EVALUATING ENVIRONMENTAL IMPACTS OF A SOLVENT RECOVERY UNIT IN A CHEMICAL FACTORY BY USING LIFE CYCLE ASSESSMENT

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ABSTRACT

EVALUATING ENVIRONMENTAL IMPACTS OF A SOLVENT RECOVERY UNIT IN A CHEMICAL FACTORY BY USING LIFE CYCLE ASSESSMENT

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In this study, Life Cycle Assessment (LCA) Technique was used to analyze the possible environmental impacts of the Solvent Recovery Unit (SRU) of a chemical factory. Firstly, the impact assessment of the SRU where a solvent of dimethylacetamide (DMAc) is currently being recovered by distillation, was performed using LCA with the help of SimaPro software, Eco-Indicator 99 method. Functional unit of the analysis was set as 1 kg of waste solvent recovered.

Secondly, the case in which a solvent of dimethyl sulfoxide (DMSO) is used in the plant as an alternative solvent was assessed. It was found that the environmental impact of these solvents are almost compensated by their recovery. Overall total impact scores for the recovery of DMAc and DMSO in the SRU were found as 0.00457 Pt and 0.00451 Pt, respectively.

Thirdly, end-of-pipe treatment and incineration were considered for both solvent types, DMAc and DMSO. Functional units were selected as 1 kg waste solvent treated and 1 kg waste solvent incinerated, respectively. In case of end-of-pipe treatment, DMAc and DMSO increased the overall impact of the baseline end-of-pipe treatment by 4,125 and 3,137 times, respectively. In case of waste solvent incineration, DMSO resulted in less impact than DMAc in all impact categories.

Comparison of three solvent handling methods revealed that environmental impact of the solvent recovery by distillation is the smallest whereas the end-of-pipe treatment is the highest for both DMAc and DMSO cases.

Finally, financial comparison of the solvent recovery and end-of pipe treatment handling methods indicated that solvent recovery is economically favorable option. Financial comparison was performed for DMAc case only, as the plant cost data was available only for DMAc recovery.

Keywords: end-of-pipe treatment, life cycle assessment, SimaPro software, solvent recovery, waste incineration

ÖZ

KIMYASAL ÜRETİM YAPAN BİR FABRİKADA, SOLVENT GERİ KAZANIM UNİTESİNİN ÇEVRESEL ETKİLERİNİN YAŞAM DÖNGÜSÜ ANALİZİ İLE DEĞERLENDİRİLMESİ

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Bu çalışmada, kimyasal üretim yapan bir tesiste, solvent geri kazanım ünitesi (SGKU) için, yaşam döngüsü analizi ile birlikte olası çevresel etkilerin değerlendirilmesi yapılmıştır. İlk olarak; SimaPro yazılımı ve Eco-Indicator 99 metodunun yardımı ile solvent geri kazanım ünitesinde fabrikada kullanılmakta olan dimetil asetamit (DMAc) solventinin distilasyon yöntemiyle geri kazanımının çevresel etkisinin değerlendirilmesi amacıyla yaşam döngü analiz (YDA) çalışması SimaPro yazılımı yardımıyla, Eco-Indicator 99 yöntemi kullanılarak yapılmıştır. Fonksiyonel birim 1 kg geri kazanılan atık solvent olarak belirlenmiştir.

İkinci olarak, tesiste alternatif solvent olarak dimetil sülfoksit (DMSO) kullanılması durumu değerlendirilmiştir. Bu solventlerin çevresel etkilerinin, solvent geri kazanımı ile kompanse edildiği görülmüştür. Toplam etki değerleri, DMAc ve DMSO için, sırasıyla, 0,00457 birim ve 0.00451 birim olarak bulunmuştur.

Üçüncü olarak, her iki solvent için, DMAc ve DMSO, boru-sonu arıtma ve yakma ele alınmıştır. Fonksiyonel birimler, sırasıyla, 1 kg arıtılan atık solvent ve 1 kg yakılan atık solvent olarak belirlenmiştir. Boru-sonu arıtma durumunda, DMAc ve DMSO, referans boru-sonu arıtmanın etkisini, sırasıyla, 4.125 kat ve 3.137 kat artırmıştır. Atık solventin yakılması durumunda, DMAc tüm etki kategorilerinde DMSO'ya göre daha düşük etki ile sonuçlanmıştır. Atık solvent için uygulanabilir üç bertaraf yöntemi karşılaştırıldığında, distilasyon yöntemiyle solvent geri kazanımının çevresel etkisinin en düşük, boru-sonu arıtmanın çevresel etkisinin ise en yüksek olduğu görülmüştür.

Son olarak, boru-soru arıtma ve solvent geri kazanım yöntemlerinin ekonomik olarak karşılaştırılması sonucunda, solvent geri kazanımı yönteminin ekonomik açıdan tercih edilir olduğu anlaşılmıştır. Bu ekonomik analiz, maliyet rakamlarının DMAc geri kazanımı için mevcut olması nedeniyle sadece DMAc için yapılmıştır.

Anahtar Kelimeler: atık yakma, boru-sonu arıtma, SimaPro yazılımı, solvent geri kazanımı, yaşam döngü analizi

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Finally, i would like to dedicate my thesis to my family and friends.

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ABBREVIATIONS

CH_4 : Methane

C(n) : Revenues in time period (n)

CO_2 : Carbon dioxide

d_{DMAc} : Density of DMAc

d_{DMSO} : Density of DMSO

DMAc : Dimethylacetamide

DMSO : Dimethyl sulfoxide

FV : Future Value

i : Discount Rate

LCA : Life Cycle Assessment

LCI : Life Cycle Inventory

LCIA : Life Cycle Impact Assessment

n : time period, year

NPV : Net Present Value

O&M : Operation and Maintenance

Pt : Point

mPt : milli-point

r : Interest Rate

R(n) : Revenues in time period (n)

RO : Reverse Osmosis

RW : Recycled Water Tank

SRU : Solvent Recovery Unit

TFE : Thin Film Evaporator

WWTP : Wastewater Treatment Plant

CHAPTER 1

INTRODUCTION

1.1 General

Solvents are chemical substances which are usually organic liquids used to dissolve or dilute other substances. Also, they can be used as chemical intermediates, fuels and components of many products including cleaning and degreasing materials, paint removers, paints, varnishes, adhesives, inks and ink removers, pesticides and toiletries. Engineering, construction, chemicals, printing, rubber, plastics, ink manufacture, pharmaceutical and paint manufacture, footwear, textiles, foodstuff, woodworking and dry cleaning are the industries where solvents are commonly used [1].

On the other hand, solvents are associated with many health problems as disruptions on the nervous system, skin, respiratory tract and cancer. Many organic solvents have adverse impact on the function of central nervous system depending on the vapour concentration, exposure time and solvent toxicity. Absorption of solvent through the skin makes the skin dry, scaly and cracked. Irritation of all types of organic solvents can affect the upper airways, nose, throat and trachea. Long term exposure may cause chronic or persisting cough. Also, some solvents are classified as carcinogenic like benzene or possible human carcinogens as dichloromethane, ethyl acrylate, tetrachloroethylene and styrene [2].

Additionally, solvents have also environmental impacts. They can partition into air, water and soil. An organic solvent with a high solubility in water can move into groundwater, rivers and lakes. Dissolved solvents in water can volatilize into the atmosphere or soil. Also, transforming or degradation of an solvent into its components is possible in water, air and soil. Volatilization is the other important property of a solvent for the movement from one point to another based on soil-water content, airflow rate, humidity, temperature, adsorption and diffusion characteristics of the soil. Therefore, depending on the both environmental and health impacts, control of hazardous wastes is deemed necessary [3].

In this respect, the aim of the Regulation on Control of Hazardous Wastes, Turkey [4] is to prevent pollution and protect the environment and human health by providing a control over hazardous wastes in terms of their production, disposal, transportation as well as by providing technical and administrative requirements in their management. Type of substances in the waste, their concentration, their characteristics, such as, chemical reactivity, pH, toxicity, carcinogenicity, corrosivity, flammability, mobility/ and persistency in the environment, explosivity, and being an oxidizing power or irritant agent, could make any waste as hazardous. Also, to deal with wastes easier, not mixing a hazardous waste with another kind of waste is essential. Waste reduction, waste recycling, energy/ and material recovery and waste incineration are the main options for dealing with hazardous wastes.

In this respect, solvent recovery is usually implemented in the industrial area, supporting green initiatives and helping to reduce hazardous waste generation in a company. In addition to these environmental and regulatory compliance benefits, it also provides a serious economical benefit.

The economical advantages of solvent recycling/recovering are minimizing costs of storage, disposal and purchasing the chemical. Additionally, considering the high cost and continously increasing unit prices of solvents, recycling or recovery of solvent within a plant remains as a very cost-effective option to apply [5].

Indeed, there are some studies in the literature, investigating the waste solvent treatment/handling alternatives, such as distilation (as a means of solvent recovery), incineration and adsorption [6]. However, reported results do not cover all types of solvents. Moreover, it is diffucult to draw a general conclusion from these studies since the appropriate technology depends highly on the type of solvent [6]. For example, Amelio et al., [7] reported that solvent recovery option is the best technology for some solvents (i.e. solvents with high impact during their production) while incineration is favorable alternative for some others (i.e. solvents with low impact during thier production). Furthermore, none of these studies did compare the solvent recovery option with the end-of-pipe treatment option (i.e. handling via the wastewater treatment plant - WWTP).

