The efficiency of the manufacturing of chemical products through the overall industrial metabolism

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Abstract: This contribution reports a detailed efficiency analysis of the manufacturing of chemical products through the overall industrial metabolism. Based on the life cycle database of ecoinvent, we consider 26 plastics, 59 organic solvents, 33 inorganic chemicals as well as 12 plastic monomers and analyse their production efficiency by quantifying the raw materials extracted from natural environment. Based on the concept of exergy and the database of cumulative exergy extraction from the natural environment (CEENE), three indicators are used to determine the resource efficiency for each group: (1) exergy content of the final products, MJ exergy per kg product, (2) CEENE score, i.e. MJ raw materials extracted from natural environment per kg product, (3) cumulative degree of perfection (CDP), the ratio of the exergy of the final product to the CEENE value to make the product. Finally, a comparison in metabolic efficiency among different sectors is made.

The results show that the production of 1 kg plastics needs on average the largest input of natural resources, being 130.08 MJ. In contrast, the production of inorganic chemicals requires on average the lowest resource intake, being 43.56 MJ/kg. Overall, the fossil resources are the main natural resource base to manufacture the chemicals, with about 76% of the total requested exergy extracted from the environment.

The study has also shown that in the production of plastics, organic solvents and plastic monomers, these industrial chemicals processes are quite efficient if they are compared to natural processes. In these three groups the average CDP values are all higher than 30%. However, in the production of inorganic chemicals, the production efficiency is quite low (8.99%), as it is compared with other groups.

Keywords: chemicals, plastics, industrial metabolism, exergy, Cumulative Exergy Extracted out of the Natural Environment (CEENE)

1. Introduction

Today, people enjoy a set of chemical products that are delivered through an industrial complex network. It is obvious that the resources that are the basis for this production chain are limited. A number of them such as fossil fuels are exhaustible. So, in this sense sustainable technology should be able to maximize the conversion efficiency of resources into products. The method to quantify the efficiency is based on thermodynamics: exergy. Exergy has been put forward as an indicator for the quality of resources. Exergy measures are traditionally applied to assess efficiency, regarding the exergy losses in a process system. However, the measure can be utilised as an indicator of resource quality demand when considering the specific resources that contain the exergy. Such an exergy measure indicates the required resources and assesses the total exergy removal from nature in order to provide a product, process or service. In this work, the exergetic content of the final chemical products is quantified. At the same time, the cumulative exergy extracted out of the natural environment as resources are quantified.

Based on the life cycle database of ecoinvent, different subgroups of chemical products are considered (plastics, organic solvents, inorganic chemicals and plastic monomers). Next to the efficiency, a distinction will be made for the kinds of resources which are used in the conversion processes to show the bottlenecks and opportunities for each sector.

2. Material and methods

2.1 Materials studied

The ecoinvent LCA database, which contains over 3900 datasets of products and services (processes), is the product of the Swiss Centre for Life Cycle Inventories. In order to quantify the resources which are extracted out of the natural environment, based on the life cycle data of ecoinvent, different groups are considered, such as plastics, organic solvents, inorganic compounds and plastic monomers. As for each group, some major products are studied as presented below. In the group of plastics, it should be noticed that some polymers have more than one type of final products. To produce each type of those products, the specific manufacture processing is required. For polyethylene (PE), for example, there are three different types of final plastics, such as high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). All reactions for the production of plastics, organic solvents, inorganic compounds and plastic monomers are provided in specific ecoinvent report [1].

The list of plastics which are selected from ecoinvent database are: acrylonitrile-butadiene styrene, ethylene vinyl acetate, nylon 66, polybutadiene, polyethylene terephthalate, polyethylene HDPE, polyethylene LDPE, polyethylene LLDPE, polymethyl methacrylate, polypropylene, polystyrene EPS, polystyrene GPPS, polystyrene HIPS, polyvinyl chloride, polyvinylidene chloride, terephthalic acid, styrene-acrylonitrile copolymer, polyphenylene sulfide,

The list of plastic monomers which are selected are: acrylic acid, vinyl chloride, bisphenol A, propylene, butadiene, styrene, butane, toluene diisocyanate, ethylene, vinyl acetate, methyl methacrylate, methylene diphenyl diisocyanate.

