CASE STUDY • PETROCHEMICAL SOLVENT PRODUCTION ROUTES

A comprehensive environmental assessment of petrochemical solvent production

Christian Capello · Gregor Wernet · Jürgen Sutter · Stefanie Hellweg · Konrad Hungerbühler

Abstract

Background, aim, and scope Organic solvents are used in large quantities in the chemical, metal and electronics industries as well as in many consumer products, such as coatings or paints, and are therefore among the most important chemicals. The petrochemical production of organic solvents is a relevant environmental issue because fossil resources are needed (crude oil and natural gas), synthesis processes are energy-intensive and cause considerable amounts of emissions. So far, comprehensive data on the environmental impact are rather scarce. The aim of this paper is to therefore present a systematical environmental assessment of the main petrochemical solvent production routes using the Life Cycle Assessment (LCA) method. *Methods* Fifty organic solvents were selected covering the most important representatives from the various chemical groups (e.g., alcohols, esters, ketones). To conduct the LCA, 40 new Life Cycle Inventories (LCI) were established and existing LCI were improved. The petrochemical solvent production was structured into four production routes. In these production routes, the single chemical unit processes (e.g. esterification, carbonylation or hydrogenation) were analyzed in order to determine characteristic environmental impacts.

Results and discussion The four solvent production routes including the unit processes and intermediates are presented. Additionally, energy profiles of these production routes are shown using the Cumulative Primary Energy Demand (CED) as an indicator for the environmental impact. The results were cross-checked with the Global Warming Potential and the Eco-indicator 99 method and good correlations were found. Processes that show high environmental impacts are the dehydration of butylene glycol to tetrahydrofuran, the carbonylation of methanol to methyl formate, the hydrogenation of acetone to methyl isobutyl ketone, and the Reppe synthesis of formaldehyd/ acetylene to butylene glycol. Based on the energy profiles, ranges of environmental impacts are determined for all unit processes. On the one hand, esterification and alkylation processes cause high CED values because complex ancillaries are needed and hydroformylation and carbonylation processes are energy-intensive. On the other hand, in hydration, hydrogenation, hydrolysis, and oxidation processes, ancillaries with low CED are added to the chemical structure that result in low CED ranges for these unit processes. Dehydrogenation and molecular sieve separation processes seem to be energy efficient and no ancillaries are required. Therefore, these unit processes cause the lowest CED values.

Perspectives Subject of further research in this field should be the environmental analysis of further process steps that include the presented unit processes and a subsequent statistical analysis in order to derive reliable data ranges for all unit processes. Such statistically robust ranges could be used in the approximation of missing life-cycle inventory data of other chemical products and intermediates.

C. Capello (✉) · G. Wernet · J. Sutter · K. Hungerbühler
Institute for Chemical and Bioengineering,
Swiss Federal Institute of Technology,
Wolfgang-Pauli Str. 10, HCI 8093 Zurich, Switzerland
e-mail: capello@gmx.ch

S. Hellweg
Institute of Environmental Engineering,
Swiss Federal Institute of Technology,
Wolfgang-Pauli Str. 15, HIL 8093 Zurich, Switzerland

1 Background, aim, and scope

Organic solvents are used in large amounts by a wide
variety of industrial sectors. In Europe, the annual con-
sumption of fresh solvents was estimated to be 4 million
tonnes in 2004 (European Solvents Industry 2007). The
largest demand for solvents comes from the paint and
coatings industry which relies on almost 2 million tonnes
every year. The next largest use is in the chemical industry
(pharmaceuticals, agricultural chemicals, specialty chem-
icals), followed by the use of solvents in metal cleaning and
degreasing as well as in the electronics industry. Other
important end markets include rubber and polymer manu-
facture, detergents, and personal care products (European
Solvents Industry 2007; Whim and Johnson 1996).

Most of the organic solvents are synthesized in the
petrochemical industry. Thus, they are mainly derived from
either crude oil or natural gas. Aliphatic hydrocarbons are
produced by refining and distilling various cuts, fractions
and aromatics either by cracking or reforming naphtha
streams. The production of oxygenated solvents requires
methane, ethylene, propylene, butylenes, air and water as
main building blocks for most of the important ones (Whim
and Johnson 1996; Wypych 2001).

The large amounts of organic solvents used combined
with the fact that their production causes the depletion of
non-renewable resources makes the manufacture of sol-
vents such a relevant environmental issue. To quantify the
corresponding environmental impacts arising from the
petrochemical production of solvents, environmental as-
sessment tools such as Life Cycle Assessment (LCA)
should be applied. In spite of the potential environmental
relevance of solvents, only little Life Cycle Inventory (LCI)
data of solvents has been published in databases (see, for
example, the ecoinvent database ecoinvent Centre 2004).
Some LCAs of chemicals have been carried out in other
works (Kralisch et al. 2005), but these only cover limited
amounts of chemicals. Frequently, chemical inventories are
estimated (Geisler et al. 2004; Wernet et al. 2008). Other
inventory analyses of chemicals have been carried out in
the chemical industry, e.g., at BASF (Saling et al. 2002),
Ciba (Bretz RaF 1996) or GlaxoSmithKline (Jiménez-
Gonzalez et al. 2004). However, these efforts are usually
not published due to confidentiality issues. Therefore,
publicly available data is scarce. Additionally, the existing
inventories of solvents have so far not been analyzed
systematically in the context of full production routes in
order to identify key production steps that contribute
substantially to the environmental impacts.

The aim of this paper is to present a comprehensive
environmental assessment of the main petrochemical
solvent production routes using the LCA method, including
the quantification of environmental impacts of all single
unit process operations applied in these production routes.
An additional goal is to provide inventory data ranges for
chemical unit process operations based on these results,
which may be used to estimate inventory data of other
chemical productions.

To achieve these goals, a selection of 50 representative
organic solvents was made based on amounts used and a
survey about the importance of solvents in chemical
industry. The petrochemical production of the selected
solvents was structured according to the most important
production routes, which were then analyzed in detail.

2 Methods

2.1 Solvent selection

A large number of solvents are used in the various
industries. For example, the number of solvents generally
available to chemists is between 250 and 300 (Reichardt
2003). Since it is impossible to include all solvents within a
study, 50 important solvents were selected for our work
according to the following criteria:

The selection covers

(1) solvents of various chemical groups (alcohols, alde-
    hydes, aliphatic hydrocarbons, amides, aromatic hydro-
    carbons, esters, ethers, halogenated hydrocarbons, and
    ketones).
(2) quantitatively important representatives of all groups
    according to technical literature (Whim and Johnson
    1996; Wypych 2001; Stoye 2000; Marcus 1998; Flick
    1998).
(3) solvents used particularly in the chemical industry
    where a large variety of solvents are employed. This
    selection is based on results of a comprehensive survey
    on the Swiss chemical industry (see Seyler et al. 2006).

