Ranking of Refrigerants by Different Assessment Methods

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Key-words

Life Cycle Assessment, energy consumption, CFC-substitutes, refrigerants, partial order theory, mobile air conditioning, Kyoto Protocol

1. Introduction

All chemicals and products have certain impacts on the environment, e.g. according to their energy consumption, toxicity, and contribution to climate change. The aim of a life cycle assessment (LCA) is to investigate and evaluate the environmental impact of a product or service and to find the least harmful option. Because of its holistic nature, LCA is an important instrument for decision making in the environmental sector. For that reason, various approaches have been developed using different calculation factors (Dreyer et al. 2003, Gloria et al. 2006, Guinée et al. 2002, Goedkoop & Spriensma 2001).

Because of the commitments in the Kyoto Protocol, hydrofluorocarbons (HFC) and perfluorocarbons (PFC) must be phased out and suitable replacements must be found. This applies also to the air-conditioning systems (A/C) in passenger cars. In almost all A/C the refrigerant nowadays used is 1,1,1,2-tetrafluoroethane (R134a) with an annual market growth in Germany of about 4 %, the largest in the field of refrigeration and air-conditioning. According to the German Federal Environmental Agency (Schwarz 2005), the A/C sector of passenger cars is the main emission source of fluorinated greenhouse gases in 2002, followed by commercial and industrial refrigeration. In combination with the high fleet number of air-conditioned cars, and the fact that the percentage of passenger cars equipped with A/C is at 95 % (Schwarz 2005), this sector is of great interest regarding potential impact reduction for ozone depleting substances (ODS), greenhouse gases, and energy consumption. In the present work, the main focus is on comparison of three assessment methods, used to evaluate the environmental impact of refrigerants used in A/C by means of partial order.

2. Scope Definition of LCA

The application examined in this LCA study is an A/C system as functional unit of a standard European passenger car. Its function is to keep the passenger compartment at a comfortable temperature of about 20 °C. The technical outlay of the system is based upon the principle of liquid evaporation and vapour compression. They currently most commonly used refrigerant in A/C in passenger cars is R134a, the HFC R152a, the hydrocarbons (HC) R290 and R600a, and carbon dioxide (R744) are possible replacements. The environmental impact of dichloromethane (R30) was assessed for comparison. The hydrofluoroethers (HFE) E125, E134, E7000, E7100, and E7200 are included as well as they are of interest because of their thermodynamic properties. The chemical formulae and names are listed in Tab. 1.

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Refrigerant	Chemical formula	Chemical name
R30	CH_2Cl_2	Methylene chloride
R134a	$C_2H_2F_4$	1,1,1,2-Tetrafluoroethane
R152a	$C_2H_4F_2$	1,1-Difluoroethane
R290	C_3H_8	Propane
R600a	C_4H_{10}	Isobutane
R744	CO_2	Carbon dioxide
E125	$CF_3\text{-}O\text{-}CHF_2$	Pentafluorodimethyl ether
E134	$CHF_2\text{-}O\text{-}CHF_2$	1,1,1',1'-Tetrafluorodimethyl ether
E7000	$C_3F_7\text{-}O\text{-}CH_3$	Heptafluoropropyl methyl ether
E7100	$C_4F_9\text{-}O\text{-}CH_3$	Nonafluorobutyl methyl ether
E7200	$C_4F_9\text{-}O\text{-}C_2H_5$	Nonafluorobutyl ethyl ether

Tab. 1: Refrigerants applied to A/C system in the present study

The A/C system is operated with respect to average German climate conditions within a 10 years lifetime of the passenger car. In general, the scope of the LCA comprises input and output of production, operation (including servicing/refilling), and disposal phase. Inventory data are literature values. The main focus is on energy consumption during the operation phase of the A/C system, assuming that the additional fuel consumption due to the operation of the A/C system represents the amount of energy necessary to compress the refrigerant under defined cycle conditions. The energy input is represented by the change of enthalpy of the refrigerant during the process of compression. Under certain pressure and temperature conditions (Ghodbane 1999; Delphi Corporation 2006), this is calculated from data provided by the National Institute of Standards and Technology (NIST 2005), the database DIPR (Heberle 2007), and 3M (3M 2007). Calculation is in principle based on the well-known Mollier diagram. It is assumed that the A/C circuit's temperature profile and the efficiency of the A/C compressor are constant. Energy consumption due to operating fans and pumps are neglected as they do not depend on the refrigerant.