The following organic solvents are analysed: 1-pentanol, cyclohexane, 2-butanol, cyclohexanone, 2-methyl-1-butanol, diethyl ether, 2-methyl-2-butanol, dimethyl sulfoxide, 2-methylpentane, dimethylamine, 3-methyl-1-butanol, dioxane, 3-methyl-1-butyl acetate, ethylene glycol, diethyl ether, 4-methyl-2-pentanone, ethylene glycol dimethyl ether, N,N-dimethylformamide, dichloromethane, N-methyl-2-pyrrolidone, ethanol, acetic acid, ethyl acetate, acetic anhydride, formic acid, acetonitrile, isobutyl acetate, acrylonitrile, isopropyl acetate, benzal chloride, methyl formate, monochlorobenzene, propanal, o-dichlorobenzene, butyl acetate, tetrahydrofuran, benzaldehyde, butane-1,4-diol, benzyl alcohol, methylcyclohexane, benzyl chloride, acetone, isopropanol, 1-butanol, methanol, ethylene glycol, monoethyl ether, methyl ethylketone, ethyl benzene, methyl tert-butylether, formaldehyde, pentane, toluene, xylene, hexane, heptane, methylcyclohexane, isobutanol, isohexane, methyl acetate and 1-propanol.

The list of inorganic chemicals selected is: ammonia (partial oxidation), ammonia (steam reforming), ammonium bicarbonate, calcium carbide, calcium chloride, carbon monoxide, hydrochloric acid 30%, ammonium chloride, diborane, iron (III) chloride 40%, lithium hydroxide, lithium chloride, nitric acid 50%, phosphoric acid 70%, phosphoric acid 85%, phosphoryl chloride, potassium carbonate, potassium perchlorate, sodium carbonate, sodium chlorate, sodium chloride brine solution, sodium chloride powder, sodium hydroxide 50%, sodium hypochlorite, sodium perchlorate, sodium sulphate and sulphuric acid.

2.2 Methods

The calculation of the exergetic content for each plastic, plastic monomer and solvent was performed either by using the group contribution method or directly taking from the reference of Szargut [2]. In the group of inorganic compounds, the exergy data of a part of products are directly obtained from [2]. If not available, the chemical exergy can be calculated on the basis of the chemical formation reaction, utilising the Gibb's free energy of formation ΔG_r (kJ/mol) [3].

Extraction of resources out of the environment is considered in order to quantify the Cumulative Exergy Extraction from the Natural Environment (CEENE) for virgin production. In CEENE, the acquired data set is coupled with a life cycle inventory database, ecoinvent. CEENE consists of eight categories of resources withdrawn from the natural environment: renewable resources, fossil fuels, nuclear energy, metal ores, minerals, water resources, land resources, and atmospheric resources. CEENE calculation has been illustrated in previous work [4]. The reference state for the environment in the calculations is taken as in [2]. The CEENE data for the different products are obtained from the CEENE database developed by Dewulf et al. [4].

When analyzing the production of materials and energy flows, in order to assess the thermodynamic efficiency of production process, the CEENE value can be compared with the exergy of the product, as a measure of efficiency. The ratio between the specific exergy content of the product itself and the CEENE is defined as the Cumulative Degree of Perfection (CDP). The higher the CDP is, the higher the thermodynamics perfection degree of the overall industrial system is.

3. Results and discussion

3.1 Plastics

The chemical exergies of 26 plastics are calculated straightforward as (MJ/kg): acrylonitrile-butadiene-styrene copolymer (ABS): 40.37, ethylene vinyl acetate (EVA 1, copolymer): 29.37, ethylene vinyl acetate (EVA 2, film): 29.37, nylon 6 (1): 33.00, nylon 6 (2, glass filled): 33.00, nylon 66 (1): 33.00, nylon 66 (2, glass-filled): 33.00, polybutadiene (PB): 45.16, polyethylene terephthalate (PET 1, amorphous): 23.76, polyethylene terephthalate (PET 2, bottle grade): 23.76, high density polyethylene (HDPE): 46.44, low density polyethylene (LDPE): 46.44, linear low density polyethylene LLDPE: 46.44, polymethyl methacrylate (PMMA 1, beads): 27.16, polymethyl methacrylate (PMMA 2, sheet): 27.16, polypropylene (PP): 46.31, polystyrene (EPS): 41.95, general purpose polystyrene (GPPS): 41.95, high impact polystyrene (HIPS): 41.95, polyvinyl chloride (PVC 1, bulk polymerised): 19.81; polyvinyl chloride (PVC 2, emulsion polymerised): 19.81, polyvinyl chloride (PVC 3, suspension polymerised): 19.81, polyvinylidene chloride (PVDC): 12.28, terephthalic acid (TPA): 20.85, styrene-acrylonitrile (SAN): 38.72, polyphenylene sulfide (PPS): 34.69.

