	60%
Benzene from toluene dealkylation	2.96	2.20	0.550	0.50%	26%
Benzene from toluene disproportionation	5.57	2.20	0.303	0.50%	61%
Benzene from toluene/xylenes	4.12	2.20	0.550	0.50%	47%
Benzene from unspecified raw materials	4.12	2.20	0.550	0.50%	47%
Caprolactam from cyclohexane (via cyclohexanone)	17.94	5.98	6.513	2.80%	67%
Caprolactam from cyclohexanone (phenol or cyclohexane-based)	8.70	1.00	0.789	2.80%	89%
Caprolactam from phenol (via cyclohexanone)	18.28	5.98	0.789	2.80%	67%

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[6] References: SEC and GHG are based on SRI data, literature and licensor information, incremental improvement factors are based on the chemical manufacturer's survey.
[7] In fact 20 products are listed here, but benzene, toluene and mixed xylenes are grouped as one product (BTX) in the figures of the core document.

Caprolactam from toluene	6.93	2.31	0.679	2.80%	67%
Cumene from propylene and benzene	3.80	2.07	0.119	0.50%	46%
Ethylene from butane	12.47	9.52	0.764	0.22%	24%
Ethylene from condensate	12.37	9.45	0.759	0.22%	24%
Ethylene from deep catalytic cracking of VGO	8.47	6.08	0.603	0.22%	28%
Ethylene from ethane	16.00	12.00	0.964	0.22%	25%
Ethylene from ethane/propane	16.00	12.19	0.694	0.22%	24%
Ethylene from ethyl alcohol	0.75	0.57	0.377	0.22%	24%
Ethylene from gas oil	12.02	8.60	0.240	0.22%	28%
Ethylene from LPG (propane/butane)	12.79	9.77	0.799	0.22%	24%
Ethylene from mixed feedstocks	12.79	9.77	0.799	0.22%	24%
Ethylene from naphtha	16.50*	12.00	0.700	0.22%	33%
Ethylene from naphtha with BZ	16.50*	12.00	0.700	0.22%	33%
Ethylene from propane	16.00*	9.00	0.799	0.22%	44%
Ethylene from refinery off-gases	12.79	9.77	0.799	0.22%	24%
Ethylene from selected gas streams from coal-to-oil	13.16	12.00	0.964	0.22%	9%
Ethylene from Superflex technology	12.56*	7.33	0.783	0.22%	42%
Ethylene Glycol from ethylene oxide (hydration)	5.94	4.95	0.763	1.58%	17%
Ethylene Oxide from ethylene (direct oxidation)	10.00	8.33	1.159	0.70%	17%
HD**PE** Gas Phase	2.25	1.87	0.272	0.58%	17%
HDPE Slurry	3.06	2.55	0.285	0.58%	17%
HDPE Solution	3.67	3.06	0.366	0.58%	17%
LDPE Autoclave	4.15	3.46	0.585	0.58%	17%
LDPE Tubular	5.23	4.36	0.601	0.58%	17%
LLDPE Autoclave	3.77	3.14	0.385	0.58%	17%
LLDPE Gas Phase	3.78	3.15	0.385	0.58%	17%
LLDPE Slurry	2.95	2.23	0.298	0.58%	24%
LLDPE Solution	2.67	2.46	0.209	0.58%	8%
LLDPE Tubular	2.95	2.23	0.298	0.58%	24%
LLDPE Unidentified	2.95	2.23	0.298	0.58%	24%
Methanol from coal-derived synthesis gas	24.00	20.10	2.830	0.40%	16%
Methanol from coke oven off-gases	24.00	20.10	2.830	0.40%	16%
Methanol from heavy oil-derived synthesis gas	16.50	15.10	1.602	0.40%	8%
Methanol from LPG-derived	13.90	9.0-10.0	0.520	0.40%	27%

synthesis gas					
Methanol from methane via synthesis gas	13.90	9.00	0.520	0.40%	35%
Methanol from naphtha-derived synthesis gas	11.00	10.10	1.061	0.40%	8%
Methanol from unspecified raw materials	11.00	10.10	1.487	0.40%	8%
Methanol recovered from DMT-based PET production	11.00	10.10	1.487	0.00%	8%
Mixed Xylene from catalytic reformate	6.09	2.20	0.280	0.50%	64%
Mixed Xylene from coal tar	5.57	2.43	0.550	0.50%	56%
Mixed Xylene from coke oven light oil	5.57	2.43	0.550	0.50%	56%
Mixed Xylene from mixed xylenes via toluene disproportionation (MSTDP)	5.57	3.10	0.550	0.50%	44%
Mixed Xylene from mixed xylenes via toluene disproportionation (MTPX)	5.57	3.10	0.550	0.50%	44%
Mixed Xylene from propane/butanes (Cyclar)	5.57	3.10	0.550	0.50%	44%
Mixed Xylene from pyrolysis gasoline	5.50	2.20	0.280	0.50%	60%
Mixed Xylene from toluene disproportionation	5.57	3.10	0.550	0.50%	44%
Phenol from benzene via benzenesulfonic acid	13.62	11.35	0.884	0.50%	17%
Phenol from cumene	13.62	11.35	0.884	0.50%	17%
Phenol from natural	13.62	11.35	0.884	0.50%	17%
Phenol from tar acids	13.62	11.35	0.884	0.50%	17%
Phenol from toluene (via benzoic acid)	13.62	11.35	0.884	0.50%	17%
Phenol from unspecified raw materials	13.62	11.35	0.884	0.50%	17%
Polypropylene from propylene (PP bulk)	3.32	2.27	0.400	1.15%	32%
Polypropylene from propylene (PP gas phase)	2.40	2.27	0.287	1.15%	5%
Polypropylene from propylene (PP other)	2.40	2.27	0.287	1.15%	5%
Polypropylene from propylene (PP slurry)	3.32	2.27	0.400	1.15%	32%
Propylene, ethylene coproduct-	16.50*	12.00	0.700	0.22%	33%