2.2 Life cycle assessment of solvents

Life Cycle Inventories for some organic solvents have already
been published in the ecoinvent database (ecoinvent Centre
2004). However, with regard to most of the 50 solvents, new
LCI data had to be collected and are now published in the
ecoinvent v2 database. In order to comply with the quality
standards of the ecoinvent database, all solvent inventories
were established according to the guidelines presented in

Frischknecht et al. (2005) and Hischier et al. (2004). Thus, all data are presented on a unit process level. Whenever possible, actual production data was used to determine inventory flows. In case such data was not available, basic information from technical reference books (e.g., Ullmann's Encyclopedia of Industrial Chemistry 2006) together with additional assumptions and simplifications were used, as described in Hischier et al. (2004). With this procedure, missing inventory data of energy consumption, process efficiency, water consumption, emissions to air and water, transports, and infrastructure can be estimated. The procedure offers clear, step-by-step guidelines on how to deal with missing data and what models to use. Additionally, inventory flows were estimated taking advantage of the fact that the petrochemical production of solvents is based mostly on a small number of different chemical reaction steps such as, for example, esterification, chlorination or carbonylation. Thus, if process data for such operation steps was available for a specific solvent it was used as an approximation for other solvents. The use of this procedure offers two advantages: consistency in approach over the whole set of solvents, and consistency with the ecoinvent data. As cases of missing data are never avoidable, this approach was deemed the most reasonable way to handle incomplete data sources.

To quantify the environmental impact of petrochemical solvent production, the Cumulative Primary Energy Demand (CED) (Jungbluth and Frischknecht 2004) was used as a screening indicator because it has been shown that the use of energy is related to several environmental impacts (Huijbregts et al. 2006). The CED is composed of all process and feedstock energies required during the production cycle, including upstream processes and energy conversion. Its unit is MJ-equivalents, the equivalent energy content of the primary energy carriers, e.g., solar energy as well as oil or uranium in the ground. However, in order not to neglect potentially important emission-related impacts, the CED impact scores were cross-checked with the results of other impact assessment indicators such as Eco-indicator 99 and Global Warming Potential.

2.3 Petrochemical solvent production

The petrochemical production of solvents can be structured in four main production routes that are of importance on an industrial scale (Ullmann's Encyclopedia of Industrial Chemistry 2006; Chauvel and Lefebre 1989a, b; Asinger 1971; Wells 1991). The routes differ with regard to their starting materials and key processes. Figure 1 gives a simplified overview of the petrochemical processing of natural gas and crude oil with focus on the production of the starting materials for the solvent production routes.

The four solvent production routes are briefly characterized in the following:

Route A: In the *methanol route*, methanol from natural gas is used as starting material. Important solvents such as acetic acid, formaldehyde or tetrahydrofuran are produced via this route.

Route B: In the *naphtha/steam cracking route*, naphtha from crude oil is treated in a steam cracking process that results in a large variety of alkenes and alkanes. Based on these intermediates, many alcohols such as ethanol, butanol or propanol are produced and further processed to acetates.

Route C: In the *BTX/naphtha route*, naphtha from crude oil or BTX reformate is separated in a molecular sieve to obtain alkanes such as hexane and heptane.

Route D: In the *BTX splitting route*, BTX reformate or pyrolysis gasoline are split to obtain aromatic solvents such as toluene or xylene. Toluene and the intermediate benzene are further processed to cyclohexane, acetone, and benzaldehyde.
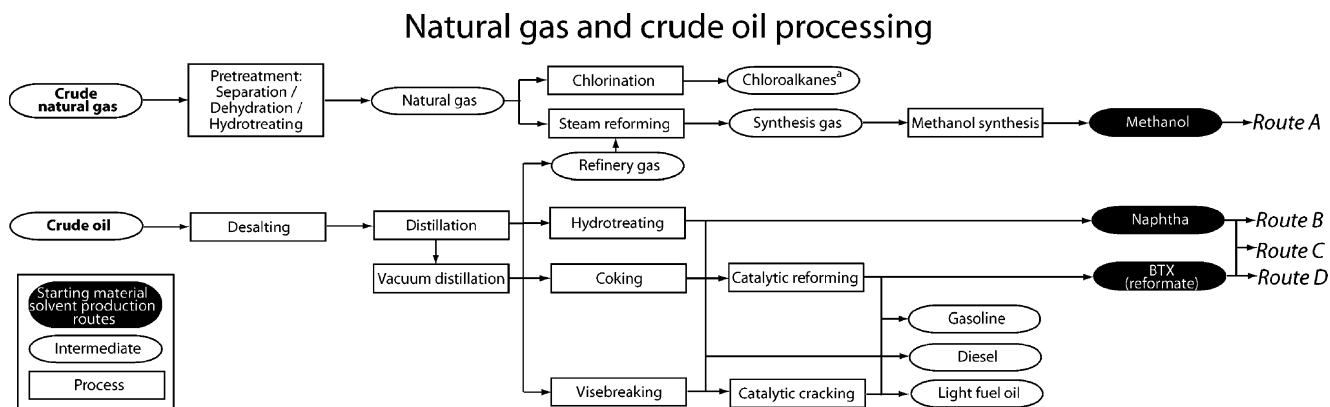
Fig. 1 Simplified overview of the petrochemical processing of natural gas and crude oil with focus on the starting materials for the four organic solvent production routes (shaded in black). [a]Chloroalkanes: methyl chloride, dichloromethane, trichloroethylene, tetrachloroethylene

Table 1 The 50 selected solvents for this study with corresponding data quality indicators