Therefore, it was deemed necessary to investigate the environmental impact of solvent recovery implementation in comparison to both incineration and end-of-pipe treatment option, taking the solvent type into consideration.

1.2. The Objectives and Scope of the Study

The main purpose of the study is to assess the possible environmental impacts of the Solvent Recovery Unit (SRU) of a chemical factory by using Life Cycle Assessment (LCA) technique. The assessment was performed for the currently used solvent, dimethylacetamide (DMAc), in the plant, as well as for a possible substitutive solvent, dimethyl sulfoxide (DMSO). Then, environmental impacts of recovering the solvent were assessed in comparison to end-of-pipe treatment and incineration options for both solvent cases.

In this respect, the study was performed mainly in three parts:

Firstly, the impact assessment of SRU where a solvent of DMAc is currently recovered in the plant studied, was performed using LCA. The boundary of the study was selected as “cradle to gate” for the SRU. To this purpose, all the inputs and outputs of the SRU system have been identifed in order to construct mass and energy balances. Then, LCA was conducted using SimaPro version 7.2.4 Software. Among the end-point methods used to conduct LCA, Eco-Indicator 99 was selected for impact assessment. The functional unit was selected as 1 kg of solvent recovered in the SRU to assess the environmental impacts.

Secondly, the case in which a solvent of DMSO is used in the plant as an alternative solvent (i.e. if solvent substitution is implemented) was assessed in the same manner as with DMAc case.

Thirdly, comparisons of solvent recovery with end-of-pipe treatment and incineration were performed in two scenarios based on solvent type, DMAc and DMSO. System boundaries were set as “cradle to gate” for the end-of pipe treatment and functional units were selected as 1 kg waste solvent treated and 1 kg solvent incinerated.

Also, economic analysis was performed to put forward the profitability of the solvent recovery over the end-of-pipe treatment waste handling method.

CHAPTER 2

LIFE CYCLE ASSESSMENT (LCA)

2.1 Principles and Context of Life Cycle Assessment (LCA)

LCA is a systematic technique that evaluates all steps of the process of using natural sources and the effects of products/by-products due to the process in order to meet our requirements within the limited natural systems. It helps to interpret the environmental aspects and potential impacts of a certain product or service [8,9].

The International Organisation For Standardisation (ISO), has standardized the framework by the series ISO 14040 on LCA. ISO 14040 is about the principles and framework for life cycle assessment (LCA). The series of ISO 14040 are like that;

ISO 14041 : Goal and Scope Definition and Inventory Analysis (1998)

ISO 14042 : Life Cycle Impact Assessment (2000)

ISO 14043 : Life Cycle Interpretation (2000)

ISO/TR 14047: Examples of the phase of Life Cycle Impact Assessment (LCIA- ISO 14042)

ISO/TS 14048: The requirements and a structure for a data documentation format (2002)

ISO/TR 14049: Examples of the Life Cycle Inventory (LCI) - ISO 14041(2000) [10].

LCA also concerns with the energy efficiency of technologies. It asks how much input energy is needed for the process, energy benefits and losses, identification of optimal services depending on ‘sustainable’ levels of effects. Therefore, LCA includes not only main inputs but also other materials that are fed into the process.

The main four phases of LCA are: defining the goal and scope, life cycle inventory (LCI) analysis, life cycle assessment and interpretation.

1) Defining Goal and Scope

In LCA, defining goal and scope and involving the functional units in the study are very important. The functional unit describes the study precisely and helps to make quantification of the process. In the scope analysis, the system boundaries should be determined. Also, the scope should include the limits of the analysis in terms of identification the production, disposal and recycling of the substances, all inputs and outputs, emissions and wastes produced, services for both pre-consumption and post-consumption. The efficiency of LCA depends on the assumptions and decisions made by the modeller and data employed in the study [8,9].

2) Life Cycle Inventory Analysis (LCI)

LCI analysis is about creating an inventory of flows from and into the system that involves inputs of water, energy, and raw materials and outputs to the air, land, and water. For LCI, the construction of a flow model of the technical system by including the data that should reflect the functional units, is a must. It makes the technical system boundaries more clear [8,9].

3) Life Cycle Impact Assessment (LCIA)

This phase is about qualifying the level of potential environmental effects according to the LCI analysis. The main elements are;

- the determination of impact categories, indicators and the method that will be used in the study,
- the classification of the parameters based on the specific impact categories,

- impact measurement by a LCIA methodology for each unit to accomplish an overall impact of the specified system.

LCIA does not quantify actual impacts of a process or a product specifically. It analyses a system and its potential effects and makes comparison between them. e.g. release of 900 tons of CO_2 (carbon dioxide) and 500 tons of CH_4 (methane). LCIA can say which process/product has more adverse impact on the environment.

The common life cycle impact categories are;

Global; global warming, stratospheric ozone depletion, human health, resource depletion.

Regional; acidification, human health, resource depletion, land use, water use.

Local; acidification, eutrophication, photochemical smog, terrestial toxicity, aquatic toxicity, human health, resource depletion, land use and water use [8,9].

Steps of LCIA:

1) *Selection of Impact Categories:* determination of the relevant impact categories as global warming, acidification etc. An environmental release can affect human health and/or the environment. In general, LCIA analyses has three main categories; human health, environment and resource depletion [8,9].

2) *Classification:* defining and assignment of the impact categories depending on their ability for contribution to different problem areas. In other words, it is about classifying LCI results into the impact categories. e.g. assigning CO_2 into global warming. LCI result can contribute partially when effects are dependent on each other. Also, LCI results can contribute to an impact category or to all relevant impact categories if effects are independent of each other. e.g. assigning nitrogen dioxide to both ground level ozone (100%) and acidification (100%) [8,9].

3) *Characterization:* calculating impact results and converting them into common units to aggregate within categories. This part is about using science-based conversion/ equivalency factors to combine LCI results into representative category indicators. e.g. estimation of the relative terrestial toxicity between lead, chromium and zinc or expression of all greenhouse gases as CO_2 to provide a general indicator of relevant impact category.

Characterization also gives an idea on quantities of different indicators in terms of their impacts. e.g. 10 pounds of methane have more adverse effects than 20 pounds of chloroform on global warming depending on their conversion factors [8,9].

4) *Normalization:* calculating impact indicator data for making comparison across impact categories. On the other hand, normalization depends on calculating the magnitude of the indicator based on the reference values with respect to different impact results that can be expressed on a common scale to make comparison within impact categories.

e.g. comparison of the impacts of acidification can not be done with impacts of aquatic toxicity. However, calculation of CO_2 equivalent value on global warming is possible by normalization [8,9].

5) *Grouping:* The aim is to make interpretation by sorting indicators according to specific areas of concern such as emissions like air or water emissions [8,9].

6) *Weighting:* This step is about assignment weights or relative values of different impact categories according to their importance or relevance. Weighting can be combined across impact categories. Meanwhile, the unweighted data should be assigned with the weighted data to make assigned weights more clear [8,9].

7) *Evaluating and Documenting the LCI Results:* This part must include defining the system and its boundaries, describing the methodology, making necessary

assumptions and mentioning uncertanities. However, some limitations can exist. In terms of limitations, some examples are;

Spatial Resolution; same amount of release in a stream will be worser than river.

Temporal Resolution; same amount of release during one month will be worser than within a year [8,9]

The results of an LCA will be different according to types of the methods; midpoints or endpoints. Their focus are on different stages in the cause-effect chain in the impact analysis. A midpoint method interested on an earlier step along the cause-effect chain while an endpoint method looks at the end of the chain (Table 1) . The advantage of the endpoint method is including impact on human health, ecosystem quality and resource depletion [11].

Table 1: Midpoint and endpoint impact categories [12]

<table>
<tr><th>Mid-point impact categories</th><th>End-point impact categories</th></tr>
<tr><td>Carcinogens</td><td rowspan="6">Human Health</td></tr>
<tr><td>Non-carcinogens</td></tr>
<tr><td>Respiratory inorganics</td></tr>
<tr><td>Ionizing radiation</td></tr>
<tr><td>Ozone layer depletion</td></tr>
<tr><td>Respiratory organics</td></tr>
<tr><td>Aquatic ecotoxicity</td><td rowspan="6">Ecosystem Quality</td></tr>
<tr><td>Terrestrial ecotoxicity</td></tr>
<tr><td>Terrestrial acid/nutrients</td></tr>
<tr><td>Land occupation</td></tr>
<tr><td>Aquatic acidification</td></tr>
<tr><td>Aquatic eutrophication</td></tr>
<tr><td>Global warming</td><td>Climate Change</td></tr>
<tr><td>Non-renewable energy</td><td rowspan="2">Resources</td></tr>
<tr><td>Mineral extraction</td></tr>
</table>

There are several impact assessment methods making end-point impact assessment, such as Eco-indicator-99, Impact-2002+ which have been commonly used. Table 2 compares these two methods.

It is reported in the literature that different evaluation methods produce different results and a proper LCIA method should be selected based on professional judgement depending on the relevant assessment results [13].