chemical grade					
Propylene, ethylene coproduct-polymer grade	16.50*	12.00	0.700	0.22%	33%
Propylene from deep catalytic cracking of VGO	8.47	7.33	0.869	0.22%	14%
Propylene from metathesis of ethylene and butylenes	0.39	0.33	0.374	0.22%	16%
Propylene from selected gas streams from coal-to-oil--polymer grade	11.59	7.33	0.783	0.22%	37%
Propylene from Superflex technology	12.56*	7.33	0.783	0.22%	42%
Propylene, propane dehydrogenation-polymer grade	13.48	11.24	1.231	0.22%	17%
Propylene, refinery byproduct-chemical grade	8.71	7.00	0.300	0.22%	20%
Propylene, refinery byproduct-polymer grade	8.71	7.00	0.491	0.22%	20%
Propylene, refinery byproduct-refinery grade	8.71	7.00	0.491	0.22%	20%
Propylene Oxide from cumene and propylene (hydroperoxidation)	36.26	30.2	3.523	0.50%	17%
Propylene Oxide from propylene (chlorohydrin process)	31.74	25.16	1.794	0.50%	21%
Propylene Oxide from propylene (unknown process)	31.74	25.16	1.794	0.50%	21%
Propylene Oxide from propylene and hydrogen peroxide	28.6	23.98	2.009	0.50%	17%
Propylene Oxide, peroxidation of propylene and ethylbenzene	16.79	14.00	2.176	0.50%	17%
Propylene Oxide, peroxidation of propylene and isobutene	6.88	5.73	1.278	0.50%	17%
p-Xylene from mixed xylenes	8.59	3.87	0.709	0.57%	55%
p-Xylene from mixed xylenes via toluene disproportionation (MSTDP)	22.90	17.78	1.206	0.57%	22%
p-Xylene from mixed xylenes via toluene disproportionation (MTPX)	31.77	24.24	1.638	0.57%	24%
Styrene from ethylbenzene	8.34	3.76	0.475	0.33%	55%

(catalytic dehydrogenation)					
Styrene from pyrolysis gasoline	8.34	3.76	0.475	0.33%	55%
Styrene peroxidation of propylene and ethylbenzene	16.79	14.00	2.192	0.33%	17%
Terephthalic Acid (TPA) from p-xylene	7.27	5.68	0.875	1.40%	22%
Toluene from catalytic reformate	2.43	2.20	0.280	0.50%	9%
Toluene from coal tar	2.43	2.20	0.280	0.50%	9%
Toluene from coke-oven light oil	2.43	2.20	0.280	0.50%	9%
Toluene from propane/butanes (Cyclar)	5.50	3.10	0.550	0.50%	44%
Toluene from pyrolysis gasoline	5.50	2.20	0.550	0.50%	60%
Toluene from unspecified raw materials	5.50	2.20	0.550	0.50%	60%
Vinyl Chloride Monomer (VCM) from ethylene and ethylene dichloride	5.75	4.79	0.445	0.59%	17%
Vinyl Chloride Monomer (VCM) from ethylene dichloride (pyrolysis)	7.53	6.27	0.493	0.59%	17%

*per t HVC (see discussion on energy allocation for multi-product processes in Annex 1)

Annex 5: Hydrogen option

For the hydrogen based processes described under the hydrogen option, the energy burden for the production of hydrogen is included in the SEC of the process. This is a deviation from the earlier SEC definition, in which the energy content of feedstocks is excluded[8].

Table 6: Calculations for the energy consumption of hydrogen and subsequent MeOH and ammonia production

Process step	kWh/Nm^3	GJ/Nm^3	kg H_2 or N_2 /Nm^3	GJ/t	mol H_2/Nm^3	kWh/mol	kWh/t	
Water electrolysis	4.7	0.017	0.08987	188.27	44.64	0.105	52225.56	
ASU	1.0	0.004	1.17	3.08	**Energy Consumption GJ/t prod.**			
H_2 based processes	mol H_2/mol prod.	mol prod./ kg	mol H_2 /kg prod.	t H_2/t prod.	Hydrogen production	Hydrogen compression	ASU	SEC H_2	Total SEC hydrogen based
Ammonia	1.5	58.72	88.08	0.178	33.43	2.137	0.41	1.35	37.33
Methanol from CO_2	3.0	31.21	93.63	0.189	35.54	1.520	0	1.50	38.56
Methanol from C[9]	2.0	31.21	62.42	0.126	23.69	0.507	0	1.50	25.70

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[8] See discussion of SEC definition in Annex 1, section on Boundary conditions for the DECHEMA model.
[9] The coal energy content is not included in the SEC here, as it has also not been included in the standard coal partial oxidation route.

Table 7: Industrial CO_2 sources that can be utilized for chemical CO_2 utilization

CO_2 source	Available amount [Mill. t]	CO_2 concentration
Oil refineries	850	3-13%
Natural gas sweetening	20	depending on NG
Ammonia synthesis	155	~ 100%
Ethylene and other petrochemical processes	150	<5%
Ethylene oxide	10	~ 100%
Cement production	1000	15-33 vol.%
Iron & steel production	850	14-27 vol.%
Coal fired power plants	>9000	3-4 vol.% 12-14 vol.% for IGCC

Energy associated with hydrogen production

Commercial electrolysers (NREL, 2004) require about 53 kWh/kg hydrogen (or 4.7 kWh/Nm^3) at a capacity of up to 380 t/year and unit. This corresponds to 188 GJ/t hydrogen. In relation to ammonia production, 33.4 GJ per tonne of ammonia are required for the hydrogen supply, as 0.18 t hydrogen are required per tonne of ammonia. Likewise, for methanol production with coal as carbon source, 23.7 GJ/t methanol and for methanol production with CO_2 as carbon source 35.5 GJ/t methanol are required.