The CEENE values and the fraction in total exergy inputs are presented in table 1.

Table 1 CEENE values and fraction of fossils for plastics

Product	CEENE (MJ/Kg)	Fossil (%)
ABS	106.02	87.76
EVA(1)	86.67	85.78
EVA(2)	113.26	72.97
Nylon 6(1)	136.83	87.90
Nylon 6(2)	121.98	79.95
Nylon 66 (1)	168.38	72.79
Nylon 66(2)	136.09	73.88
PB	100.53	95.14
PET(1)	87.25	82.39
PET(2)	92.71	80.55
HDPE	78.40	91.79
LDPE	80.94	87.79
LLDPE	80.03	88.45
PMMA(1)	132.24	91.43
PMMA(2)	148.95	88.94
PP	76.93	92.09
EPS	97.93	87.73
GPPS	94.78	89.37
HIPS	95.07	89.32
PVC(1)	59.26	68.09
PVC(2)	93.99	54.82
PVC(3)	81.20	57.56
PVDC	87.40	72.83
TPA	63.51	85.26
SAN	101.50	89.12
PPS	860.35	85.37

Eight different categories of resources withdrawn from the natural environment for producing the target product are shown in figure 1. It is obvious that exergy extraction for plastics made from polymers is dominated by exergy from fossil energy to provide the typical fuels and feedstocks with an average of 81%. However, the second largest exergy source for each plastic production is not the same in the CEENE categories, such as nuclear energy or water resources. The difference in categories can be explained by the fact that the manufacture processing and systems needed are different to achieve the specific properties of the plastics.

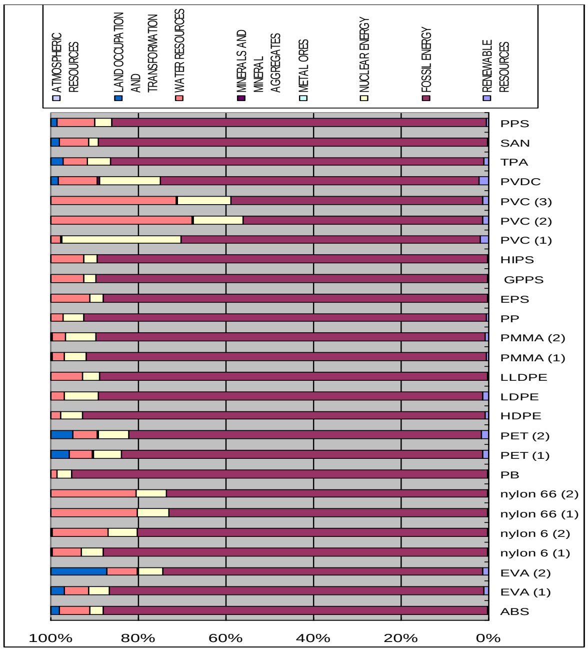

Figure 1 Comparison of the composition of CEENE for 26 plastics productions

In order to evaluate the thermodynamic efficiency of production process, the CDP values of all plastics products are separated into two groups, as represented in Figure 2.

In group (1), PP has the highest CDP value (60.2%) and the lowest one is PS (42.83). The average is 51.37%. In group (2), the range of CDP values is between 38.18% (ABS) and 14.04% (PVDC), except for PPS (4.03%).