Assessment characteristics for midpoint and endpoint categories and relevant units are presented in Table 3.

Table 2: Comparison of Eco-indicator-99 and Impact-2002+ Methods [14].

Impact	Eco-Indicator 99	Impact 2002+
Carcinogens	+	+
Non-Carcinogens	-	+
Human Toxicity	-	-
Respiratory Organics	+	+
Respiratory Inorganics	+	+
Climate Change	+	-
Global Warming	-	+
Radiation	+	+
Ozone Layer Depletion	+	+
Aquatic Acidification	+	+
Terrestrial Acidification		+
Terrestrial Ecotoxicity	-	+
Aquatic Eco-toxicity	+	+
Aquatic Eutrophication	+	+
Freshwater Eutrophication		-
Non-renewable Energy	-	+
Land use	+	+
Photochemical oxidation	-	+
Mineral Extraction	+	+
Fossil (Fuels)Depletion	+	-

+ : exists in the method; **-**: does not exist in the method

Table 3. Midpoint and endpoint categories and relevant units [15].

Midpoint Category	Midpoint reference substance	End-point category	Damage unit	Weighting unit
Human toxicity (carcinogens + non-carcinogens)	kg Chloroethylene into air$_{-eq}$	Human health	DALY	Point
Respiratory (inorganics)	kg $PM_{2.5}$ into air$_{-eq}$	Human health		
Ionizing radiations	Bq Carbon-14 into air$_{-eq}$	Human health		
Ozone layer Depletion	kg CFC-11 into air$_{eq}$	Human health		
Photochemical Oxidation (Respiratory organics for human health)	kg Ethylene into air-eq	Human health		
		Ecosystem quality	n/a	n/a
Aquatic ecotoxicity	kg Triethylene glycol into water$_{eq}$	Ecosystem quality	PDF.m^2.yr	Point
Terrestrial ecotoxicity	kg Triethylene glycol into soil$_{-eq}$	Ecosystem quality		
Terrestrial acidification/ nutrification	kg SO_2 into air$_{-eq}$	Ecosystem quality		
Aquatic acidification	kg SO_2 into air$_{-eq}$	Ecosystem quality		
Aquatic eutrophication	kg PO_4^{3-} into water $_{-eq}$	Ecosystem quality		
Land occupation	m ^{2} Organic arable land$_{-eq}$ y	Ecosystem quality		
Water turbined	inventory in m^3	Ecosystem quality		
Global warming	kg CO_2 into air$_{-eq}$	Climate change (life support system)	kg CO_2 into air$_{-eq}$	Point
Non-renewable energy	MJ or kg Crude oil$_{eq}$(860 kg/m^3)	Resources	MJ	Point

[DALY: Disability-Adjusted Life Year, PDF.m^2.yr: Potentially Disappeared Fraction of species per m^2 per year, MJ: Mega Joule, eq: equivalent].

4) Interpretation

This is the last phase of LCA, which is about identifying, controlling and analysing the results of both the LCI and the LCIA. It sets conclusions and recommendations. Also, it evaluates the study by considering completeness, consistency, sensitivity, limitations and assumptions [8,9].

Totally, the main phases of the LCA can be seen from Figure 1.

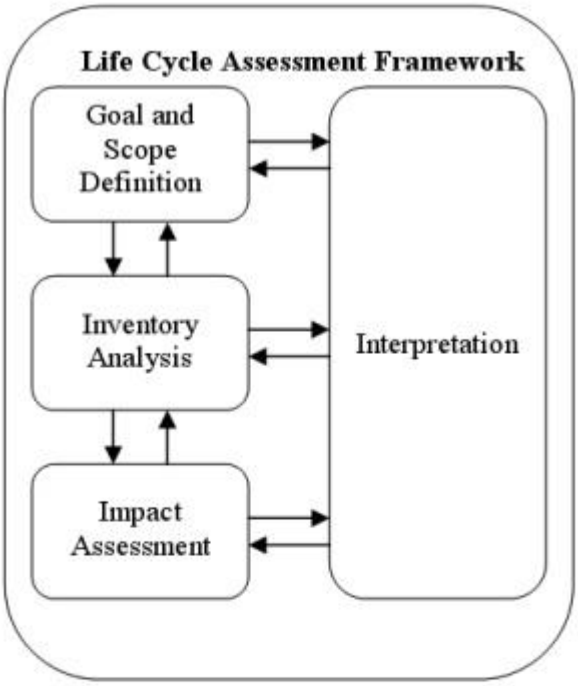

Figure 1: LCA framework [16].

2.2 LCA in Practice

In general, LCA involves many practices and approaches with different strengths and weaknesses. There are variations due to the questions asked, the quality and quantity of the data, changes in environmental and socioeconomic conditions and preferences on the services. However, at the same time, it sets common and basic elements for all practices.

In the scope determination, there are three main effective variances like;

- The number of life cycle stages
- The number of environmental impacts that should be analysed.
- The quantity and quality of the obtained data for the study.

The certain characteristics of LCA are;

- The determination of suitable functional units is a challange since options might have secondary functions.
- The boundaries of the system should be determined.
- Flows within the system, inputs and outputs to air, water and soil like carbon dioxide, nitrogen and heavy metals should be included.
- Bottom-up process starts at the bottom of the chain and individual unit processes are added for making up the product's system. At the bottom-up process, asking the appropriate question to set the main goal and scope is essential.
- The type of LCA can be streamlined. The aim is to simplify and decrease the time, cost and effort by representing the most important environmental burdens, determining the key impact areas, leaving out some life cycle stages, using available and qualified data, targeting specific issues and narrowing the system boundaries.
- Interpretation is essential for all LCAs, as well as for all stages of LCA's.

Normally, consideration of linear cause and effect relationship is not suitable for objective result. In fact, environmental problems are not simple and LCA should take as much as complexities into account to meet more objective truth. However, LCA has little to say about the adaptability of the system, risks and potential depending on the assumptions used. Therefore, LCA can not reach objective truths but it can produce efficient answers [17].

In general, LCA considers long time from hundreds to thousands of years, all environmental effects regardless of where they belong and data can be added up along supply chains. e.g. emissions.

In LCA, indicators are used for measurement of adverse impacts. Water as an indicator is for similar fashion but it is basically a measurement as a source depletion. Both the electricity and water used for infrastructure can be neglected when compared with the operational usage.

LCA is a decision support tool. The most important characteristic of LCA is providing definite quantiable results, however, it can reveal the points where fixation is needed by changes. The tool used affects the result of any analysis.

LCA focuses on the functional units. The function can be multifaceted and the type of function will affect the results accordingly [17].

CHAPTER 3

SOLVENT USE AND ITS RECOVERY

3.1 Solvent use in manufacturing industry

Solvents are used to dissolve or dilute other substances in many industries. They are commonly used in engineering, construction, chemicals, printing, rubber, plastics, ink manufacture, pharmaceutical and paint manufacture, footwear, textiles, foodstuff, woodworking and dry cleaning. The summary of industries, products and relevant areas of solvent usage is:

- Cosmetics and Personal Care Products; nail polish, nail polish remover, fragrences, hair dyes, general cleaners, hair sprays and setting lotions,
- Textiles; dry cleaning, spotting and textile finishing processes,
- Electronic Industry; halogen-free solvents in semi-aqueous cleaners,
- Fabricated metal products; metal cutting and forming, surface cleaning and paintings,
- Food Industry; extracting vegetable oils,
- Ground Transportation; refurbishing and maintenance,
- Iron and Steel Industry; finishing processes,
- Lumber and Wood Products; wood preservatives,
- Medical Applications; pacemaker leads, peripheral and central catheters, feeding tubes, balloons, condoms, surgical gloves, instrument and appliance covers and wound dressings,
- Metal Casting; mold-making process, die casting, finishing processes,
- Motor Vehicle Assembly; cleaning, preparation and painting operations,
- Paints and Coatings,

- Petroleum Refining Industry; extracting aromatics from lube oil feedstock, deasphalting lubricating base stocks, sulfur recovery from gas stream, production of solvent additives for motor fuels and cleaning operations,
- Pharmaceutical Industry; drug substances and drug products,
- Polymers and man-made fibers; dissolving or diluting monomer and reactants, facilitating the transportation of the reaction mixture throughout the plant,
- Printing Industry; imaging, platemaking, printing and finishing operation,
- Rubber and Plastics Industry; surface cleaning, cleaning of an equipment, adhesives used in finishing operations,
- Shipbuilding and Ship Repair Industry; building, repairing, repainting and alteration of marine and fresh water vessels,
- Stone, clay, glass and concrete; decoration materials,
- Textile Industry; printing, finishing, scouring, cleaning knit goods, desizing and coating [18].

3.2 Solvent Waste Handling

The treatment technologies for wastes which include solvent are incineration, fuel substitution, distillation, steam stripping, biological treatment and activated carbon adsorption. The preference of technologies depends on applicability, removal efficiency of constituents of concern, operating factors, process residuals and emissions and waste characteristics. The quantity of waste also plays an important role on selection of a technology. The size of an equipment, volume of raw materials needed, pollution control and disposal requirements are relevant with the quantity of waste. Therefore, recycling is more economically attractive for larger quantities of waste. Recycled/reused wastes have lower costs compare with virgin materials usage. In general, within the treatment technologies, solvent extraction is the most expensive treatment process due to high need for extraction agents and relavant equipment whereas carbon adsorption is the least expensive treatment process.