As Table 8 shows, this is by far the highest energy consuming process step in the overall scheme and dominates all subsequent steps, such as hydrogen compression and, in the case of ammonia production, the air separation unit for production of nitrogen from air.

Table 8: Energy consumption of process steps related to the hydrogen option[10]

Process	Hydrogen amount [t/t product]	SEC H$_2$ production [GJ/t product]	Compression [GJ/t product]	N$_2$ from ASU [GJ/t product]	SEC H$_2$ to product [GJ/t product]	Total SEC [GJ/t product]
Ammonia	0.178	33.43	2.14	0.41	1.35	37.3
MeOH from CO$_2$	0.189	35.54	1.52	-	1.50	38.6
MeOH from coal	0.126	23.69	0.507	-	1.50	25.70

Costs of hydrogen production

The supply of hydrogen from water electrolysis is subject to intensive public funding programmes and public private partnerships. Examples are the European Fuel Cells and Hydrogen (FCH) Joint Undertaking (http://www.fch-ju.eu/) in Europe or the US Department of Energy (DOE) Hydrogen and Fuel Cells Program (http://www.hydrogen.energy.gov/). According to (NREL, 2011) capital costs for a central 20 kt/year plant are estimated at M$ 60 with operational costs estimated at M$ 3.3/year.

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[10] Details on the calculation see Annex 5: Hydrogen option.

IEA (IEA, 2007) compared hydrogen costs and sensitivity to energy prices of different technologies, i.e. coal/biomass gasification, natural gas steam reforming and electrolysis. For a price of 35$ per MWh electricity, hydrogen can be produced via electrolysis at 3.6 $/kg, whereas steam reforming of natural gas at 6 to 9 $ /GJ NG results in hydrogen costs of 1.2 to 1.8 $/kg. Hence costs for hydrogen from electrolysis are roughly twice of those from gas steam reforming. Benner et al. (Benner, 2012) estimated costs for future hydrogen based ammonia production compared to conventional natural gas based ammonia production. They conclude investment costs of a centralised water electrolysis plant to be one third of the investment costs of a conventional natural gas based plant of equivalent production capacity. Total specific production costs for ammonia based on estimated power production costs for hydropower and wind power in 2050 given in recent reports of SRREN and EWEA were estimated to be competitive for cheap hydropower, but to require a surcharge between € 0–175/tonne NH_3 in case of hydropower and € 350-500/tonne NH_3 in case of wind-power based production. For the scenario of 30% ammonia and methanol production to be based on hydrogen in 2050 (see Figure 10 of the roadmap) 2.4 EJ energy would be required, of which 1,16 EJ or roughly 318 TWh would be supplied as electricity from renewable sources[11].

Annex 6: Biomass based process routes

Considered routes

The following routes are considered as part of the biomass gamechanger option:

1.   Lignocellulosic biomass gasification and subsequent methanol synthesis, followed by an MTO process to olefins

2.   Direct fermentation of sugar/starch rich biomass (e.g. sugar cane, sugar beet or maize starch) to ethanol, subsequent dehydration to ethylene, evtl. followed by polyethylene synthesis.

Different bioethanol routes are well described and either operated on industrial scale or close to commercial entry. For the other routes investigated, sufficient data is available by design studies and demonstration and pilot plant operation to provide a realistic assessment. Related routes such as hydrolysis of lignocellulosic biomass and subsequent fermentation to ethanol or biomass gasification and syngas fermentation to ethanol are not considered here, as these routes are still predominately determinded by R&D activities and limited data is available on potential energy consumption on commercial scale.

Database

A number of studies and papers are dedicated to biomass routes to ethylene, propylene or polyethylene as final products. Ren (Ren, 2009) analysed the energy consumption and GHG emissions of sugar-cane based ethylene production and biomass based methanol with subsequent olefin production with napthta steam cracking. The well-to-wheel report (Edwards, 2011) describes different processes for producing, transporting and manufacturing of fuels and the respective energy and GHG balances for the various routes. Table 9 lists the different numbers from these studies and

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[11] This assumes that hydrogen production, nitrogen separation by the ASU and gas compression would be electrically based, whereas the final reaction step of ammonia or methanol synthesis are still based on fossil fuels (compare Table 8).

supplementing data from other studies. The row entitled "Total process chain" in the table provides the cumulated numbers for the entire process chain from primary feedstock production to the olefins as product.

Comparison of a biomass route with a fossil fuel based process also has to be done for the respective entire process chains, as the energy use in production of the respective primary feedstocks (biomass, oil, gas, coal), secondary feedstocks and intermediates (e.g. naphtha for fossil based ethylene, ethanol for biomass based ethylene) are largely different for the compared routes. Comparison of only the last reaction step in the respective processes would result in a biased picture on energy consumption (see similar discussion in the methanol to olefin chapter and (Ren, 2009) for a more detailed analysis). This is a deviation from the SEC definition, as already described in the emerging technologies section of Annex 4 and the hydrogen option in Annex 5. For further explanation please refer to the discussion of SEC definition in Annex 1, section on "Boundary conditions for the DECHEMA model".