Selected solvents				Available inventory information				
No.	Name	Synonym(s), Abbreviation	CAS-no.	Input material	Water consumption	Energy consumption	Emissions to air	Emissions to water
Alcohols (estimated worldwide production: $3*10^6$ tonnes per year (Whim and Johnson 1996))								
1	tert-Amyl alcohol	2-Methyl-2-butanol	75-85-4	3	3	2	3	3
2	Benzyl alcohol		100-51-6	1	1	1	1	1
3	1-Butanol	n-Butyl alcohol	71-36-3	ecoinvent v1.2. dataset				
4	2-Butanol	s-Butyl alcohol	78-92-2	1	1	1	3	3
5	Isobutanol	2-Methyl-1-propanol	78-83-1	1	1	1	3	3
6	1,4-Butylene glycol	1,4-Butanediol	1100-63-4	1	1	1	1	1
7	Ethanol	Ethyl alcohol	64-17-5	1	1	1	3	3
8	Methanol	Methyl alcohol	67-56-1	ecoinvent v1.2. dataset				
9	1-Pentanol	n-Pentyl alcohol	71-41-0	3	3	2	3	3
10	1-Propanol	n-Propyl alcohol	71-23-8	1	1	1	1	1
11	Isopropanol	2-Propanol, Isopropyl alcohol	67-63-0	ecoinvent v1.2. dataset				
Aldehydes (estimated worldwide production of the specific aldehydes listed below: $7.1*10^6$ tonnes per year (Brühne and Wright 2004; Consulting 2003; Chemicals 2002))								
12	Benzaldehyde		100-52-7	3	3	1	3	3
13	Formaldehyde		50-00-0	ecoinvent v1.2. dataset				
14	Propionaldehyde	Propanal	123-38-6	3	3	2	3	3
Aliphatic hydrocarbons (estimated worldwide production: $4.1*10^6$ tonnes per year (Whim and Johnson 1996))								
15	Cyclohexane		110-82-7	1	1	1	3	3
16	n-Heptane		142-85-5	1	1	1	1	1
17	Isohexane	2-Methyl pentane	96-14-0	3	3	1	3	3
18	n-Hexane		110-54-3	1	1	1	1	1
19	Methyl cyclohexane		108-87-2	3	3	2	3	3
20	n-Pentane		109-66-0	ecoinvent v1.2. dataset				
Aliphatic carbon acids (estimated worldwide production of the specific acids listed below: $5.8*10^6$ tonnes per year (Reutemann and Kieczka 2002; Cheung et al. 2002))								
21	Acetic acid	Ethanoic acid	64-19-7	ecoinvent v1.2. dataset				
22	Formic acid	Methanoic acid	64-18-6	1	1	1	3	3
Aromatic hydrocarbons (estimated worldwide production: $2*10^6$ tonnes per year (Whim and Johnson 1996))								
23	Ethyl benzene		100-41-4	ecoinvent v1.2. dataset				
24	Toluene	Methyl benzene	108-88-3	ecoinvent v1.2. dataset				
25	Xylene	Dimethyl benzene	1330-20-7	ecoinvent v1.2. dataset				
Chlorinated hydrocarbons (estimated worldwide production: $1.1*10^6$ tonnes per year (Whim and Johnson 1996))								
26	Chlorobenzene	Monochlorobenzene	180-90-7	1	1	1	1	1
27	Dichloromethane	Methylene chloride	75-09-2	ecoinvent v1.2. dataset				

No.	Solvent	Synonyms	CAS						
Esters (estimated worldwide production: 0.9*10⁶ tonnes per year (Whim and Johnson 1996))									
28	Butyl acetate		123-86-4	3	3		2	3	3
29	Ethyl acetate		141-78-6	1	1		1	3	3
30	Isoamyl acetate		628-63-7	3	3		2	3	3
31	Isobutyl acetate		110-19-0	3	3		2	3	3
32	Isopropyl acetate		108-21-4	3	3		2	3	3
33	Methyl acetate		79-20-9	1	1		1	3	3
34	Methyl formate		592-84-7	1	3		1	3	3
Ethers and glycol ethers (estimated worldwide production: 1.1*10⁶ tonnes per year (Whim and Johnson 1996))									
35	Dioxane	Diethylene oxide, Diethylene ether	123-91-1	3	3		1		3
36	Ethyl ether	Ether, Diethyl ether, Ethoxy ethane	60-29-7	1	1		1	3	3
37	Ethylene glycol diethyl ether	Diethoxyethane	629-14-1	3	3		3	3	3
38	Ethylene glycol dimethyl ether	Dimethoxyethane, DME	110-71-4	3	3		3	3	3
39	Ethylene glycol monoethyl ether	2-Ethoxyethanol, Cellosolve	110-80-5	3	3		3	3	3
40	Methyl *tert*-butyl ether[a]	MTBE	1634-04-4	1		3	3	3	3
41	Tetrahydrofuran	THF	109-99-9	3	3		1	3	3
Ketones (estimated worldwide production: 1.8*10⁶ tonnes per year (Whim and Johnson 1996))									
42	Acetone[a]	2-Propanone, Dimethyl ketone	67-64-1	3		3	3		3
43	Cyclohexanone		108-94-1	1			1	3	3
44	Methyl ethyl ketone[a]	MEK	78-93-3	3		3	1	3	3
45	Methyl isobutyl ketone	Methyl pentanone, MIK	108-10-1	1			1	1	1
Miscellaneous solvents (estimated worldwide production of the specific solvents listed below: 2.4*10⁶ tonnes per year (Bipp and Kieczka 2002; Harreus 2002; Kirk-Othmer Encyclopedia of Chemical Technology 2006))									
46	Acetic anhydride[a]		108-24-7	1	1		1	3	3
47	Acetonitrile	Methylcyanide, Ethanenitrile	75-05-8	1	1		1	3	3
48	Dimethyl sulfoxide	DMSO	67-68-5	3	3		3	3	3
49	Dimethylformamide	DMF	68-12-2	3	3		1	3	3
50	n-Methylpyrrolidone	NMP	872-50-4	3	3		3	3	3

1 data available from literature or manufacturers, *2* estimated from similar processes, *3* estimated according to Hischier et al. (Hischier et al. 2004)

[a] existing ecoinvent processes were improved with better data

In all four production routes, the single unit processes (e.g., esterification, carbonylation or oxidation processes) are analyzed in order to determine characteristic environmental impacts for such process steps or full production routes. To this end, energy profiles of the production routes are established and interpreted.

3 Results

3.1 Solvents under study

The 50 organic solvents under study are presented in Table 1. The selection covers the quantitatively most important solvent groups. Their estimated worldwide production volume is also shown in Table 1. With regard to 10 solvents, inventory data had already been published in the ecoinvent database (ecoinvent Centre 2004). For the other 40 solvents, new inventories were established or existing inventories were improved with better data. The inventory data was reviewed by experts of the ecoinvent framework and are now published as part of the ecoinvent v.2.0. The 40 new solvent inventories vary with regard to data quality. Table 1 shows the data quality specifically for input materials (amount of educts, ancillaries), water consumption (process water and cooling water), energy consumption (process energy and feedstock energy), emissions to air and water. If process data was available from literature or manufacturers it is indicated with "1" in Table 1. In case no information was found, either inventory data of good quality were used as an approximation for solvent production steps that require the same unit processes (e.g., energy data of the esterification of ethyl acetate are used as an approximation for the esterification of butyl acetate) (indicated as "2") or the inventory data were estimated according to Hischier et al. (2004) (indicated as "3").