The energy consumption for compression is multiplied with the operation time of the A/C system. To estimate the system's operation time, the A/C operating model for Europe (Duthie et al. 2002), average monthly temperatures in Germany (WMO 2006), and the New European Driving Cycle (NEDC) are used. In Europe, 90 % of the drivers turn on their A/C system at an outside air temperature of 22 °C, which is the case in Germany, for 2 months or sixty days per year. The average mileage driven per year is 16,000 km; according to NEDC, two thirds are urban traffic (ca. 20 km/h) and one third is extra-urban traffic (ca. 60 km/h). Typical driving conditions in Germany are 1.5 h per day under urban and 0.24 h under extra-urban conditions. Consequently, the A/C system runs 104 h per year in this particular scenario.

Life cycle phase	Refrigerant emission	Average direct refrigerant emissions [% refrigerant charge]
Manufacture	Production of refrigerant	0.5
	Loading of tanks and bottles	2
	Charging of A/C system	2
Usage	Regular emissions	77
	Irregular emissions	33
Disposal	Disposal of End-of-Life vehicle	50
Total		164.5 of charge + 0.2 kg*)

*) Additional refrigerant for two servicing during lifetime (Schwarz/Harnisch 2003).

Tab. 2: Direct emission scenarios within the life cycle of an A/C system

The refrigerant leakage within the life cycle is set to be independent of the refrigerant but dependent on the different life stages. An average emission scenario is defined and the leakage rates of the different life phases were estimated (Tab. 2). The direct refrigerant emissions (in CO_2-equivalents) during the entire lifecycle are calculated using the direct emission scenario, the characteristic refrigerant charge of the A/C system, and the GWP_{100} of the different refrigerants. During the usage phase, the A/C is serviced and re-filled twice, resulting in an emission of 100 g refrigerant per service. The A/C is emptied and then refilled with new refrigerant.

The recovered refrigerants from servicing and end-of-life processes are burned assuming total combustion, resulting in H_2O, CO_2, HF, and HCl. For the inventory, the actual amount of the incineration products HF and HCl that are emitted to the atmosphere is set to 1 %, H_2O and CO_2 from incineration processes are completely released to the atmosphere.

3. Assessment Methods

Three different assessment methods were applied to the results of the life cycle inventory in order to find the least harmful refrigerant to the environment. The results of three methods, i.e. the Dutch Handbook method (CML02), Total Equivalent Warming Impact (TEWI), and Eco-Indicator 99 (EI99) are compared by means of partial order and the software WHASSE (Brüggemann et al. 1993, 1999a and b, 2001).

3.1 CML02

In this study, ten impact categories were considered following the mid-point assessment method CML02 (Guinée et al. 2002) to evaluate the environmental impact of certain refrigerants in A/C systems in cars:
- Demand of non-renewable primary energy (PE)
- Depletion of abiotic resources (excluding primary energy sources) (ADP)
- Climate change (GWP)
- Stratospheric ozone depletion (ODP)
- Human toxicity (HT)
- Photo-oxidant formation (POCP)
- Acidification (AP)
- Eutrophication (EP)

- Fresh water aquatic toxicity (FAETP)
- Terrestrial ecotoxicity (TETP)

3.2 TEWI

The so-called TEWI is the sum of the direct and indirect impacts on the global warming (FKT 2005). The direct TEWI component is determined by the refrigerant loss created by leakage and recovery loss, the indirect one by the energy consumption of the system. This concept has become widely used in valuating the environmental impact of refrigerant systems.

$$TEWI = \{L*m*T*GWP_{100}\} + \{z*x*GWP_{100}\} + \{GWP_{100}*m*((c+d)/100)\} + \{E*S_L*r*T\}$$

With:

L	average annual loss of refrigerant [% of refrigerant charge]
m	refrigerant charge [kg]
T	lifetime [years]
GWP_{100}	global warming potential in units CO_2, time horizon of 100 years
z	number of recharges/servicings per lifetime
x	refrigerant loss during recharge/servicing
c	refrigerant loss during production and charging
d	refrigerant loss during disposal
E	energy consumption [kWh/h]
S_L	annual operation hours [h/yr]
$r-$	emission of CO_2 + other greenhouse gases by energy generation [kg CO_2/kWh]

3.3 EI99

The EI99 is a damage-oriented impact assessment method for LCA which constitutes the basis for the calculation of eco-indicator scores for materials and processes (Goedkoop and Spriensma 2001). The endpoint method is divided into different steps such as fate, exposure, effect, and damage analysis which are combined in the damage factors which are applied to the emissions arising during the life cycle. Overall, the methodology is compatible with ISO 14042 requirements. The method includes normalisation and weighting of the three damage categories Human Health, Ecosystem Quality and Resources, resulting in one index.