Table 9: Energy consumption and GHG emissions of bio-based ethylene (HVC) production compared to ethylene (HVC) from Naphtha steam cracking

Process chain	Lignocelluloses gasification and MeOH to olefins		Sugar-cane based route via ethanol dehydration		Conventional route from oil via Naphtha	
	Efficiency as yield (wt %)[12]	Energy consumption and GHG emissions	Efficiency as yield (wt %)[14]	Energy consumption and GHG emissions	Efficiency as yield (wt %)14	Energy consumption and GHG emissions
Primary feedstock production	-	2 GJ/t lignocell.[12] 0.15 t CO_2-eq/t[12] 0.67 GJ/t wood[13] 0.09 t CO_2-eq/t[13]	-	1 GJ/t sugar-cane[12] 0.074 t CO_2-eq/t[12] 0.41 GJ/t sugar cane[13] 0.11 t CO_2-eq/t[13]	-	0.4 GJ/t crude oil[12] 0.069 t CO_2-eq/t[12] 2,4 GJ/t crude oil[13] 0.2 t CO_2-eq/t[13]
Production of inter-mediates (2nd feedstocks)	Wood to MeOH 49%	21 GJ biomass + 6 GJ fossil/t MeOH 39 GJ biofeed + 19.1 GJ add. energy/t MeOH[13, 15]**Fehler! Textmarke nicht definiert.**	Sugar cane to ethanol 19%	61 GJ biomass +7 GJ fossil/t ethanol (if electricity cogeneration is included: -11 GJ fossil/t)[14] 74 GJ biofeed + 43.7 GJ add. energy/t ethanol [13, 15] -0.22 t CO_2-eq/t[19]**Fehler! Textmarke nicht definiert.**	Naphtha 8% of crude oil	3 GJ/t Naphtha[12] 0.2 t CO_2-eq/t[12] 2.33 GJ/t Naphtha[13] 0.2 t CO_2-eq/t[13]
HVC	MeOH to	5 GJ/t HVC12	Ethanol to	2 GJ/t HVC[12]	Naptha to olefins 60%	12 GJ/t HVC[16]

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[12] From: (Ren, 2009)

[13] Based on (Edwards, 2011)

[14] Fossil energy consumption for ethanol production depends on the process configuration, which vary in energy efficiency vs. the amount of electricity co-generation.

[15] The additional energy does not differentiate between bio-based and fossil energy

[16] SEC and GHG emissions for a state of the art steam cracker, current average is higher (16.5 GJ/tHVC).

production	olefins 43%		ethylene 61%	1 GJ/t HVC[17] 0.057 t CO_2-eq/tHVC[17]		0.7 t CO_2-eq/t
Total process chain[18]	4.75 t wood/t HVC required	14.5 GJ fossil + 50 GJ biomass /t HVC[12] 1.0 t CO_2-eq/t[12] 91 GJ biofeed + 52.7 GJ add. energy[21] (CO_2-eq not reported)	8.6 t sugar cane/t HVC required	-17 GJ fossil + 100 GJ biomass /t HVC[12] -0.9 t CO_2-eq/t[12, 19] 121 GJ biofeed + 76 GJ add. energy[21] 0.64 t CO_2-eq/t		17.7 GJ fossil/tHVC[20] 1.15 t CO_2-eq/t[20]
CO_2 captured	-3.5 t CO_2-eq/tHVC[22]		-3.5 CO_2-eq		0 t CO_2-eq/tHVC	

[17] From: (Benner, 2012); for the GHG emissions it is assumed that the energy is supplied by natural gas.

[18] Based on (Ren, 2009); numbers reflect total energy consumption/GHG emissions of the process chain, taking into account the yields as weight% of the different process steps. The energy content of the final product (HVCs) as well as the carbon content (CO2eq) is excluded.

[19] Negative emissions due to the avoidance of CO_2 emissions from electricity co-generation exceeding process emissions from fossil fuel use in this process configuration.

[20] Based on (Ren, 2009); 1.67 t Naptha/t HVC are required at 60% efficiency. Hence production of this Naphtha requires 5 GJ + 0.67 GJ for oil refining (as opposed to the biomass routes, Naphtha is only one product of oil refinery, hence energy consumption for 1 t oil production (0,4 GJ) has been multiplied by the amount of required Naphtha; the same approach has been used for GHG emissions).

[21] Based on (Edwards, 2011) using the efficiencies in the table (from (Ren, 2009)).

[22] Combustion at end of life is carbon neutral in case of products made from renewable feedstocks.

Assumptions for energy consumption of biomass-based HVC production

To assess the impact of biomass based HVC production on the total energy consumption of chemical industry, the following assumptions have been made:

- Production volumes and projections as depicted in the roadmap.
- Moderate, but increasing deployment rates for biomass based HVC production: 2.5% of HVC production in 2020, 5% in 2030, 10% in 2040.
- HVC production from lignocellulosic biomass via methanol is compared to sugar cane based production via ethanol. Other sugar/starch rich biomass, in particular sugar beet might be used instead of sugarcane, potential differences in energy consumption or co-generation of electricity are not considered.

The entire process chain from primary feedstocks to HVCs is included.

Table 10 summarizes the numbers for 10% biomass-based HVC production and anticipated production volumes in 2040.

Table 10: Summary of energy consumption and GHG emissions of biomass routes to HVCs, relative to fossil route (oil via Naphtha steam cracking); numbers for 2040 and 10% assumed deployment rate

Factor	Lignocelluloses to HVC via methanol	Sugar cane to HVC via ethanol
Total energy consumption [EJ]	+2.2	+3.1
Biomass-based energy [EJ]	+2.3	+4.7
Fossil energy [EJ]	-0.14	-1.6
GHG emissions [Mill. t CO_2-eq]	110	260

Further improvement of energy efficiency of the described biomass routes as well as commercial development of alternative routes, such as lignocelluloses hydrolysis and fermentation or biomass gasification and fermentation are to be expected. However, given the relatively large total energy requirement of the biomass routes, it is not to be expected to reach the energy consumption of the conventional fossil processes any time soon. No indications are given in any of the analysed references that would imply improvement rates for the biomass-based catalytic processes to be largely different than the corresponding fossil processes.