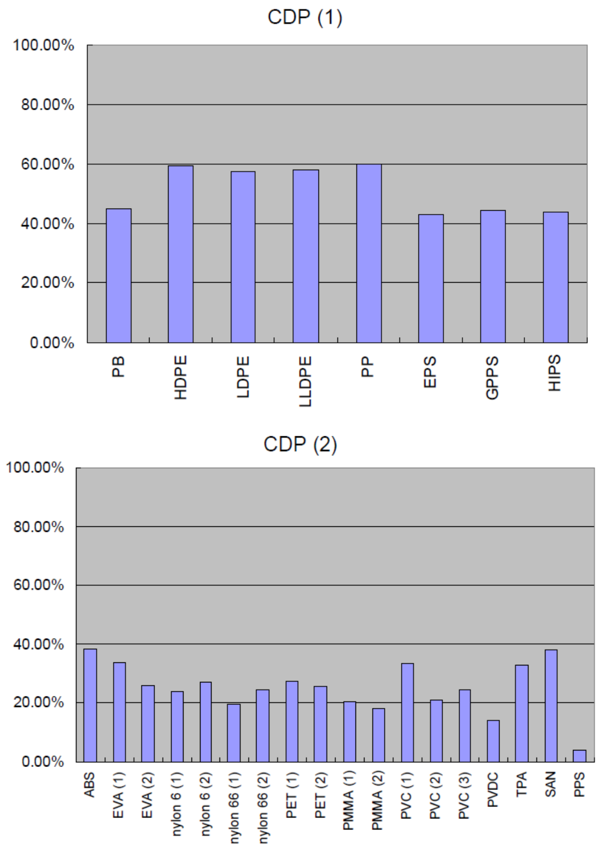

Figure 2 CDP values of plastics

The difference in the chemical exergy among polymers can be caused by the chemical structure or different degree of chemical reactions such as oxidation. In order to deliver the necessary materials and energy to the plant for the production of plastics, the industry has to extract a number of resources out of the environment. Based on the ecoinvent and CEENE database, these resources have been quantified in exergy terms. They all require exergy inputs between 59.26 (bulk PVC) and 168.38 (nylon 66) MJ per kg polymer, except for PPS (860.35 MJ/kg). The higher value for PPS is due to higher requirements of chemical inputs during the manufacturing process. To summarise the average shares of eight categories of resources intake ways within 26 plastics, it has shown that the major contribution to the CEENE scores is due to fossil energy (crude oil depletion and natural gas), accounting for instance, for 92.09% of the total in the case of PP. Secondly, in terms of thermodynamic efficiency, 32.88% (mean of CDP values) of the exergy intake is found back in the target product in case of the plastics industry.

3.2 Plastic monomers

The chemical exergy of 12 plastic monomers (MJ/kg) are calculated as: acrylic acid: 19.44, Methylene diphenyl diisocyanate: 30.16, bisphenol A: 35.02, propylene: 47.47, butadiene: 46.06, styrene: 42.42, butane: 47.22, toluene diisocyanate: 25.71, ethylene: 48.17, vinyl acetate: 24.38, methyl methacrylate: 27.51, vinyl chloride: 20.60. They range between 19.44 (acrylic acid) to 48.17 (ethylene) MJ/kg.

With respect to the CEENE values (Table 2), monomers require exergy inputs between 68.25 MJ/kg (butene) and 153.12 MJ/kg (bisphenol A). In the production of bisphenol A, one of the most important processes is the catalysed condensation of phenol and acetone. Such a reaction takes place at about 50 to 90 ℃ with a molar ratio of phenol-acetone of 15:1. An input amount of 0.916 kg phenol and 0.283 kg acetone are required for the production of 1 kg of bisphenol A. According to the analysis with respect to total resource inputs from technosphere in terms of exergy, it turns out that chemicals going into the manufacturing process of bisphenol A are predominant with a share of 81.10% of the total intake, 103.98 MJ (phenol) and 20.20 MJ (acetone), respectively, for the production of 1 kg of bisphenol A.

Eight categories of resources withdrawn from the natural environment for the production of 1 kg plastic monomers are shown in the figure 3. It can be seen that except for the fossil energy, only inputs of water resources and nuclear energy exhibit an important share of the total CEENE score. Depending on the plastic monomer, water resources make up between 1.34% (butadiene) and 27.03% (vinyl chloride) of the total exergy demand, with an average contribution of 8.41%.

A comparison of the cumulative degree of thermodynamic perfection (CDP) learns that ethylene, butene, butadiene and propylene exhibit the highest scores (65-70%). For the rest of the plastic monomers, the CDP scores are in the range of 21.05% (toluene diisocyanate) to 43.60% (styrene). The lowest CDP in the toluene diisocyanate is mainly due to the complex manufacturing process.