3.2 Analysis of the petrochemical solvent production routes

Figures 2, 3, 4 and 5 show the four production routes described in Section 2.3, including the starting material of the production route (e.g., naphtha, methanol), the subsequent process steps on the level of unit processes (e.g., esterification, oxidation) and resulting products (solvents, intermediates). As unit processes, we consider all operations that are required to achieve a change in the chemical structure (e.g., the actual reaction processes and subsequent purification and separation steps). In addition, Figs. 2, 3, 4 and 5 also show the Cumulative Energy Demand (CED) for all solvents and intermediates. These energy profiles facilitate the identification of energy-related environmental impacts within the solvent production chain.

The production routes displayed in the figures represent the most important synthesis routes with regard to the annual production volume. Variations or alternative synthesis routes also exist in the petrochemical industry. Some of them are shown in Figs. 2, 3, 4 and 5 as secondary production routes. The production of dichloromethane is not included in the figures, as the chlorination of natural gas is the most important synthesis route (see Fig. 1) (Whim and Johnson 1996).

In the *methanol route* (Route A, Fig. 2), the process steps for the production of methyl formate, butylene glycol, and tetrahydrofuran show particularly high increases of the CED (52 to 67 MJ-eq. per kg product). With regard to methyl formate, the high consumption of raw material causes the increase of the CED (1.1 kg methanol and 0.4 kg carbon monoxide per kg of methyl formate (Shouzu 2003)). In case of butylene glycol, the high energy consumption of the Reppe synthesis process is responsible for the high change in CED (Chauvel and Lefebre 1989a). The saturated diol is subsequently cyclized to tetrahydrofuran with elimination of water. This process step is material and energy intensive (1.3 kg butylene glycol per kg product because of the mass loss due to the removal of water from the chemical structure). In contrast, the production of formaldehyde and ethylene glycol dimethyl ether results in very low changes in the CED per kg product. The reason for this is that in both processes high shares of 40 to 50 wt % of raw materials with low CED are used (oxygen, ethylene oxide) in addition to the starting materials methanol and dimethyl ether.

The *naphtha/steam cracking route* (Route B, Fig. 3) is the most diverse solvent production route and also provides a variety of important starting materials for synthesis routes of chemical product groups, such as ethene (worldwide production of $80*10^6$ tonnes in 1996 (Zimmermann and Walzl 2002)) or propene (worldwide production of $30*10^6$ tonnes in 1990 (Eisele and Killpack 2002)). Processes that lead to high changes in the CED in this route are the hydroformylations to produce pentanol, isoamyl alcohol, and isobutanol as well as the production of dioxane.

With regard to the hydroformylation processes, important contributions to the high change in the CED arise out of the large amounts of starting materials that are needed, as well as the high use of synthesis gas and energy (Chauvel and Lefebre 1989a). The production of dioxane includes the dehydration and ring closure of diethylene glycol. As in the case of tetrahydrofuran, this process is material and energy intensive (1.3 kg diethylene glycol per kg product for the removal of water from the chemical structure).

The esterification to isoamyl acetate, isobutyl acetate, and butyl acetate, as well as the hydrogenation to propanol and the addition of methanol for the production of MTBE, show only a low increase of the CED per kg product
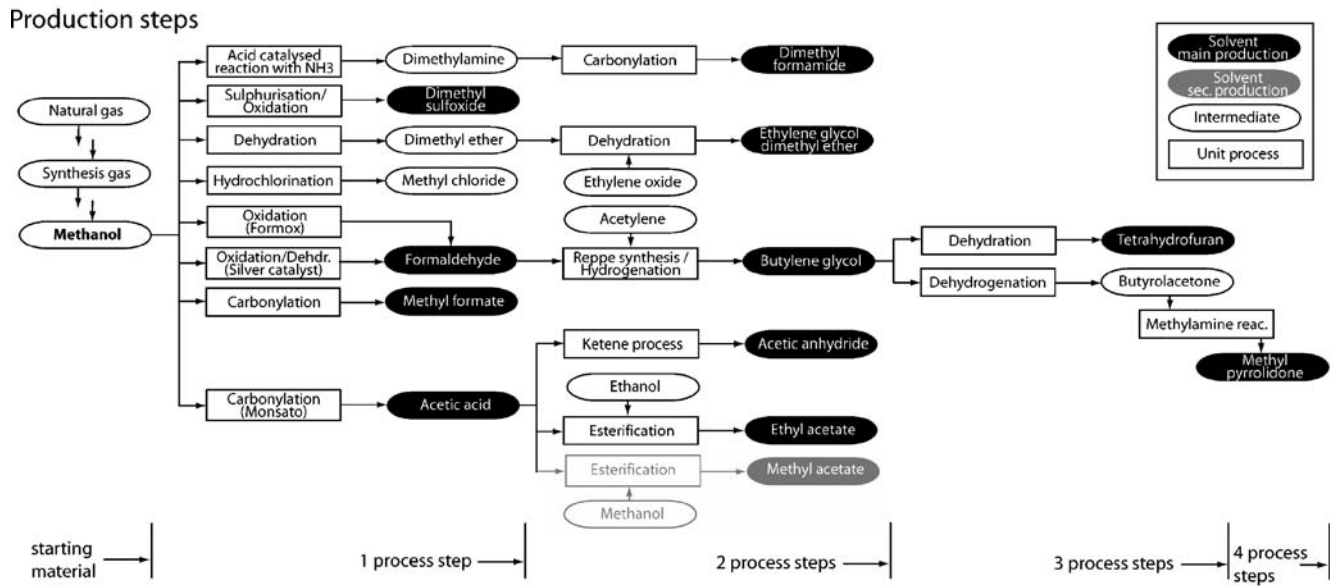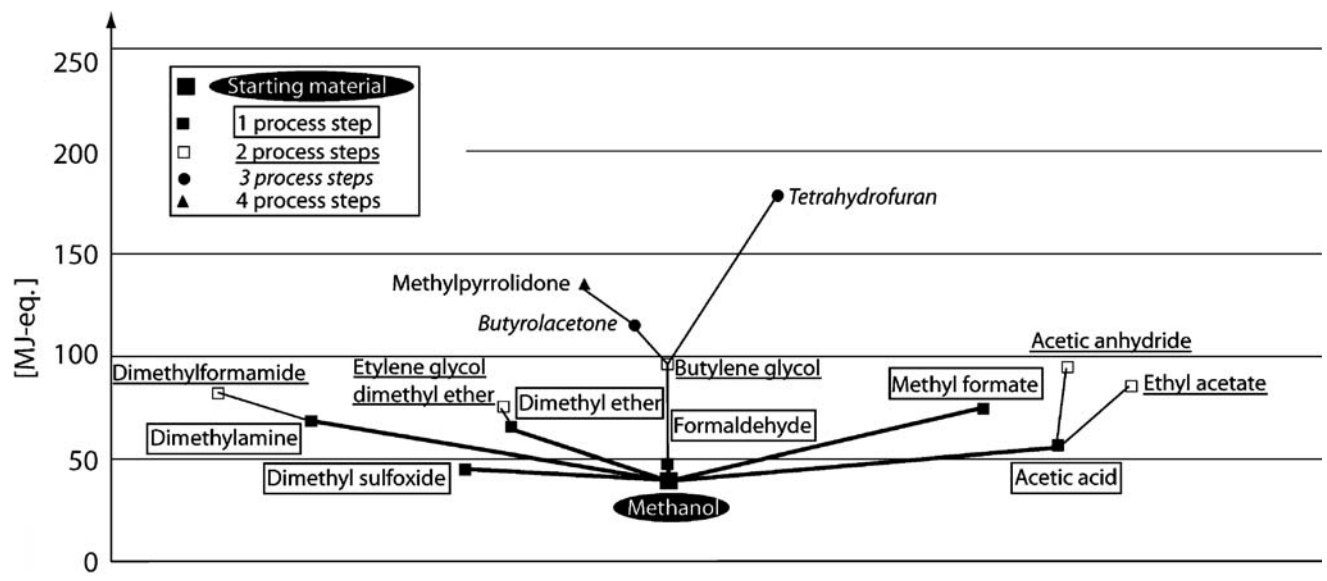
Fig. 2 Process steps and energy profile of the *methanol route*