Annex 7: Refineries

Assessing the Refining sector for energy and GHG reductions is much more difficult than the Chemicals sector. The variety of feeds in refinery units that change on a regular basis make these estimates very difficult. The feed changes are economically driven and the catalysts change based on the feeds. The SECs of catalytic refinery steps in Table 11 and the refinery cuts in Table 12 of this Annex are therefore indicative only.

Overall, the same outcomes are applicable to the refining sector as was gleaned from the Chemicals work: namely

1.) Constant improvement in catalytic processes (FCC, Reforming, Hydrocracking) are essential to reduce energy consumption in refining processes.

2.) Game changers such as bio-based feeds for liquid fuels conserves fossil fuels

3.) Game changers such as processing of heavy bitumen (tar sands) to synthetic oil and it's treatment before traditional refining operations will see greater application which brings along higher energy consumption and GHG emissions. There is a need for further R&D to develop catalytic improvements to convert heavy oils into refinery ready feedstocks.

Table 11 shows the specific energy consumption for the catalytic processes for US refineries. The table shows that BPT level plants consume 20 to 30% less energy than the average refinery. The listed theoretical minimum represents the thermodynamic minimum energy requirement –which will not be achievable in practise. Instead, a practical operational limit of 30% or higher above theoretical is assumed.

Table 11: Specific energy consumption of catalytic process steps in US oil refineries

Energy consumption [GJ/bbl]	FCC	Reforming	Hydrotreating
avg SEC US Refineries	0.19	0.28	0.086
SEC of BPT level plant	0.14	0.21	0.06
theoretical minimumFehler! extmarke nicht definiert.	0.04	0.083	0.03
Practical operational limit	0.1	0.16	0.04

Source: (Energetics Incorporated, 2006)

Catalytic process steps in refineries

Catalytic cracking in refineries is one of the most important existing technical processes. In order to use the major part of crude oil as gasoline, diesel and fuel oil, catalytic cracking is required to cut the long chain hydrocarbons of crude oil into smaller hydrocarbons. Fluid catalytic cracking (FCC) is the most important conversion process used in petroleum refineries. This process uses acidic zeolites as catalyst and produces a high yield of gasoline and LPG, while hydrocracking is a major source of jet fuel, diesel, naphtha, and LPG. One estimates that the introduction of zeolite catalysts for FCC replacing former amorphous alumosilicates saves 400 million barrels of crude oil per year (Blauwhoff, 1999).

The second important catalytic process in oil refineries is **catalytic reforming**, which increases the octane rate of naphthas and heavy straight-run gasoline by re-structuring the hydrocarbon molecules from crude oil distillation into high-octane gasoline blending components.

Finally, **catalytic hydrotreating**, which occurs at different locations of refineries includes the removal of sulfur and nitrogen impurities and the upgrading of heavy olefin feed by saturating it with hydrogen to produce paraffins.

Table 12: Refinery Cuts of Different Process Steps by Regions

	Cuts for different regions [million barrels/d]*					
Process step	USA	OECD Europe	Pacific**	China	Other Asia	Middle East
Atmosph. Distillation unit	21.5	15.96	8.63	9.83	10.69	7.75
Vacuum distillation unit	9.5	6.46	2.44	3.74	2.9	2.15
Cat Reforming	4.4	2.35	1.26	0.7	1.1	0.92
Hydrocracking	1.9	1.36	0.5	1.05	0.94	0.6
FCC	6.6	2.15	1.4	0.7	1.04	0.3

* Based on 2010 numbers from IEA.

**Pacific includes Japan, Korea, NZ and Australia

Annex 8. Description of IEA Scenarios

Box 1 describes the different IEA scenarios, which are the basis for all IEA graphs in the roadmap and in this annex.

Box 1: IEA *Energy Technology Perspectives 2012* Scenarios

The basis for all IEA graphs is the IEA's *ETP 2012* 2-Degree Scenario (2DS), which describes how energy technologies across all energy sectors could be transformed by 2050 to achieve the global goal of reducing annual CO_2 emission levels to half those of 2005 (IEA, 2012). The model used for this analysis is a bottom-up TIMES model that uses cost optimisation to identify least-cost mixes of energy technologies and fuels to meet energy demand, given constraints such as the availability of natural resources. The ETP model is a global 29-region model that permits the analysis of fuel and technology choices throughout the energy system. The model's detailed representation of technology options includes about 100 individual technologies. The model has been developed over a number of years and has been used in many analyses of the global energy sector. In addition, the ETP model is supplemented with detailed demand-side models for all major end-uses in the industry, buildings and transport sectors.

ETP 2012 considers other scenarios. The 6-Degree Scenario (6DS) assumes that no major new policies to reduce GHG emissions will be introduced in the coming decades. The 6DS is considered to be the baseline scenario in the Technology Roadmap series. Achieving the 2DS will be difficult; some of its assumed rates of change (e.g., annual change in sales of new technologies) are unprecedented. To achieve such a scenario, strong policies will be needed from governments around the world. In industry two variants are consider, one assuming low demand growth for materials and the second based on high demand.

Figure 5 depicts the expected strong increase in production of the largest high volume chemicals, as already described in the roadmap. This strong demand makes absolute energy and GHG savings challenging.