Table 2 CEENE values and fraction of fossils for monomers

Product	CEENE (MJ/kg)	Fossil (%)
Acrylic acid	69.32	89.03
Bisphenol A	153.12	81.92
Butadiene	67.59	96.97
Butene	68.25	94.80
Ethylene	68.46	95.84
Methyl methacrylate	125.48	91.66
Methylene diphenyl diisocyanate	105.97	76.48
Propylene	69.95	95.79
Styrene	97.29	85.39
Toluene diisocyanate	122.13	74.70
Vinyl acetate	79.53	77.19
Vinyl chloride	72.12	58.86

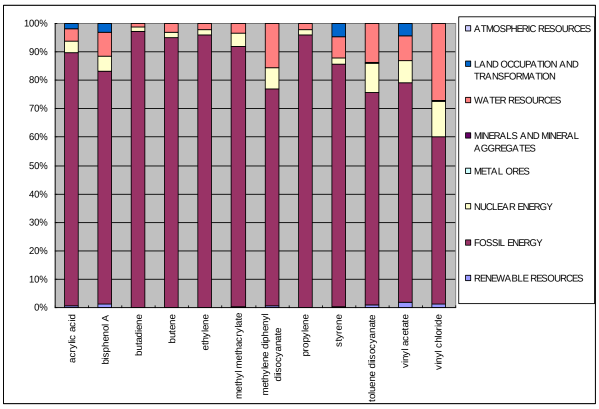

Figure 3 CEENE fingerprint of monomers

3.3. Organic solvents

For organic solvents, chemical exergies are not shown as this can be calculated straightforward. In Table 3, CEENE values are represented and in Figure 4 CEENE compositions.

Table 3 CEENE values and share of fossils for organic solvents

Product	CEENE (MJ/kg)	Fossils (MJ/kg)
1-pentanol	113.51	94.29
2-butanol	126.94	94.80
2-methyl-1-butanol	113.51	94.29
2-methyl-2-butanol	120.30	105.47
2-methylpentane	65.82	60.49
3-methyl-1-butanol	113.51	94.29
3-methyl-1-butyl acetate	130.23	105.01
4-methyl-2-pentanone	126.39	107.30
N,N-dimethylformamide	65.51	50.82
N-methyl-2-pyrrolidone	113.69	76.46
Acetic acid	62.03	47.06
Acetic anhydride	113.40	74.91
Acetonitrile	75.40	58.99
Acrylonitrile	95.41	86.02
Benzal chloride	83.27	59.45
Monochlorobenzene	494.23	433.04
O-dichlorobenzene	494.22	433.03
Tetrahydrofuran	170.75	111.83
Butane-1,4-diol	129.76	86.04
Methylcyclohexane	129.25	115.36
Cyclohexane	83.23	73.98
Cyclohexanone	118.14	102.20
Diethyl ether	50.63	46.48
Dimethyl sulfoxide	61.67	52.86
Dimethylamine	45.34	38.57
Dioxane	101.02	70.14
Ethylene glycol diethyl ether	103.45	76.05
Ethylene glycol dimethyl ether	82.84	69.43
Ethylene glycol monoethyl ether	73.63	62.05
Ethanol	50.66	46.50
Ethyl acetate	93.50	76.31
Formic acid	85.51	58.13
Isobutyl acetate	112.14	92.45
Isopropyl acetate	99.65	81.57
Methyl formate	113.11	80.33
Propanal	106.90	85.63
Butyl acetate	117.09	97.90
Benzaldehyde	146.67	104.81
Benzyl alcohol	122.72	90.01
Benzyl chloride	84.23	65.15

It can be seen that monochlorobenzene and o-dichlorobenzene have the highest CEENE values, 494.23 MJ/kg and 494.22 MJ/kg. The average CEENE value in the group of organic solvents is 103.98 MJ for producing 1 kg product. It turns out that fossil energy is the major input source, in the case of 1-pentanol, accounting for 83.07% of the total exergy inputs. Eight main intakes for the production of 1kg target organic solvent are calculated in the form of percentage (%) as presented in the figure 4.