4. Application of Partial Order

A partially ordered set (poset) formalizes the concept of a ranking of the elements of a set. It consists of a set endowed with an order relation that describes the precedence of one element over another for certain pairs of elements. Because some pairs of elements may not be ordered, a poset is not necessarily a total order. Such a poset can be visualised through its Hasse diagram.

Each of the ten impact categories of the CML02 method resulted in a specific ranking, as did EI99 and TEWI. Based on the ten indicators ADP, PE, ODP, GWP, AP, EP, HT, POCP, FAETP, and TETP of CML02 an average ranking (AV) was calculated, giving equal weights to every impact category. There-

fore, a ranking of the eleven refrigerants was set up without a numerical combination of the ten indicators. Hence, the average ranking can be compared with the ranking according to EI99 and TEWI (Tab. 3).

Refrigerant	CML02											EI99	TEWI
	ADP	PE	GWP	ODP	AP	EP	POCP	HT	FAETP	TETP	AV		
E125	5	8.5	11	3.5	1	1	1	1	9	9	5	10	11
E134	11	8.5	10	3.5	10	10	10	10	6	6	8.5	11	10
E7000	6	8.5	8	9	2	2	2	2	7	7	5.4	7	2
E7100	8	8.5	7	10	4	4	4	4	8	8	6.5	8	3
E7200	7	8.5	6	11	3	3	3	3	5	5	5.5	5	1
R134a	9	8.5	9	8	6	6	6	6	11	11	8.1	9	7
R152a	1	5	5	7	5	5	5	5	10	10	5.8	4	4
R290	2	1.5	3	3.5	7	7	7	7	2	2	4.2	1	5
R30	10	4	1	3.5	11	11	11	11	4	4	7.1	6	9
R600a	3	1.5	4	3.5	8	8	8	8	2	2	4.8	2	6
R744	4	3	2	3.5	9	9	9	9	2	2	5.3	3	8

ADP – Depletion of abiotic resources (excluding primary energy); PE – Demand of non-renewable primary energy; GWP – Climate change; ODP – Stratospheric ozone depletion; AP – Acidification; EP – Eutrophication; POCP – Photo-oxidant formation; HT – Human toxicity; FAETP – Fresh water aquatic toxicity; TETP – Terrestrial ecotoxicity; AV – average ranking of the CML02 method; EI99 – Eco-Indicator 99; TEWI – Total equivalent warming impact

Tab. 3: Ranks of the CML02 method and its average ranking (AV), ranks of the EI99 and TEWI method; High rank (11) - strong environmental impact, low rank (1) - low environmental impact.

The Hasse diagram shown in Figure 1 was achieved using the average ranking (AV) of the CML02 method and the rankings from EI99 and TEWI (Tab. 3). E134 and E125 placed highest in the Hasse diagram indicate high environmental impact. Lowest in the diagram are E7000, E7200, R152a, and R290. This means that there is no other refrigerant which has in all three indicators simultaneously lower values. R134a is less problematic than E134a but more problematic than R152a, R600a, R290, E7100, E7200, and E7000. R744 is less problematic than R30 and E134, more problematic than R600a and R290 but incomparable to the other refrigerants. Beside those incomparabilities, others occur; e.g. a) R30 with E125, E134, R134a, E7100, and E7000, b) R152a with E7000, E7100, E7200, R744, R600a, R290, and E125, c) E7200 with E7000, R152a, R744, R600a, R290, and E125.

A pairwise Spearman correlation analysis was performed (Lyerly 1952, Kendall 1975) in order to find the most strongly correlated parameters. It shows that the average ranking of CML02 correlates better with TEWI (correlation coefficient $\rho = 0.67$, at $\alpha = 0.05$) than with EI99 ($\rho = 0.514$). The correlation of TEWI with EI99 is 0.664 (at $\alpha = 0.05$).

Considering the better correlation of TEWI with the AV of CML02, a second Hasse diagram was drawn omitting EI99. In Figure 2, R152a becomes additionally comparable to E7000 and E7200, reducing the number of refrigerants with a potential low environmental impact.
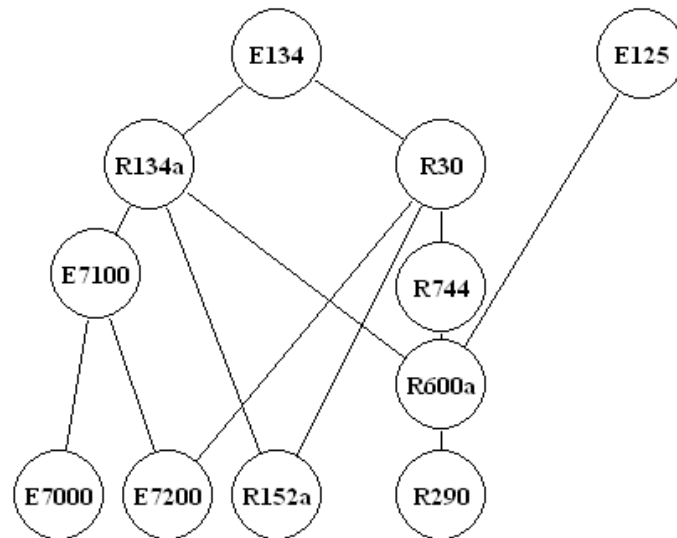
70