Figure 5: Regional HVC, ammonia and methanol production between 2009 and 2050 in 2DS.
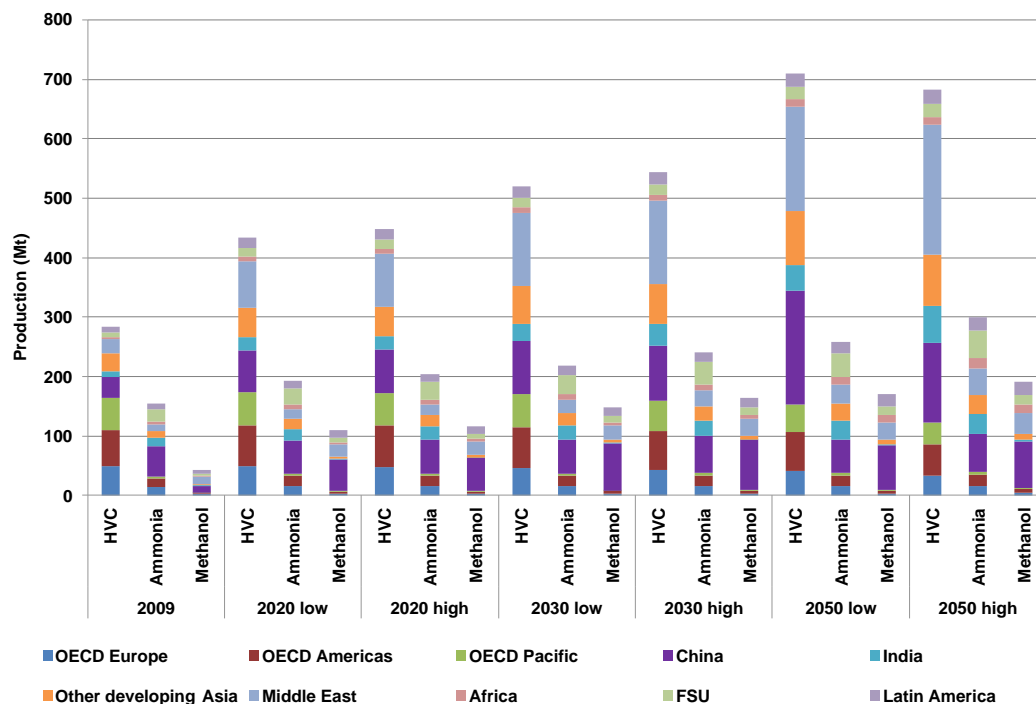

Key message: Production in the chemical and petrochemical sector is expected to increase, especially for HVCs and methanol.

Figure 6 provides a breakdown of production volumes between 2010 and 2050 across regions.

The IEA scenarios show regional CO_2 emissions grow fastest in Asia, Africa and the Middle East, with emissions in these regions increasing threefold from the current rate in the 6DS (Figure 7).

Figure 6: Predicted production growth in different world regions (SRI).
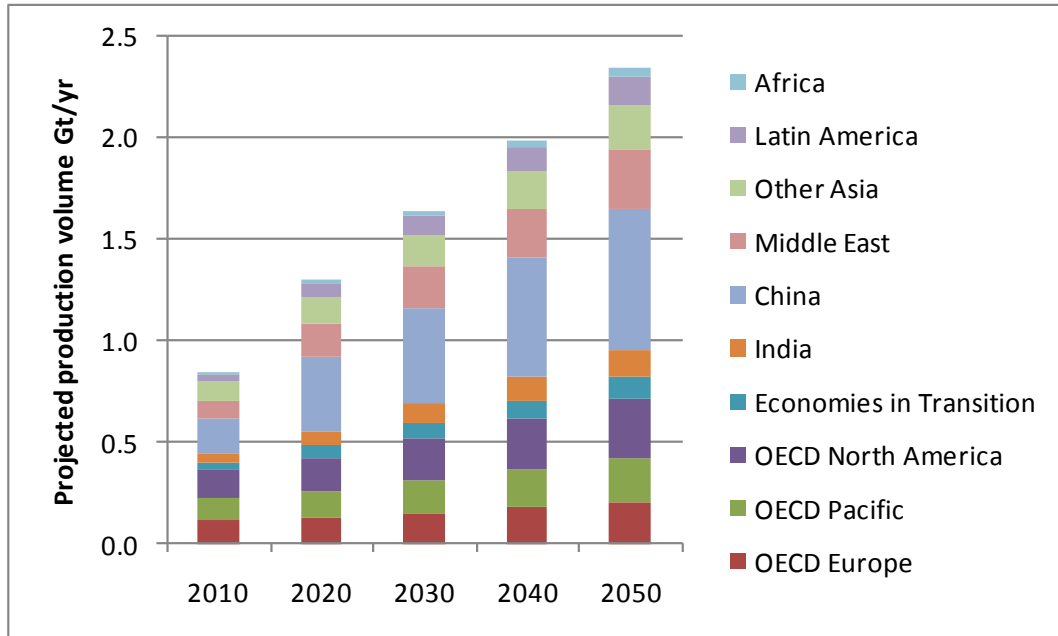
Key message: All regions are expected to increase their production, with the largest growth in China.