Source reduction which is an onsite activity and about reducing the volume and/or hazard of the generated waste and recycling are the main aspects of waste minimization. Raw material substitution, product reformulation, process modernization and waste segregation are options of source reduction. Recycling is about reclaming (purifying) waste for subsequent reuse or recovering specific constituents for reusing.

Physical treatment technologies can be classified into distillation, evaporation, steam stripping, air stripping, liquid-liquid extraction, carbon adsorption and resin adsorption. Evaporation and distillation can be applied to organic solvent wastes, however, they produce large volume of residuals in terms of organic contamination. Incineration is an option for handling this type of residual. Air stripping is used for low levels of volatile contamination, whereas steam stripping is used for higher levels of contamination. Solvent extraction are applicable for all levels of contamination. For residuals of these processes, additional biological treatment or possible adsorption processes may be required. Carbon and resin adsorption processes are used to achieve low organic concentration levels [19].

The commonly used waste solvent recycling technologies are distillation, solvent extraction and adsorption. Distillation is a liquid seperation process depending on volatilities of constituents in a solution. End products of this process have high purities. High temperature values with low pressure values increase the recovery efficiency for high boiling substances whereas larger pressure values are applied to lower boiling substances. In solvent extraction which is applicable method for recovering organic solvents from aqueous streams, a solute is transferred from one liquid phase to a immiscible liquid phase. Adsorption process (carbon and resin) are used for a single liquid phase. The aim is to dilute aqueous liquids [20].

Distillation (physical treatment) and incineration (thermal treatment) are the common waste solvent treatment technologies. Distillation is more preferable technology than solvent incineration since cost of organic solvents increase continuously. However, it is not known exactly whether waste solvent incineration or distillation is the better treatment option in terms of environmental aspects. Both treatment options can reduce the demand of non-renewable resources. Solvent incineration can substitute fuel for steam and electricity production. Also, incineration can led to a lower overall environmental impact for solvents with a lower environmental impact. As a result, the production of energy by incineration can be advantageous compared with distillation [6].

3.3 Case Studies on Solvent Recovery

A research was conducted by C. Capello in 2003 for answering the question whether a toluene containing waste solvent mixture which includes methanol, hydroxyphenylpropionic acid and water addition to toluene, should be incinerated or recovered by distillation to be advantageous environmentally. Incineration and distillation are commonly used waste solvent treatment technologies in chemical industry. Handling of solvents is a high priority environmental issue because of their volatiliy, considerable persistency in the environment and high toxicity [7]. In the Swiss Chemical Industry, incineration of a solvent is a commonly used handling method because they are used for energy supply instead of fossil fuels. However, due to their toxicity, fullfilling the low emission limits is essential by Swiss environmental regulations [7].

Life cycle assessments (LCAs) of two case studies were performed based on three different impact assessment methods; Swiss Ecopoints, Eco-Indicator 99 and primary energy demand. The functional unit was selected as 1 kg waste solvent. The data of steam and electricity supply was the net energy production by incineration without addition of fuel.

The evaluation depends on the avoided products as steam and electricity since waste solvents can be used instead of light fuel oil. Enthalpy of combustion, carbon content and the environmental impact of the petrochemical solvent production are the main properties of the waste solvents that changes the assessment evaluation. Carbon content is proportional to impact of CO_2 emissions and energy production.

According to the Eco-Indicator 99 and primary energy demand methods, distillation is better in terms of recovering non-renewable resources whereas incineration is preferable for the Swiss Ecopoints method if the focus is on emissions to air and water in terms of avoided energy production. For water type solvents, distillation is a better treatment option. However, for a waste solvent mixture which includes toluene, incineration is preferable if emissions to air and water need to be minimized.

Finally, industrial waste solvent mixtures that are produced by the petrochemical processes should be distilled instead of incineration since they have a high environmental impact [7].

It can be said that which treatment option is better in terms of environmental aspects can not be known certainly. Both treatment options can reduce the demand of non-renewable resources. Solvent incineration can substitute fuel for steam and electricity production. Furthermore, incineration can led to a lower overall environmental score for solvents less toxic. Thus, the production of energy by incineration can be preferable [6].

CHAPTER 4

STUDY APPROACH

4.1 Plant Studied

4.1.1 Applied Processes and Use of Chemicals

There are three main stages of production in the factory. Due to confidentiality agreement, the codes were given to the chemicals used for the production. The flow chart of the production is presented in Figure 2.

Further detail of these processes along with the chemicals used are provided below:

<u>Polymerization</u>

Polymerization is the first stage of the production. Chemical A, Chemical B and additives (catalyser, initiaters, pH stabilizer etc.) form polymers at this stage. Chemical F and Chemical H are fed as the reaction initiator and as the catalyst of the reaction, respectively. In the polymerization process, dyes are attached to SO_3 (Sulfite) groups. For this purpose, Chemical G is used. Additionally, since the reaction proceeds within the pH interval, 2.6 to 3.2, Chemical I is added.

It is assumed that polymer chains are formed within a 1 dwell time which is a time period needed for a substance to pass from the entrance to the exit of the reactor. At the end of the dwell time, Chemical N is sprayed to prevent the reaction continuity. Chemical N captures Fe^{++} ions which act as the catalyser, as a result, Chemical N stops the reaction. The final mixture at the reactor is called as slurry.

After polymerization, slurry is passed to the tanks where neutralization occurs by Chemical O usage. To finish the reaction at those tanks, Chemical P as the stabilizer is added.

Polymerization

1) Polymerization Reaction (Chemical A, Chemical B, Chemical F, Chemical G, Chemical H, Chemical I)

2) Polymer Washing

3) Polymer Drying

Midproduct Preparation

1) Chemical C (Solvent) Addition
2) Heat Stabilizer Addition (Chemical J)
3) Midproduct Agitation
4) Midproduct Filtration
5) Heating

Product Spinning

1) Pigment Dying (Chemical K, C-Black, Chemical L)
2) Filtration
3) Coagulation
4) Washing
5) Gel Dying
6) Chemical M/Softener Addition
7) Drying
8) Crimping
9) Annealing

Figure 2: The flow chart of main production in the factory

The next step is to wash the slurry at the drum filters. At the same time, remaining chemicals and salts produced during the reaction are removed. After washing, there are flash dryer and fluid bed mechanisms for drying the solution.

Midproduct Preparation and Product Spinning

The next main stage in the process is the midproduct preparation. In order to produce midproduct, the slurry from the polymerization unit is mixed with the Chemical C. Also, Chemical J which acts as the heat stabilizer is added to the system. Other purpose of using Chemical J is to prevent the oxidation of the product at the subsequent steps.

For an exact midproduct preparation, the mixture is agitated. Then, it is filtered by the filtre press cloth to remove the undissolved particulates and salts. After that, the midproduct is heated by the heat exchangers to decrease its viscosity. The aim of decreasing the viscosity is to increase the spinning efficiency.

According to the type of desired product, addition of certain chemicals is required. For example, Chemical K is added for matt products, some pigments are added for whiter products, carbon black is added for black products. In general, Chemical L is also used for stabilization purpose to prevent oxidation during the heating process. For special products, which are more resistant to day light and weather conditions, dying is done only by pigments. Under normal conditions, only gel dying is applied in the process.

Then, the mixed midproduct is passed through filters to prevent clogging of the spinnerets. The filtered midproduct is transported to the coagulation baths from spinnerets. When midproduct enters to the bath, it turns into final product because of the fact that polymer can not be dissolved in water although it is soluble in Chemical C. In the coagulation bath, the solvent in the midproduct enters to the water; coagulation occurs and spinning starts. The conditions during the coagulation, such as; temperature, solvent amount in the bath, number and structure of the pores of the spinnerets, effect the quality of the product directly.

The next step is washing to purge the remaining solvent on the product. After washing, gel dying which provides absorption of the dye on the product is applied. By gel dying, cationic dyes are attached to SO_3 groups.

By means of stretching applied to the product, its strength decreases and elongation increases. At the same time, chemical finish/softener is used to get antistatic and soft product. Then, product passes through the drying rollers.

Following drying, the product passes to the crimping unit. The aim is to prepare the product to the annealing unit to increase the efficiency in terms of better attachment of fiber each other.

By means of annealing which is the last step of the production, brittleness of the product decreases. Another purpose of annealing is to make colors of the product permanent.

The sketchy products via the glitches in the system are being added to the process to be used again during the production. However, negligible amount of product and some other solid particulates might merge to the solution that comes from the spinning unit and goes to the solvent recovery unit. They leave the system by the solid waste (sludge) at the end.

In short, the chemicals used for the production at polimerization part are Chemical A, Chemical B, Chemical G, Chemical F, Chemical I, Chemical O, Chemical P and Chemical N. Chemical A and Chemical B are the main chemicals at polimerization. Carbon black, other pigments/dyes, Chemical J, Chemical K, Chemical L, chemical finish (softener) and solvent (Chemical C) are the chemicals which are added at the midproduct preparation part. The amounts of chemicals used during the midproduct preparation and spinning unit are negligable as compared to the amount of solvent used, as indicated in Table 1. Nevertheless, Chemical A and Chemical B are used in comparable amounts to the solvent (Chemical C).