because ancillaries with CED values similar to the educts are needed for these reactions (acetic acid, hydrogen, methanol). Negative changes in the CED result from the oxidation to formic acid, methyl acetate, and ethylene oxide as well as from the hydration to diethyl ether, ethanol, and diethylene glycol. This is possible because the reference unit in the figures is always 1 kg of solvent, and oxygen as well as water as reactants only feature a small CED compared to the CED of the educts.

The *BTX/naphtha separating route* (Route C, Fig. 4) is characterized by processes that cause low changes in the

CED because no ancillaries are needed, the processes operate very efficiently and only little energy is required (Kim and Overcash 2003; U.S. Department of Energy 1998).

The *BTX splitting route* (Route D, Fig. 5) includes two processes that cause high changes in the CED: The productions of benzaldehyde and methyl isobutyl ketone. With regard to the former process, a high amount of benzal chlorine as starting material is required (1.6 kg per kg of benzaldehyde) due to the removal of chloride in this process (Brühne and Wright 2004). For the latter process,
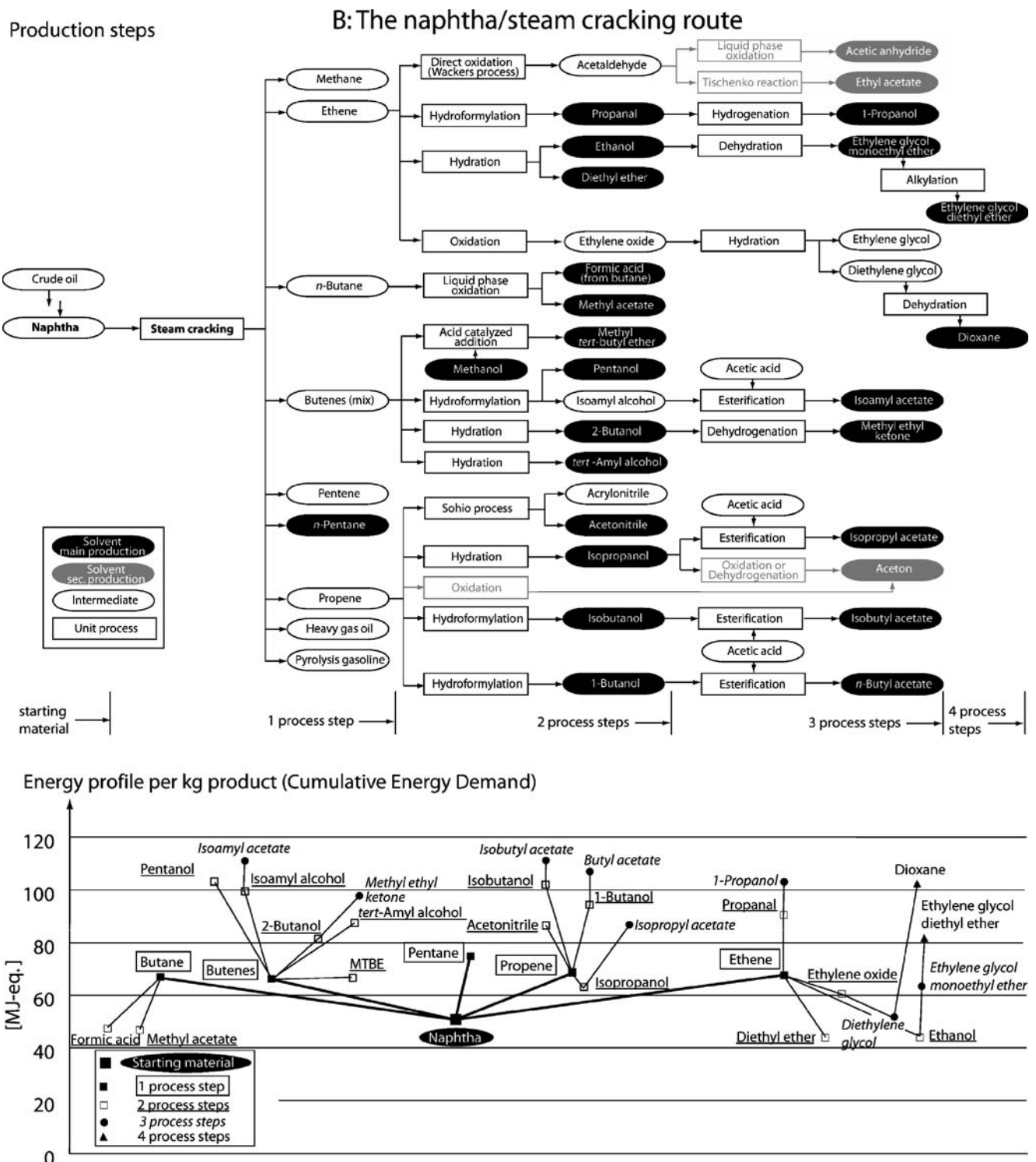
Fig. 3 Process steps and energy profile of the *naphtha/steam cracking route*

high amounts of acetone and hydrogen as starting materials are needed for the conversion to methyl isobutyl ketone (totally 1.5 kg per kg MIK (Overcash 1998)).

In comparison to these processes, the production of benzal chloride, benzyl chloride, cyclohexane, ethyl ben-

zene, cumene, phenol, acetone, and monochlorobenzene causes only low or even negative changes in the CED due to high shares (30 to 50 wt%) of raw materials with low CED (chloride, oxygen, hydrogen, ethylene, propylene) in addition to the starting materials toluene and benzene.