Figure 7: Direct CO$_2$ emissions by region and by scenario, 2009 and 2050.
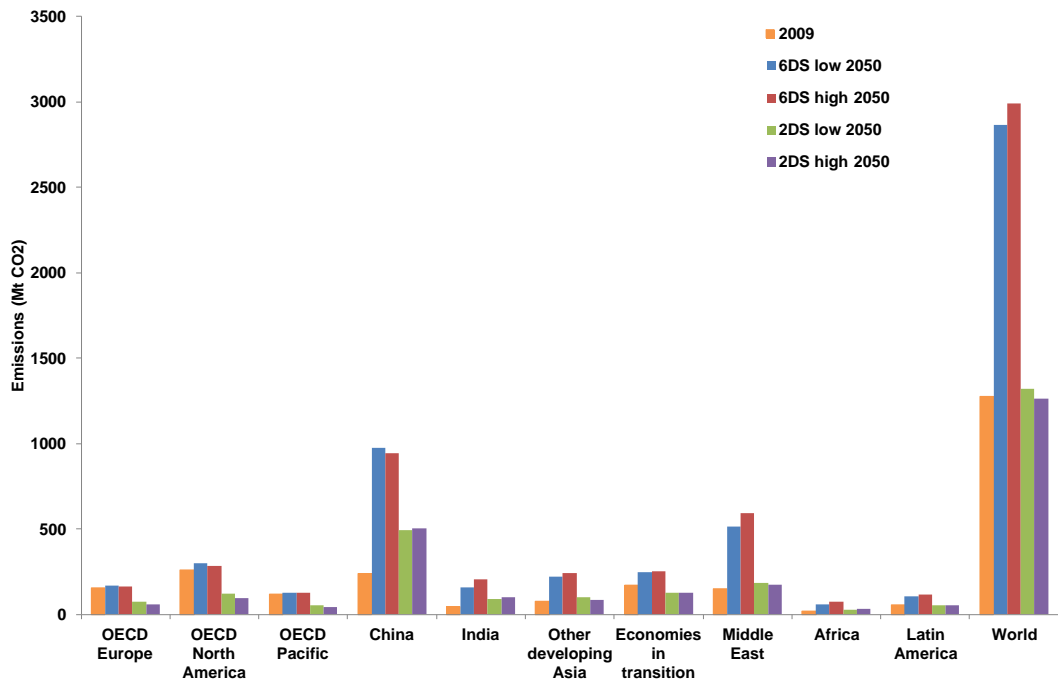
Key message: CO$_2$ emissions are expected to rise strongly in the developing countries. Developed countries see stagnation or decreases.

Annex 9. Research needs[23]

Improve feedstock efficiency

New catalytic technologies for the production of olefins and aromatic compounds or their direct secondary products from natural gas are needed. Synthesis gas is becoming an increasingly important platform both for the production of fuels like gasoline, diesel or kerosene and for the chemical industry in general.

It is very likely that natural gas will become more important for the chemical industry in the future as it is a raw material which is easy to transport and handle, and some of the heavier feedstocks are becoming heavier with greater impurities and have a supply position with a long-term question mark. In addition, the use of coal and biomass will increase due to regional needs and advantages.

The most important chemical primary products made from crude oil are olefins (particularly ethylene and propylene) and aromatic hydrocarbons (particularly benzol, xylenes) which are produced using steamcracking and reforming. Consequently, the greatest future potential for natural gas in the chemical industry therefore lies in the production of precisely these primary products. For the short-chain alkanes in natural gas, in particular for the C1 building block methane, carbon linking reactions play a decisive role. This includes improved synthetic gas based techniques such as methanol to olefins (MTO, but also direct synthesis of aromatic compounds from methane or LPG (Cyclar process) and the production of ethylene from methane.

Furthermore, for olefin production from alkanes, activation of these alkanes to introduce double bonds and subsequently other functionalities will grow important with increasing significance of natural gas. Examples of required catalytic technologies are the dehydrogenation of propane to propylene, and the partial oxidation of alkanes with oxygen for direct production of methanol from methane, ethanol or acetic acid from ethane, or propanols or acrylic acid from propane.

Synthesis gas from a variety of different raw material sources (natural gas, coal, renewable resources) with an optimized CO/H_2 ratio achieved with the aid of improved water-gas shift catalysts will represent one of the fundamental raw material sources of the future, as in principle any raw material containing carbon can be synthesized via this interim stage. Coal as the source of carbon with the lowest hydrogen content is the most problematic raw material in terms of GHG emissions and would therefore benefit from catalytic processes enabling the re-use of CO_2 as carbon source in chemical production. The conversion of biomass into synthesis gas is an alternative for the medium to long term. The following research needs can be identified:

• Production of synthesis gas from methane, coal or biogenous sources with subsequent GTL ("gas to liquids") processes via two principal routes: (a) synthesis of methanol and its conversion to dimethylether, C2 and C3 olefins as well as of gasoline, plus (b) Fischer Tropsch synthesis with subsequent conversion of the products via hydro-isomerization and hydrocracking as well as oligomerization of olefins.

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[23] Elements retrieved from GeCatS, 2010

- Continuous optimization of already established methods on the basis of synthesis gas (oxo synthesis, acetic acid, Fischer-Tropsch).
- Optimization of catalyst activity, selectivity and lifetime in gas-to-chemicals processes, with more selective process control in the process in order to avoid broad product distributions.
- The development of highly selective, direct synthesis gas conversion processes into end products like hydrocarbons or oxygenates.
- New catalysts for conversion of synthesis gas to ethanol and higher alcohols.
- Further development of methanol synthesis catalysts with performance criteria which are carefully selected to match the origin of the synthesis gas (coal, gas, biomass).
- Improved control of the water-gas shift activity in order to avoid the production of CO_2 and the resulting methanation.

In terms of chemical CO_2 utilization the following research areas shall be mentioned:

- Photocatalytic or electrocatalytic activation modeled on natural processes.
- Synthesis of products with high added value, in which CO_2 remains in the product as a C1 building block (for example polycarbonates, polyurethane)
- Hydrogenation of CO_2 with hydrogen from regenerative sources.

Fuels from gas and coal

It can be expected that the bulk of fuels for mobile applications will continue to be based on hydrocarbons. The proportion of compounds containing oxygen in the fuel pool will increase slightly, as on the one hand biogenous carbon sources are being developed and on the other hand a certain concentration of oxygen in the fuel has a positive effect in terms of combustion properties. Alongside conventional fuels from fossil sources, there will be regionally varying proportions of biogenous fuels based on renewable raw materials, such as biodiesel or ethanol.