The hourly amounts of chemicals used for the production are presented in Table 4.

Table 4: The average hourly amounts of the chemicals used for the production

	The Chemical Name	**ton/h**
Polimerization	Chemical A	31.83
	Chemical B	2.52
	Chemical G	0.94
	Chemical F	0.18
	Chemical I	0.08
	Chemical O	0.16
	Chemical P	0.001
	Chemical N	0.01
Midproduct Preparation & Spinning	Pigment/Dye	0.14
	Carbon Black	0.02
	Chemical J	0.01
	Chemical K	0.05
	Chemical L	0.002
	Chemical Finish/Softener	1.82
	Solvent (Chemical C)	101.31

4.1.2 The Solvent Recovery Unit (SRU)

4.1.2.1 Process Description

The solutions from the coagulation bath and washing part of the spinning unit which include solvent, water and some solid particulates, are collected at the storage tank before sending to the SRU (Figure 3).

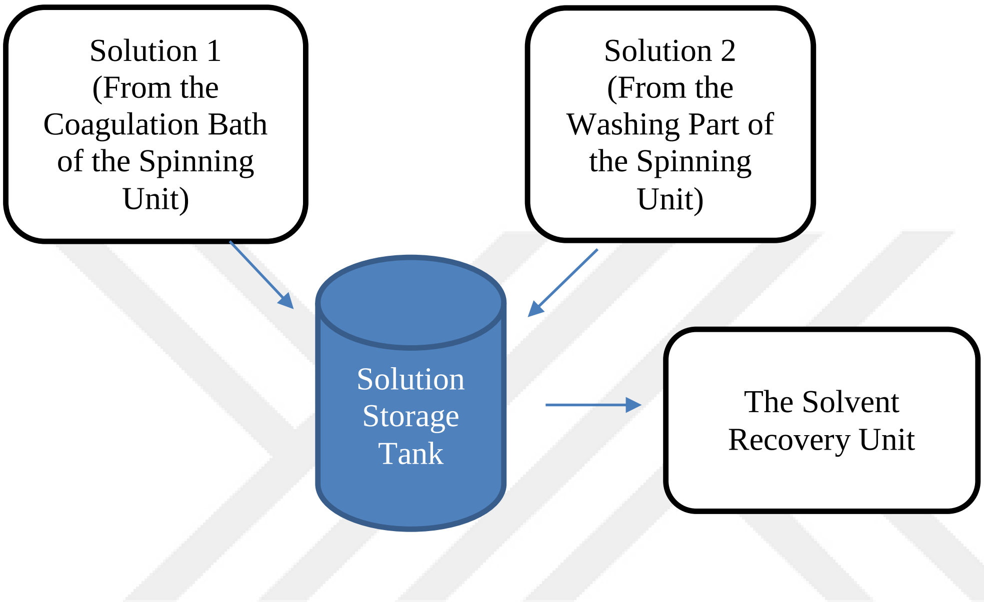

Figure 3: The pathway of the solution that comes to the SRU

One of the main purposes in the SRU is to minimize consumption of water and energy during distillation the solvent. Water and steam are always circulated by the heat exchangers so that water and heat are not wasted within the system for cooling and heating purposes.

The SRU in the factory includes three subunits, coded as 1, 2 and 3. They have same operational principles, only their capacities are different. Their capacities are 100 ton/h - 100 ton h and 60 ton/h, respectively. In this study, 2nd unit has been considered with respect to their flow chart/operational principles to explain about the environmental performance of the general SRU and the distillation principles.

Simplified flowchart of the SRU can be depicted from Figure 4.

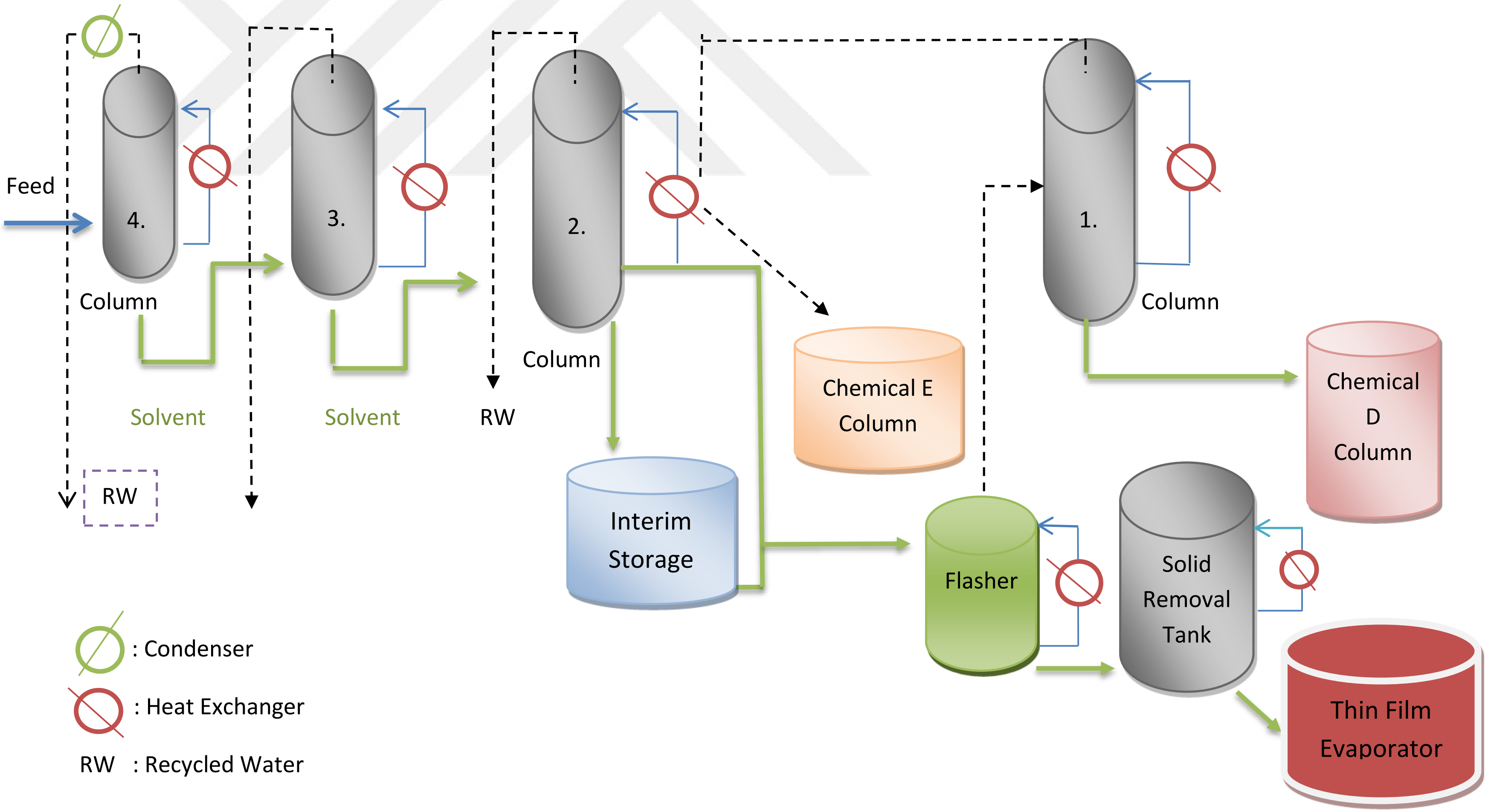

Figure 4: Simplified flowchart of the SRU

As shown in Figure 4, there are 4 columns in each subunit. The SRU starts with the 4th column. The aim of the solvent recovery unit is to distill water and solvent (Chemical C) which are present in the solution that comes from the spinning unit, based on their different boiling points/steam pressures. While the recycled water is being sent to the spinning unit, the recovered solvent is sent to the midproduct preparation unit to be used again.

The flow direction is from the 4th column to the 1st column, however, the heat transfer is from the 1st column to the 4th column. The main idea is to use the top product as a heat source for the bottom product of the previous column. As a result, while the top products are being condensed, the bottom products are being boiled.

There are heat exchangers after each column to achieve condensation. But, after 4th column of each unit, there are condensers that use air since there is not any next column to transfer heat. Except the top products of all 4th columns, all solutions from the 1st, 2nd and 3rd columns and the bottom products of the 4th columns pass through two heat exchangers that use water to maintain the condensation efficiency at maximum.

The working principles of heat exchangers in the SRU are same with the one illustrated in Figure 5. At the heat exhangers, hot and cold fluids are seperated by a heat conducting surface. There are tubes in the heat exchanger of the SRU instead of plates explained in Figure 5. Heat can be transferred from the fluid with a high temperature to the lower one. Fluids are not mixed within the heat exhangers [21,22].