Fig. 4 Process steps and energy profile of the *BTX/naphtha separation route*
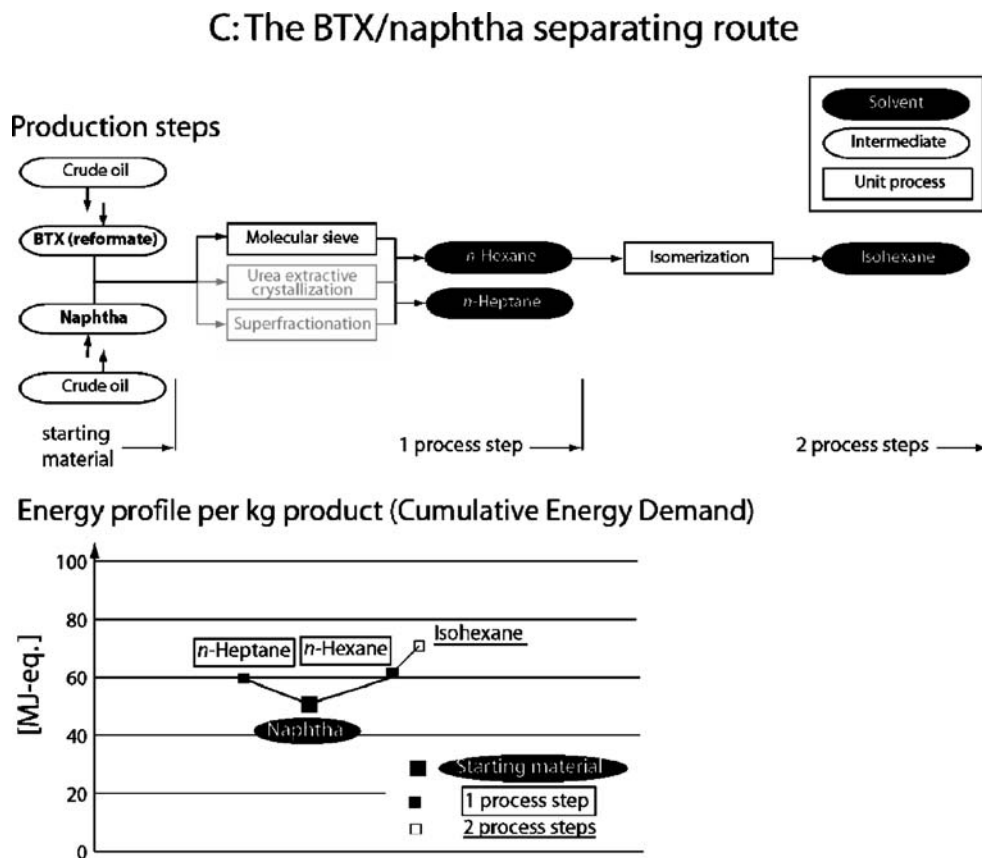
3.3 Unit processes: general results

In order to provide generally applicable results for the estimation of environmental impacts of other chemical products and intermediates, CED values of all unit processes presented in Figs. 2, 3, 4 and 5, such as esterification or chlorination, are investigated in detail. Results of the environmental impact are expressed per mole of product of the unit processes. The CED of a product i ($CED_{p,i}$, in MJ-eq./mole product) is composed of the CED of a specific unit process j ($CED_{u,j}$, in MJ-eq./mole product) that includes energy, ancillary, and resource use of the last step to product i, the CED of the educt ($CED_{e,i}$ in MJ-eq./mole educt) and the amount of educt ($m_{e,j}$, in kg educt/mole product) that is required in the unit process j (Eq. 1). As educt, we consider the solvent or intermediate that serves as starting material for the unit process, as shown in Figs. 2, 3, 4 and 5.

$$CED_{p,i} = CED_{u,j} + CED_{e,i} \cdot m_{e,j} \qquad (1)$$

$CED_{u,j}$ and $m_{e,j}$, values are unit process specific parameters. Data ranges of these parameters are presented in Table 2 for all unit processes that are part of the four solvent production routes and for which at least 2 data points are known. Detailed information of all investigated

process steps is provided in the supporting information (Table SI-1).

Many unit processes show similar results. The processes for which an adequate number of unit process data were available are shown in Table 2. However, some tendencies can be identified: First, unit processes show high CED values ($CED_{u,j}$) if complex, energy-intensive ancillaries are used, such as acetic acid (esterification) or alkyl groups (alkylation) or if the processes are energy-intensive (carbonylation, hydroformylation). Low CED values result if ancillaries with low CED values are used in unit processes (hydration, hydrogenation, hydrolysis, oxidation) and if no ancillaries and only little energy are needed (molecular sieve separation, dehydrogenation). However, also these unit processes may cause high CED values if purification steps of the product are required (high energy demand for distillation processes) or if the yield of the reaction is low (high demand on raw material).