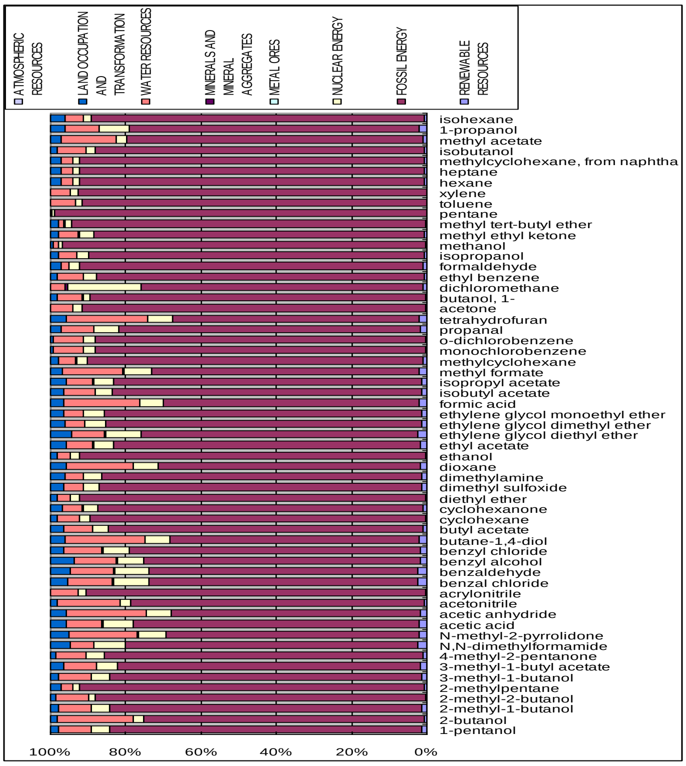

Figure 4 CEENE composition of solvents

Dimethylamine, diethyl ether, hexane, 2-methylpentane, heptane, methylcyclohexane, isohexane, toluene, methyl tert-butyl ether and xylene exhibit high CDP: above 60%. Overall low scores of CDP for methyl formate, acetic anhydride, formic acid, monochlorobenzene and o-dichlorobenzene are 14.76%, 11.29%, 7.41%, 5.78% and 4.33%, respectively. For the rest of organic solvents in the group, the values of CDP are in the range from 60% to 20%, in which the methanol has the highest value and the lowest one is for tetrahydrofuran, 58.44% and 20.37%, respectively. In the whole group of organic solvents, the average value of CDP is 38.95%.

3.4. Inorganic chemicals

Whereas exergy value calculations are straightforward (results not shown), CEENE values and share of fossils are presented in Table 4.

Table 4. CEENE values and fossil contribution for inorganic chemicals.

Product	CEENE (MJ/kg)	Fossil (%)
Ammonia (1)	56.52	92.20
Ammonia (2)	41.99	92.88
Ammonium bicarbonate	37.08	48.54
Calcium carbide	80.05	63.71
Calcium chloride	20.55	46.23
Carbon dioxide	14.59	61.00
Carbon monoxide	67.59	75.45
Hydrochloric acid	24.68	48.62
Ammonium chloride	89.59	61.39
Diborane	72.41	51.10
Iron (III) chloride	25.21	43.63
Lithium hydroxide	24.70	56.68
Lithium chloride	54.19	47.98
Nitric acid	15.65	83.07
Phosphoric acid (1)	47.65	25.18
Phosphoric acid (2)	57.65	31.22
Phosphoryl chloride	100.64	49.68
Potassium carbonate	53.79	59.49
Potassium perchlorate	133.07	48.85
Sodium carbonate	25.72	66.10
Sodium chlorate	84.94	45.91
Sodium chloride (1)	4.11	43.80
Sodium chloride (2)	5.67	44.09
Sodium hydroxide (1)	37.57	39.93
Sodium hydroxide (2)	27.99	46.45
Sodium hydroxide (3)	29.94	46.76
Sodium hydroxide (4)	31.32	44.70
Sodium hypochlorite	24.03	49.94
Sodium perchlorate	118.77	47.15
Sodium sulphate (1)	13.87	52.63
Sodium sulphate (2)	3.75	48.00
Sodium sulphate (3)	10.98	61.02
Sulphuric acid	5.67	33.51

It can be seen that potassium perchlorate (133.07 MJ/kg) and sodium perchlorate (118.77 MJ/kg) exhibit high CEENE values. The inputs of fossils are often over 40% of the total exergy extraction from the natural environment, especially for ammonia, where the fossil energy is up to 90% of the total CEENE score. This is due to the fact that fossil energy is used both as fuel and feedstock in the production of ammonia. Ammonia is produced basically from natural gas (steam reforming).