New routes to polymers

More energy-efficient methods for monomer production and polymerization will be the central topics of catalytic and process engineering research and development.

Related to the above mentioned gas based routes to olefins is the subsequent production of polymers. Polymers are generally made up of simple chemical monomers, with the olefins (ethylene, propylene, butylene, butadiene and octane) being key monomer building blocks, which are polymerized into corresponding specialized, high-performance materials using catalytic methods.

Olefins are currently still primarily produced from fossil raw materials (crude oil). In the future, natural gas (see above) and renewable raw materials will also become more important.

Research efforts are required on new techniques and catalysts for the production of monomer building blocks on the basis of new raw materials (e.g. methane -> synthesis gas -> methanol -> olefins). Here, top priority goes to the improvement of zeolite-based MTO catalysts (methanol-to-olefins). Alongside methanol as a C1 source, it makes sense to develop more efficient synthesis routes to higher alcohols (propanol, butanol), so that these products can then be converted into olefins via catalytic dehydration.

The primary objectives of catalyst development are: improvement of the mechanical stability of powdery and formed catalyst types, optimization of resistance to catalyst poisons and better control of product distribution and hence more efficient and therefore more sustainable utilization and recycling of raw materials.

Concerning biomass-based routes, research on processes and biocatalytic systems for the saccharification of lignocellulose into bioethanol as a raw material for ethylene should be strengthened. Subsequently, single-step processes for the conversion of ethylene, preferably regenerative ethylene, into propylene, e.g. via catalytic "one-pot" combination of ethylene dimerization/isomerization/ metathesis into C3 monomer could be envisioned.

Hydrogen production

R&D is required on hydrogen production from cultivated biomass or from the exploitation of secondary materials via autothermic reforming, the improvement of water electrolysis processes, both in terms of the electrocatalysts and in terms of process control and long-term efforts on photocatalytic water cleavage with new catalyst systems

State-of-the-art processes for hydrogen production include steam reforming and/or the partial oxidation of natural gas or other fossil carbon sources. For the production of large volume products such as ammonia and methanol this syngas production is integral part of the process.

Alternatively, production of synthesis gas is possible from biomass or waste materials via the modification of classic reforming. Here, the variable composition of the raw materials represents a particular challenge in terms of the robustness of the catalysts.

The process of electrolytic cleavage of water is technically already possible with energy efficiencies around 70 %. Optimized processes need to be found for non-stationary operating conditions when using regenerative energy sources. Today, nickel is used predominantly as the catalyst; platinum would be better in terms of energy efficiency but is too expensive. Cheaper electrode materials with a similarly low overvoltage to platinum could help to bring about significant progress here. In addition, it is also important to test and optimize new process variants, such as high-pressure electrolysis or gas phase electrolysis.

Photocatalytic water cleavage processes are still a long way off commercially viable space-time yields, regardless of whether they are based on solid catalysts or biochemical/biomimetic systems. The situation is similar for the (to date) undervalued alternatives of homogeneous or biocatalytic methods. In the area of biocatalysis, past work has focused particularly on discovering the fundamental biochemical principles and regulatory processes for microorganisms which can be used to produce hydrogen or fix nitrogen. As in all cases these enzymes carry a complex metal cofactor in their active center and also display a pronounced oxygen intolerance, to date they have been used only rarely in biotechnology applications. Finally, some initial progress has been made with approaches to produce hydrogen in electrochemical cells by converting CO_2 into synthesis gas. All of these techniques are still in an early stage of fundamental research, but they all have the potential to revolutionize hydrogen production in the long term.

Biomass as chemical feedstock

Efficient use of biomass as feedstock requires innovative value chains on the basis of carbohydrates instead of hydrocarbons and defunctionalization instead of functionalization as the synthesis strategy

Consequent biomass utilization as chemical feedstock requires substantial R&D effort in catalysis. To avoid competition with food production, the use of lignocellulosic biomass with the three components cellulose, hemicellulose and lignin gains importance. Starting from cellulose and hemicellulose, it is possible to generate family trees for the chemical reaction processes into chemical resources and materials. The study "Top Value Added Chemicals from Biomass" published by the US Department of Energy contains a list of 12 possible platform chemicals.

Lignin on the other hand contains various aromatic building blocks and hence could represent an important source of aromatic compounds. The main tasks for catalysis are the depolymerization of these biomass components and the defunctionalisation, as cellulose, carbohydrates and other biogenic compounds contain too many functional groups, which need to be selectively decomposed. In addition most of the biomass-based processes require aqueous systems and hence catalysts which are stable in water.

In addition to the development of efficient solutions for individual reaction steps the industrial-scale implementation of biomass-based processes requires that a large proportion of the biogenous starting materials is converted into usable end products and does not remain unused as a waste stream. This refers to the concept of biorefineries, in which sufficient value is created in the individual process streams.

These examples already show that a huge amount of fundamental R&D is required to explore these new synthetic strategies and to ultimately facilitate commercial processes.

Annex 11. Workshop Participants

Catalyst Subject Matter Experts, Paris, September 7-9, 2011

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Jesper Nerlov, Haldor Topsoe

Julia Reinaud, ClimateWorks- Inst. for Industrial Productivity

Jigar Shah, ClimateWorks- Inst. for Industrial Productivity

Policymakers, Brussels, January 23, 2012

Achim Boenke, EU Commission

Chetna Khosla, ACCRE/ DOE

Chiara Di Mambro, EU Commission/DG Climate

Christian Egenhofer, CEPS

Joachim Ehrenberg, EU Commission/DG Enterprise

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Dongmei Chen, IIP network

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Lynn Chen, Air Product

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