The amount of educt needed ($m_{e,j}$) is directly related to the stoichiometry of the chemical reaction in a unit process. On the one hand, unit processes in which parts of the chemical molecules are removed (dehydration, dehydrogenation, hydrolysis) require a high amount of educt. In these unit processes, the CED of the educt ($CED_{e,i}$) strongly
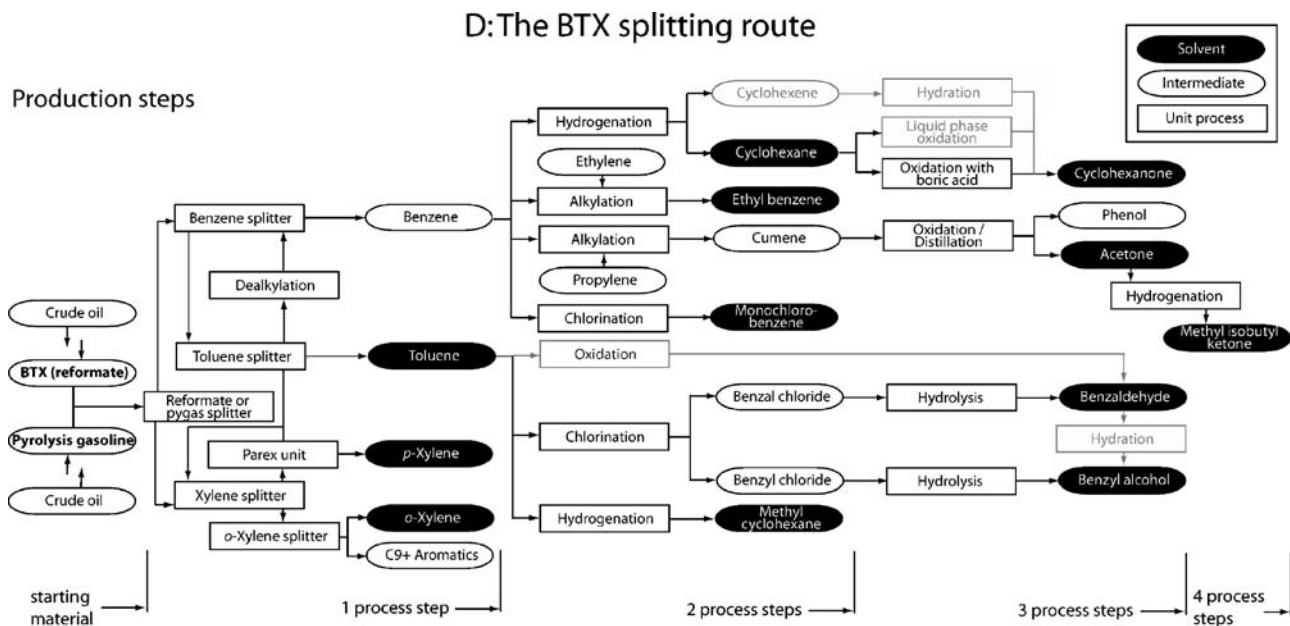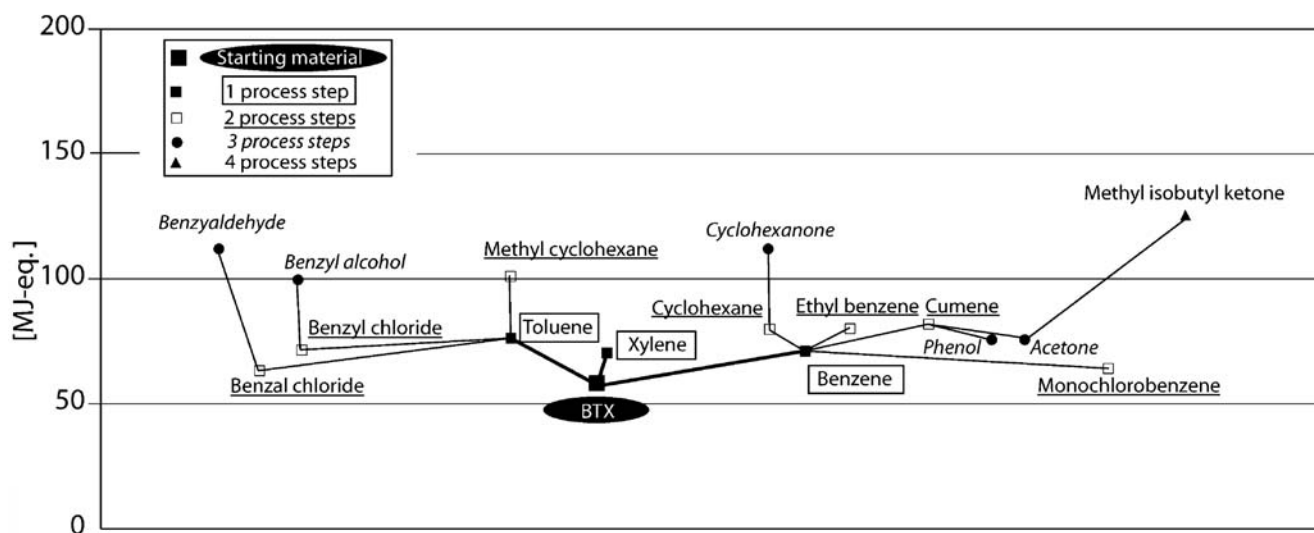
Fig. 5 Process steps and energy profile of the *BTX splitting route*. The CED of the BTX reformate is a rough estimation. CED scores for Toluene, Xylene, and Benzene, however, are based on cumulated industry data of high quality (see ecoinvent (ecoinvent Centre 2004))

influences and often dominates the CED of the product. On the other hand, unit processes in which ancillaries are added require a little amount of educt and the $CED_{u,j}$ is therefore more important for the total CED ($CED_{p,i}$) of the product (e.g., hydration, oxidation).

As all products have been purified by drying, extraction or distillation, for instance, this is considered to be part of the process step and the results in Table 2 reflect the values for the process including purification of the product.

3.4 Comparison of the CED results with other impact assessment methods

In order to verify whether the CED is a suitable indicator for the environmental impact of the petrochemical solvent production, the 50 selected solvents (see Table 1) were also assessed with the Global Warming Potential (GWP, 100 year perspective (IPCC 2001)) and the Eco-indicator 99 (Ei-99) method (hierarchist perspective (Goedkoop and Spriensma 2000)). Both impact assessment methods correlate with the

Table 2 Unit process specific results (CED values and amounts of educt)

Unit process j	Description	CED$_{u,j}$ [MJ-eq. / mole product]			m$_{e,j}$ [kg educt / mole product]			Data points
		Min	Max	Average	Min	Max	Average	
Alkylation	Replacement of a hydrogen in a chemical structure by an alkyl group (e.g., methyl, ethyl groups).	2.79	3.97	3.38	0.081	0.082	0.081	2
Carbonylation	Addition of carbon monoxide in a chemical structure.	2.20	5.19	3.20	0.031	0.112	0.063	3
Chlorination	Addition of chlorine in a chemical structure.	1.95	3.07	2.38	0.072	0.093	0.086	3
Dehydration	Removing of water from a chemical structure.	0.38	3.69	2.82	0.067	0.118	0.094	6
Dehydrogenation	Removing of hydrogen from a chemical structure.	0.56	0.69	0.62	0.080	0.086	0.083	2
Esterification	Reaction of an acid with an alcohol to form an ester.	4.88	5.59	5.26	0.055	0.090	0.071	5
Hydration	Addition of water in a chemical structure.	0.29	3.01	1.14	0.029	0.070	0.056	6
Hydroformylation	Transformation of an olefin to an aldehyde.	3.32	5.32	4.22	0.029	0.056	0.050	5
Hydrogenation	Addition of hydrogen in a chemical structure.	0.67	2.12	1.43	0.058	0.142	0.095	4
Hydrolysis	Cleavage of a chemical structure using water.	1.64	1.17	1.40	0.127	0.169	0.148	2
Molecular sieve separation	Absorbance of chemical structures in the pore systems of the sieve.	0.52	0.59	0.56	0.089	0.100	0.094	2
Oxidation	Addition of oxygen in a chemical structure.	0.10	3.74	0.97	0.029	0.078	0.052	7

results of the Cumulative Energy Demand (Fig. 6), in particular the results of Eco-indicator 99. These findings correspond well with the results presented by Huijbregts et al. (2006) considering material production processes.