It can be seen from Figure 5 that except for fossil energy, the inputs of water resources and nuclear energy as well as land occupation also take up an important share of the total intake. The exergy of land use contributes on the average to 12.60% the total exergy demand, but to more than 50% in the production of phosphoric acid. It is mainly due to the large amounts of raw materials (phosphate rock and sulphuric acid) and process water needed.

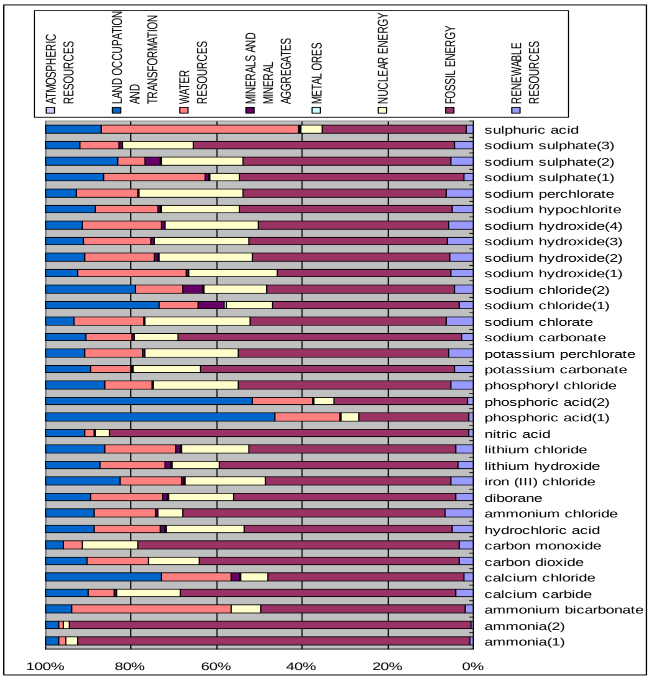

Figure 5 Composition of CEENE of inorganic chemicals

The CDP values are illustrated in Figure 6. They are obviously lower than for organics with a range of 0.93% to 50.50%, and an average value of 8.99%.

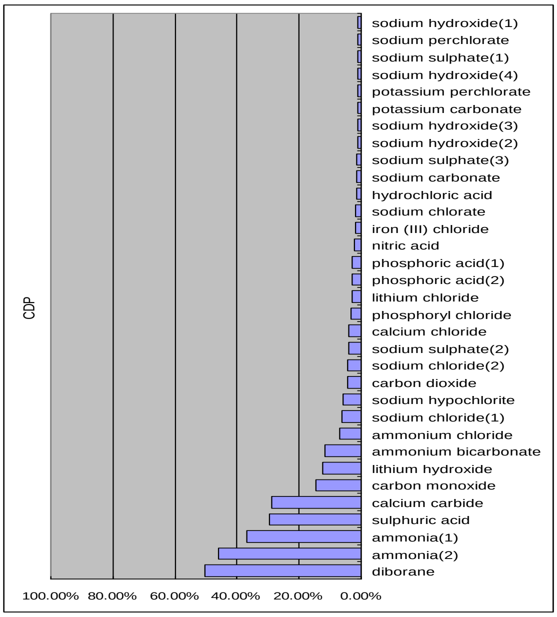

Figure 6 CDP values for inorganics

4. Conclusions

First of all, this work shows that the exergy concept can be operationalized in product life cycle assessments. Due to the consideration of the quality of energy and the integration of non-energetic resources, CEENE enables to account for very different natural resource intakes. This approach is helpful in substantiating the argument on sustainable use of the natural environment by humans: it expresses the physical chemical price the natural environment pays for the withdrawal toward our industrial society. Through the eight different resource categories, and the integrated development with the up-to-date life cycle inventory in ecoinvent, it shows the nature of the resources that are consumed in the chemical industry.

In terms of production efficiency, we have seen that plastics, organic solvents and plastic monomers are generally manufactured with efficient use of resources if they are compared to natural processes. In these three groups the average CDP values are all higher than 30%. The production of inorganic chemicals, the efficiency is quite low (8.99%). Overall, it can be stated that through combination of CEENE with an up-to-date life cycle inventory such as ecoinvent, decision-makers can obtain a comprehensive LCIA methods taking into consideration the impact of resource input as well as production efficiency.

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