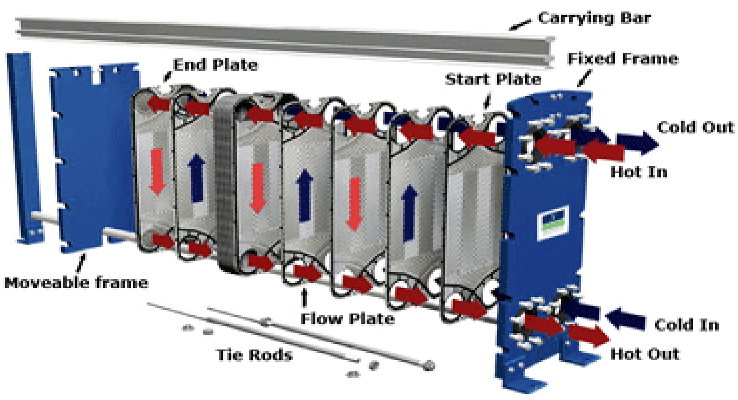

Figure 5: Heat exchangers working principles [22]

The little amount of vapor from each column which is not condensed while passing through the heat exchangers is sent to the ejectors in order to create vacuum at the tops of the columns. The operational mechanisms of the ejectors depend on the pressure and velocity of the vapor. The vapor enters the ejector with a high pressure and low velocity. At the throat of the ejector, the vapor is at high velocity and low pressure. When the ejector reaches the desired pressure, the suction valve opens. Concurrently, the vapor starts to discharge, the empty part of the chamber starts to fill with the top product. Both the vapor and the top product move together within the ejector [23].

After vapor is condensed, some part of it is used as reflux and the remaining part is sent to the recycled water tank (RW). The aim of the reflux is to make the vapor more pure, which moves upward at the column to separate vapor and liquid phases in a better way. At each column of the whole unit, reflux is made by the condensed top products.

The first step is filtration by the cartridge filter just before the entrence to the 4th column to decrease solid particulates in the solution. However, only ~ 10% of the solid particulates can be handled by the cartridge filter.

The feed to the 4th column is the combination of water (51.9%), solvent (48.0%) and Chemical D (0.1%). Finally, at the 4th column; 57.8% solvent, 42.1% water and 0.1% Chemical D solution are obtained from the bottom while 99.9% water and 0.1% Chemical D solution are obtained from the top.

After the top product of the 4th column is condensed with the large condenser, the solution is sent to the RW. The bottom product of the 4th column is reboiled by the top product of the 3rd column.

The feed from the 4th column to the 3rd column includes solvent (57.8%), water (42.1%), Chemical D (0.1%). In the 3rd column, while the solution contains solvent (68.7%), water (31.2%) and Chemical D (0.1%) at the bottom, the solution contains solvent (0.1%) and water (99.9%) at the top. The top product of the 3rd column is vacuumed by the pressure application with a negative value. The top product of the 3rd column is condensed during heating the bottom product of the 4th column. After passing through two heat exchangers, while the uncondensed part, is sent to the ejector, the condensed part is sent to the RW. Also, some part of the condensed top product is used as reflux in the 4th column.

The feed to the 2nd column contains water (31.2%), solvent (68.7%) and Chemical D (0.1%). In this column, while the bottom solution includes water (11.9%), solvent (88%) and Chemical D (0.1%), the top product contains water (99.9%) and (0.01%). The function of the top product of the 2nd column is same with that of the 3rd column. The applied pressure has a negative value at the top of the 2nd column as 4th and 3rd columns. The bottom product of the column is heated by the top product of the 1st column.

At the 2nd column, contamination starts to be seen in the system due to the accumulation of solid particulates. There are the flasher and interim storage tank between the 1st and 2nd columns. Some part of the bottom product of the 2nd column is fed to the flasher, other part is sent to the interim storage tank.

While the vaporized solution of the 2nd column is being transferred to the 1st column, the bottom solution which includes solid particulates is passed to the solid removal tank. The aim of the flasher is to supply pure solution with the negligible amount of solid particulates to the 1st column which is the last column in the system, therefore the contamination at the 1st column will be minimized. The solution at the flasher is heated by the 21 barg steam to increase the temperature for the 1st column.

The first column pressure at the top has a positive value. There is not need for vacuuming at the top of the 1st column as the vapor moves upward in the column spontaneously. The solution includes solvent (99.6%), water (0.2%), Chemical D (0.2%) at the bottom and the solution includes water (99.8%) and Chemical D (0.2%) at the top.

It can be inferred that while the temperature of the top product increases, the required pressure to create a vacuum decreases.

Due to the high pressure and temperature values at the 1st column, hydrolysis of the solvent occurs. The solvent decomposes into two components: Chemical D and

Chemical E. While the bottom product (i.e the mixture of the Chemical D and solvent) is passing to the Chemical D column, the top product (i.e the mixture of Chemical E and water) is sent to the Chemical E column to be distilled. The obtained Chemical D and Chemical E are transferred to the solvent production unit.

The aim of the solid removal tank is to remove solid particulates as much as possible before sending it to the last part of the system, namely; thin film evaporator. The solution in the solid removal tank involves water (3.6%) and solvent (96.4%). The obtained vaporized solution from the solid removal tank is sent to the 2nd column instead of 1st column to minimize contamination of the 1st column due to solid particulates coming from the solid removal tank. The bottom product is passed to the final part, the thin film evaporator.

In the SRU, the energy is cycled by the use of temperature and pressure differences within the columns. As a result, heat loss within the system is minimized. Heat transfer is made by the heat exchangers.

For the components of the solvent (Chemical D and Chemical E), there are also different columns of them in the unit. There is not any heat exchanger after those columns since they are sent to the solvent production unit, directly. There is not any solution sent to the solid removal system from these columns.

The last part of the solvent recovery unit is the thin film evaporator (TFE). Additionally, there is a pandryer system which is more simple than TFE. However, pan dryer is a separate system and it is being used for the solution comes from the neighbour company.

The operational principle of the pan dryer system is like a pressure cooker with a simple mixer. However, the main principle of the TFE is to form a thin film at the wall so that vaporization will be better while solution goes down.

TFE can be used for highly concentrated and viscous liquids at high temperatures. Also, the final solid waste of the pan dryer system contains solvent by 30-35%, however, the final solid waste (sludge) of the TFE contains solvent by 10-15%.

The diagram of the TFE can be seen from Figure 6.

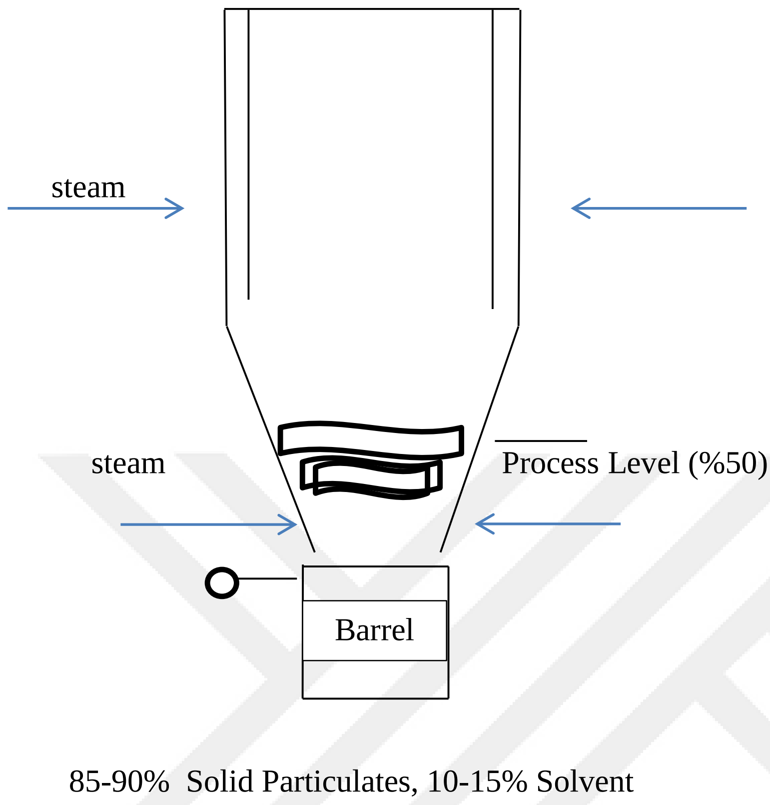

Figure 6: TFE diagram

The amount of the solution coming to the SRU is about 240 ton/hr. Initially, 6% of the solution is Chemical D. By hydrolysis due to the high temperature at the 1st column, 160.3 kg/hr (3847 kg/d) Chemical D is produced. The bottom product of the 1st column (the mixture of the solvent and Chemical D) with the amount of 212.5 kg/hr (5,100 kg/d), is sent to the Chemical D column. The remaining amount of the Chemical D is sent to the spinning part to be used again in the production of solvent which is the final product of the SRU. There is no loss of Chemical D within the system.

By hydrolysis, also Chemical E is obtained. Its amount is about 120 kg/hr. 300 kg/hr of the Chemical E and water mixture (the top product of the 1st column) is transferred to the SRU. The solution is 30% concentrated and the transferred amount contains 90 kg/hr (2,160 kg/d) Chemical E which means that 25% Chemical E as 30 kg/d (0.03 ton/hr) is lost.

4.1.2.2 Steam, Electricity and Water Consumption and Produced Solid Waste Amounts

The factory produces its own electricity and steam by the the coal fired power plant to be used during the production. In Table 5, energy consumption amounts of vapor and electricity in the SRU can be found.