Fig. 1: Hasse diagram using three parameters: the average ranking (AV) of the CML02 method and the rankings from EI99 and TEWI.
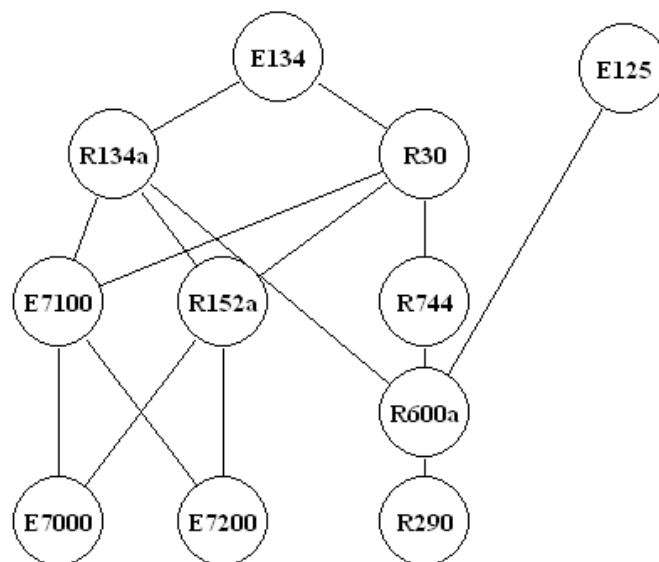

Fig. 2: Hasse diagram with the average ranking of the CML02 method and the ranking from TEWI.
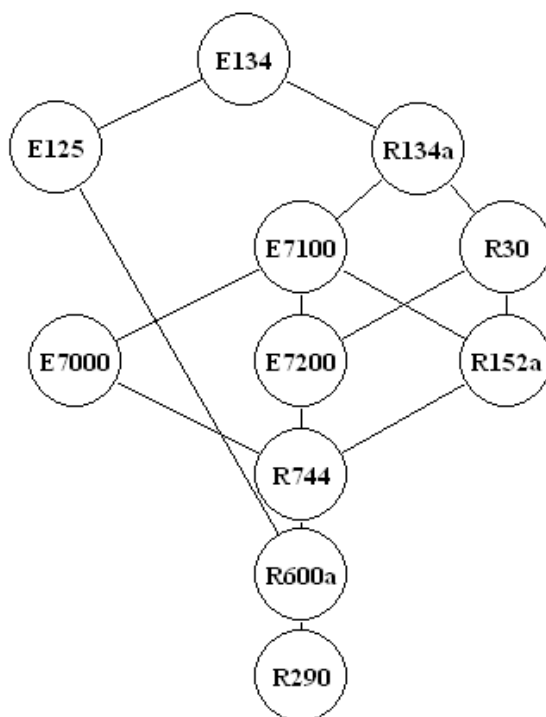
71

Fig. 3: Hasse diagram with the average ranking of the CML02 method and the ranking from EI99.

Although the AV of CML02 and EI99 are less correlated, the Hasse diagram using their rankings as parameters (Figure 3) show E134 as the refrigerant with the highest and R290 with the lowest environmental impact of the studied refrigerants. In both rankings, from AV of CML02 and EI99, E125 holds a rank lower than E134. E7000 and E7200 become comparable to R744, R600a, and R290 and are placed higher than those, implying a greater impact on the environment.

5. Discussion

In A/C systems in passenger cars, the polyfluorinated dimethylethers E134 and E125 do not seem to be suitable replacements for R134a. The perfluoroalkyl-alkyl-ethers E7000, E7100, E7200, and the HC R600a and R290 have smaller environmental impact than R134a with all three assessment methods. Using the more holistic assessment methods CML02 and EI99, R744 is also ranked lower than R134a.

The Spearman correlation analysis shows that there is a discrepancy of the rankings resulting from different assessment methods. Therefore, one must choose carefully the method for assessing the environmental impact of one substance. Even of more advantage is the performance of more than one assessment and to use partial order theory in order to visualise similarities in the rankings of substances as it was done in this work. The weaknesses and advantages of each method have to be made transparent. The next step is to examine the crucial factors that lead to the incomparability of the rankings by the mentioned assessment methods.

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