With regard to the GWP, outliers are observable: Dichloromethane shows a high GWP compared to the CED because of CFC-12 emissions (Boustead 1997). The production of butylene glycol requires a high amount of energy (Reppe synthesis, see Fig. 2) that originates partially from coal

combustion (European electricity and heat production mix). The low net calorific value (approx. 30 MJ/kg (Perry and Green 1998)) and therefore low CED of coal compared with its high share of carbon (80 to 90% (Perry and Green 1998)) leads to a relatively higher impact of the GWP. As a consequence of the use of butylene glycol as starting material for the production of methyl isobutyl ketone (MIK), MIK also has a relatively high GWP compared to the corresponding CED results.
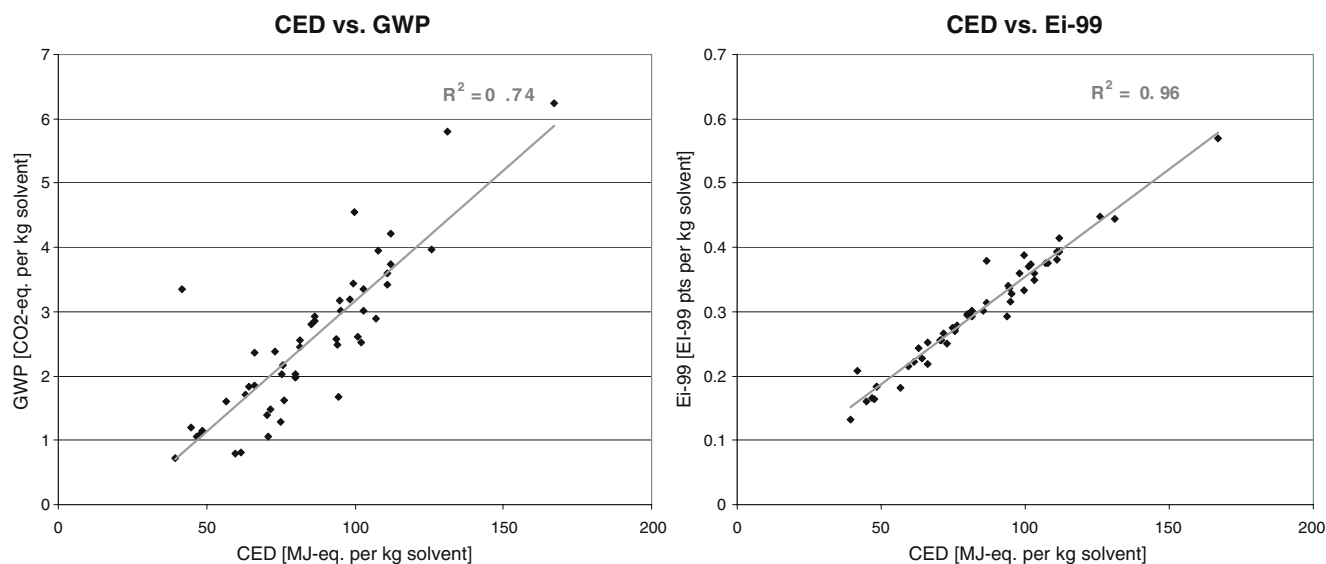
Fig. 6 Correlation of the CED values of the 50 selected solvents (Table 1) with the results of impact assessment methods of Global Warming Potential (100a) and Eco-indicator 99 (H/A)

4 Summary, discussion, and perspectives

The present paper provides a comprehensive overview on the environmental impact of petrochemical solvent production based on a selection of 50 important organic solvents. To conduct the LCA, new or updated Life Cycle Inventories were established for 40 out of the 50 solvents. The inventory data differ in terms of data quality. However, about half of the solvent inventories are based on reliable data taken from technical reference books or solvent manufacturers (see data quality indicators presented in Table 1). With regard to the other solvents, assumptions and estimations were made according to the ecoinvent guidelines (Frischknecht et al. 2005; Hischier et al. 2004) to provide transparent and reliable inventory data for these cases as well.

The graphical presentation of petrochemical process chains with focus on the solvent production gives a broad overview of the industrially relevant processes involved (Figs. 2, 3, 4 and 5). Such comprehensive process trees are novel since existing diagrams of petrochemical production pathways mainly focus on the refinery and on first generation intermediates (see e.g., Chauvel and Lefebre 1989b; Asinger 1971; Schmidt and Romey 1981)). The energy profiles of the four solvent production routes allow for an identification of key processes with regard to the environmental impacts of petrochemical solvent production processes. Such key processes are the dehydration of butylene glycol to tetrahydrofuran, the carbonylation of methanol to methyl formate, the hydrogenation of acetone to methyl isobutyl ketone, and the Reppe synthesis from formaldehyd/ acetylene to butylene glycol (see Figs. 2 and 3).

Generally applicable results for unit processes used in the chemical industry are presented (see Table 2). Although many unit processes show similar results, some tendencies can be identified. On the one hand, esterification and alkylation processes cause high CED values because complex ancillaries are needed ($CED_{u,j}$ of 5.26 and 3.38 MJ-eq. per mole of product, see Table 2) and hydroformylation and carbonylation processes are energy-intensive ($CED_{u,j}$ of 4.22 and 3.2 MJ-eq. per mole of product, see Table 2). On the other hand, in hydration, hydrogenation, hydrolysis, and oxidation processes, ancillaries with low CED are added to the chemical structure that result in low CED ranges for these unit processes ($CED_{u,j}$ of 0.97 to 1.43 MJ-eq. per mole of product, see Table 2). And finally, dehydrogenation and molecular sieve separation processes seem to be energy efficient and no ancillaries are required. Therefore, these unit processes cause the lowest increase in CED values ($CED_{u,j}$ of 0.62 and 0.56 MJ-eq. per mole of product, see Table 2). However, ranges of $CED_{u,j}$ values per unit process can vary largely, e.g., from 0.38 to 3.69 MJ-eq. per mole of product in case of dehydration processes. Such observations indicate that the environmental impact of a process step in the petrochemical industry is, on the one hand, influenced by the general characteristic of the chemical reaction that is conducted in a unit process (e.g., addition of a specific ancillary in the chemical structure). On the other hand, particularly high amounts of input material due to low reaction yield, the use of highly complex ancillaries or energy-intensive purification steps of the product can dominate the overall result for a specific reaction. The results in this paper are a first attempt to present unit process specific environmental impacts. The determination of additional data points for all unit processes and a subsequent statistical analysis in order to derive reliable data ranges for all unit processes could be the subject of further research in this field.

Further potential applications of the presented process chains with the corresponding energy profiles as well as the unit process-specific changes in CED values are to use them as a starting point to establish Life Cycle Inventories of more complex chemicals or as approximations of additional petrochemical products and intermediates. Such approximations may help to abridge the large data gap that we are still facing today when it comes to inventory data of chemicals.

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