Table 5: Steam, electricity and water consumption and produced solid waste amounts in the SRU

	Unit	**June 2014**	**July 2014**	**August 2014**	**Average Amounts (3 months)**
Electricity Consumption by the SRU	kWh/h	2,184	2,220	2,054	2,153
Steam Usage by the SRU	ton/h (kWh/h)	66.34 (62.59)	64.78 (60.93)	59.22 (56.14)	63.45 (59.89)
Average Amount of Water Usage for Cleaning the Subunits	ton/h	0.86	0.86	0.86	0.86
The Solid Waste Amount	ton/h	0.091	0.057	0.102	0.083
Disposal Cost of the Solid Waste	$/h	32.58	20.25	35.41	30.31

[2153 kWh/h = 7551 MJ/h for 1 kWh = 1MJ and for the calculation on disposal cost of the waste; 1$=2.12 TL in June, 2014, 1$=2.12 TL in July, 2014 and 1$=2.16 TL in August, 2014] [24,25].

In 2015, a new subunit was added to the SRU, therefore, data belonging to the year 2014 was used in the study for making more accurate analysis that reflects the three subunits.

The operational cost mentioned in Table 5, includes maintenance, power transmission line, labour, natural gas, coal and electricity use.

Note that in the SRU, to prevent energy consumption, ejectors are being used instead of pumps to produce vacuum at the top of the columns. The centrifugal pumps are being used only to send the solution to the higher points in the system.

4.1.2.3 Water Usage

RW with a 1000 ton capacity stores recycled water and deionized water. The recycled water is obtained from the SRU (140 ton/h) and all of it is pumped from the RW to the spinning unit to be used again. The water used in the spinning unit is obtained from the SRU as recycled water and it is always circulated in the process to minimize losses in terms of mass and energy. Normally, spinning unit consumes 165 ton/h water. Therefore, 25 ton/h deionised water is used as make-up in the RW.

The water consumption of the SRU is only due to cleaning of the heat exchangers and columns.

There are 17 heat exchangers in the SRU. To wash polluted heat exchangers at every 20 days period, hydrants are used. However, to wash each subunit at every 40 days and for the general cleaning once a year, recycled water is used. In short, it can be said that averagely; 17 heat exchangers are washed at every 40 days based on the each subunit cleaning requirement and 15 heat exchangers are washed once a year depending on the pollution levels of the heat exhangers.

Based on the data available, it can be said that 250 ton water is used for each subunit at every 40 days (Considering the fact that each unit is also out of service for cleaning and maintanence purposes once every 40 days).

Additionally, on the average 500 ton recycled water per unit is used for general cleaning purpose in a year.

As a result, for 3 units (by assuming 360 days in a year to analyse water consumption for every 40 days time intervals);

- 250 * 3 * 8 = 6,000 ton/yr water (for standarg cleaning of each subunit every 40 days period except the general cleaning once a year),
- 500 * 3 = 1,500 ton/yr water (for a general cleaning of each subunit once a year) is consumed.

Hence, totally, it can be inferred that 7,500 ton/yr = 20.5 ton/d = 0.86 ton/h water is needed at the SRU for cleaning, ignoring the amount of escaped vapor from vents into the atmosphere due to the glitches within the system. The water used for cleaning is being sent to the wastewater treatment plant by meshes around the SRU.

Additionally, for the three subunits of the SRU, for heating the solution, the amount of needed vapor is 63.45 ton/h (59.89 MWh/h).

The vapor is not consumed; after vapor is condensed, it is sent to the power plant to be heated and then is directed back to the SRU.

4.1.2.4 Emissions

Because of the high temparature at the 1st column (122 ^{o}C at the top and 200 ^{o}C at the bottom), hydrolysis takes place and the solvent (Chemical C) digests into its components (Chemical D and Chemical E). Due to fluctuations and glitches in the system, Chemical E can escape to the atmosphere from the vents of the scrubbers and tanks of both the solvent recovery and the solvent production units. However, there is no loss of Chemical D within the system. The reason is that they have different tendency for rising through the column based on their boiling points.

The unused part of the Chemical D at the solvent production unit is being turned back to the SRU. There is a circuit within the units to minimize losses.

For both the solvent recovery unit and the solvent production unit, the total loss amount of Chemical E is about 30 kg/h (0.03 ton/h) (Figure 9). This equals to 1/4 of the total amount of Chemical E production. The escape due to its very low boiling point can take place from the scrubbers of the SRU, vents or the brackets of the lines.

The emission values of the power plants are not taken into consideration separately in this study since the impact of them are already calculated under the entered electricity data in the SimaPro Program. The emission values are also controlled by The Ministry of Environment and Urbanisation via the online system. All emission values are within limits under normal conditions according to the Regulation on Control of Industrial Air Pollution (dated 07/03/2009 and Official Gazette number 27277).

4.1.2.5 The Summary of the SRU

- The total solution (42% solvent and 58% water) amount that comes to the SRU is about 240 ton/h. At the end of distillation, 100 ton/h solvent and 140 ton/h recycled water are produced.
- Within the columns, the energy and mass flows follow counter-current flow mode.
- There is a cartridge filter with 15 micrometer (μm) diameter at the inlet of the SRU unit which can retain 10% of solid particulates, approximately.
- The vacuum at the top of the columns is maintained by means of the ejectors.
- The top product of the 1st column includes 0.05 – 0.1% Chemical D.
- From the flasher, the solution is sent to the 1st column in the gas phase, and the solid particulates are accumulated at the bottom. At the flasher, another aim is to fix the highest concentration of the solids in the solution as 1%, constantly.
- The solution comes to the solid removal tank which exists before the thin film evaporator, includes 1% solid particulates, 4% water and 95% solvent.
- The end product of the solid removal tank includes 30% solid and the flow rate to the thin film evaporator is 12 ton/h.

- The amount of solid waste (sludge) produced from the thin film evaporator is about 0.083 ton/h with 90% solid concentration. The thin film evaporator is much more efficient than the pan dryer system since the final waste of the pan dryer contains 65% solid particulates and 35% solvent. The disposal cost is also higher for the pan dryer system since it includes more solvent.
- For the 90 tons of solution, 24 tons of steam is needed for the system. (The incoming solution to the SRU is 240 ton/h and 64 ton/h steam is required).
- The recycled water is being sent to the spinning part to be used again.
- Average electricity consumption by the SRU (three subunits) is 2153 kWh/h = 7551 MJ/h (where 1 kWh = 1MJ).
- Both the steam for heating and water used in the system are not wasted, they are circulated.
- Normally, wastewater is produced due to the cleaning of the columns and heat exchangers within the SRU. The resulting wastewater amount due to the cleaning is very little as compared to the total amount of wastewater production by the factory.

4.2 LCA Approach

This LCA study was conducted by using SimaPro ver. 7.2.4 software developed by PRé Consultants [26].

4.2.1 Goal and Scope

In this study, the main goal is to determine the overall environmental performance of the SRU. SRU includes three subunits, one of which is illustrated in Figure 4. Each of them has the same working mechanism while their capacities are different (100 ton/h – 100 ton/h – 60 ton/h). The solution comes from the spinning part and it consists of water and solvent that involves also chemicals used in the process. The studied system boundary was described as “cradle to gate 2” where the “cradle” represents the solvent production (including its raw materials and processes) while “gate 2” represents the exit gate of the SRU (i.e. the end of TFE). The entry of the

SRU was described as "gate 1". The main plant was excluded from the system boundary. Therefore, it can be said that the system boundary is a 'cradle to gate 2'. Figure 7 shows the system boundary of the SRU-LCA study. In this figure, only solvent and water components of the system were represented while the decomposition products (acetic acid and dimethylamine) were not shown to avoid complexity. Functional unit was set as 1 kg of solvent recovered.

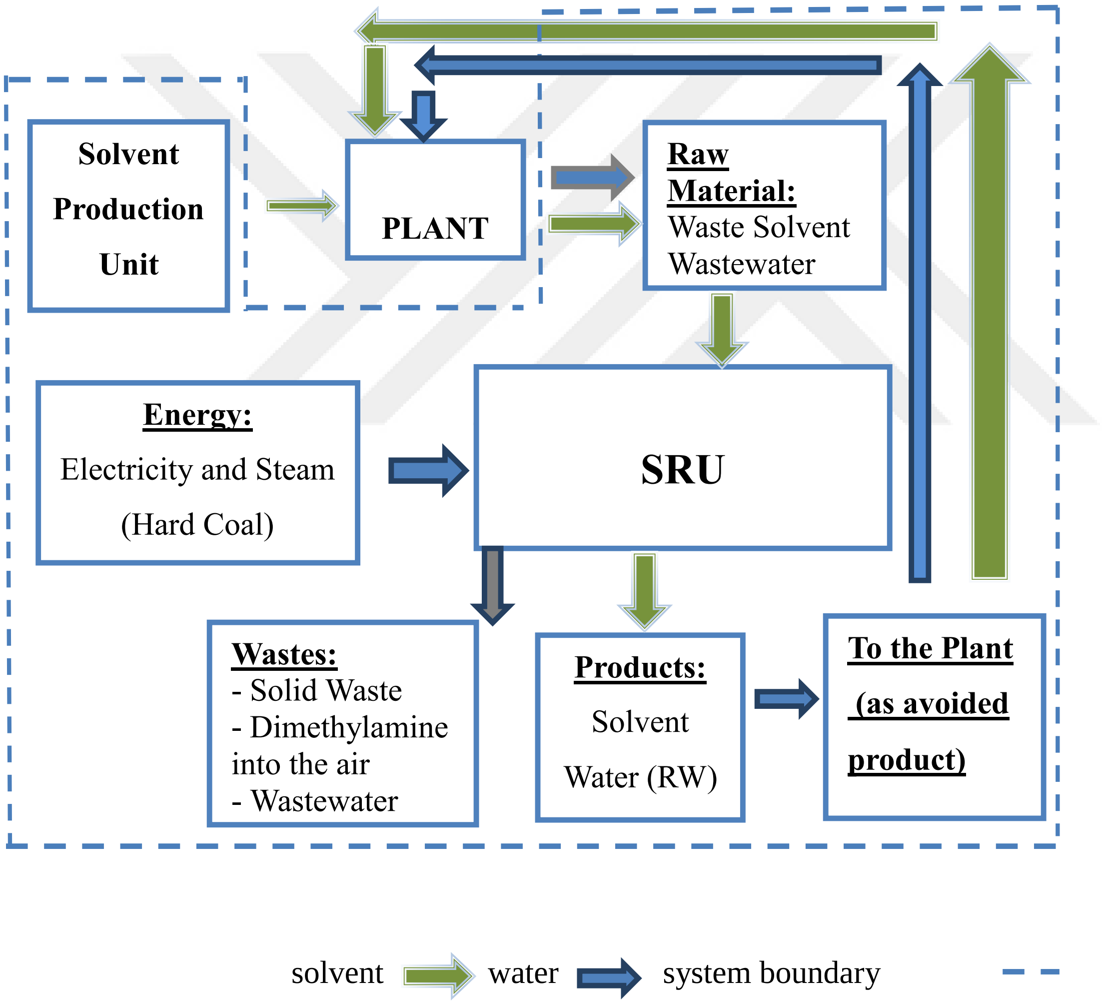

Figure 7: System boundary for the LCA-SRU study

To understand the impact of recovering solvent on wastewater treatment, application of end-of pipe treatment was analysed. For the end-of-pipe treatment of the solvents part of the study, system boundary starts with the inlet of the WWTP and ends with sludge digestion. The functional units were set as 1 kg waste solvent treated.

An alternative method to distillation, solvent incineration was also analysed. For the incineration of solvents part of the study, the system boundary starts with the inlet of the incineration system and ends with flue gas cleaning. The functional unit was set as 1 kg waste solvent incinerated.

All waste handling methods were analysed for both DMAc and DMSO.

In SimaPro, the following selections were made as entry on the goal and scope section;

- DQI Requirements (Data Quality Indicators) under the goal and scope section were entered, namely; time, type of the technology and system boundaries, as the known data.
- Time; '2000-2004', '1985-1989' and 'before 1980' were chosen as the time intervals of each subunit.
- Type; 'average technology', 'modern technology' and 'data from a specific process and company' were signed as the type of the technology and representativeness.
- 'less than 1% (environmental relevance) for the cut-off amount and 'second order (material/energy flows including operations)' inside the "system boundaries" part were selected

The related screenshots can be seen through Figures B.1-B.3 in Appendix B.

4.2.2 Inventory

This section is about gathering inventory data related to all inputs and outputs of the systems (SRU, end-of-pipe treatment and incineration) studied.

Primarily Ecoinvent and Ecoinvent Unit Processes databases were preferred; in case the information was not available in these databases, the other databases were used.

Geographical conditions specified in the databases were accepted as appropriate for the location of the plant studied.

4.2.2.1 For the SRU

For the SRU-LCA study, since the system boundary was “cradle to gate 2”, necessary data including *upstream* processes of the SRU (i.e. solvent production) should be available. For the “gate 1 to gate 2” part of this analysis, data were obtained through the site investigation in the plant studied. Detailed mass balance was constructed for the entire SRU. Compilation of this data was also summarized in Table 6. This set of data formed a basis for the calculation of the inputs, outputs and avoided products for the SRU as indicated in Figure 8.

Data which could not be obtained from the plant were gathered from the Databases provided in SimaPro software. For example, data regarding the “cradle to gate 1” part (upstream processes, e.g. production of solvents, DMAc and DMSO) were extracted from the “Ecoinvent Unit Processes” database of SimaPro. Regarding the production of the solvents, units selected were “Input as Dimethylacetamide, at plant/GLO U” and “Dimethyl Sulfoxide, at plant/RER U” from the database[1]. Note that these units were the only available ones provided in the SimaPro for DMAc and DMSO production. The further detail about these unit processes are provided in Sec. 4.2.2.1 under remarks.

The other relevant databases and their properties can be seen in the following subsections.

Note that the use of water for cooling within the system was ingored since it is always circulated for the same purpose and the amounts of the input and output are equal. Also, entered amount of electricity usage includes the electricity consumption of the circulation of the cooling water and steam.

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[1] *Extension U in the names of the units refers to the library which contains 4100 unit processes which show the specific inputs and outputs and have links to the other processes. Extensions GLO and RER refers to location as “global” and “regional” respectively.*

For DMAc

Dimethylacetamide is an organic, colorless, volatile and hazardous liquid. It is miscible in most organic solvents, aromatic compounds, esters, ethers and ketones [28]. The summary of inputs, outputs and avoided products of entire SRU for DMAc are presented in Figure 8.

The screenshot of data entry in terms of inputs and outputs for DMAc can be depicted from Figure B.4 in Appendix B. As seen from this figüre, electricity (hard coal) and process steam (from heavy fuel oil) used in the plant are 2153 Kwh and 59.89 Kwh, kg of waste solvent recovered, respectively.

<u>Database Characteristics of Recovering DMAc</u>

Impact Assessment Method: Eco-Indicator 99.

Input/Output: Dimethylacetamide, at plant/GLO U

Functional Unit: 1 kg DMAc recovered.

Data treatment extrapolations: energy consumptions and emissions are estimated.

Included processes: Production of N,N-dimethylacetamide including materials, energy uses, infrastructure and emissions.

Remark: The process "N,N-dimethylacetamide, at plant, GLO" is modelled for the production of N,N-dimethylacetamide from dimethylamine and acetic acid in the world. Raw materials are modelled with a stoechiometric calculation. Energy consumptions and emissions are estimated. Infrastructure and transports are calculated with standard values.

CAS number: 000127-19-5; *Formula:* C_4H_9NO; *Geography:* The inventory is modelled for the world.

Technology: Amination of acetic acid.

Database name: “Ecoinvent unit processes”

Table 6: Mass balance of the solvent recovery unit based on the 100 ton solution (DMAc)

STREAM	**1**		**2**		**3**		**4**		**5**	
FLUID	Feed to the 4th Column		Bottom Product of the 4th Column		Top Product of the 4th Column		Feed to the 3rd Column		Bottom Product of the 3rd Column	
STATE	liquid		liquid		vapor		liquid		liquid	
MASS FLOW RATE kg/h	100000.00		80929.50		21834.60		80929.50		68080.00	
COMPONENTS	kg/h	%	kg/h	%	kg/h	%	kg/h	%	kg/h	%
CHEMICAL E		0.0		0.0		0.0		0.0		0.0
WATER	57900.0	57.9	34071.3	42.1	21801.9	99.9	34071.3	42.1	21243.6	31.2
SOLVENT	42000.0	42.0	46777.2	57.8	10.9	0.0	46777.2	57.8	46776.7	68.7
CHEMICAL D	100.0	0.1	81.0	0.1	21.8	0.1	81.0	0.1	59.7	0.1
MASS BALANCE	**100000.00**	**100**	**80929.50**	**100**	**21834.60**	**100**	**80929.50**	**100**	**68080.00**	**100**

Table 6: Mass balance of the solvent recovery unit based on the 100 ton solution (DMAc) - continued

STREAM	6		7		8		9		10		11	
FLUID	Top Product of the 3rd Column		Feed to the 2nd Column		Bottom Product of the 2nd Column		Top Product of the 2nd Column		Feed to the Flasher		Feed from the Flasher to the 1st Column	
STATE	vapor		liquid		Liquid		vapor		mixed		vapor	
FLOW RATE kg	17564.90		69847.00		64330.60		18502.40		65330.60		60330.60	
COMPONENTS	kg/h	%	kg/h	%	kg/h	%	kg/h	%	kg/h	%	kg/h	%
CHEMICAL E		0.0		0.0		0.0		0.0		0.0		0.0
WATER	17545.2	99.9	21802.4	31.2	7658.0	11.9	18485	99.9	7807	11.9	7549.5	12.5
SOLVENT	8.8	0.1	47984.9	68.7	56611	88.0	9.2	0.1	57461	88.0	52725	87.4
CHEMICAL D	5.7	0.0	59.7	0.1	61.3	0.1	2.8	0.0	62	0.1	56.5	0.1
MASS BALANCE	**17559.7**	**100**	**69847**	**100**	**64330.3**	**100**	**18497**	**100**	**65330**	**100**	**60331**	**100**

Table 6: Mass balance of the solvent recovery unit based on the 100 ton solution (DMAc) – continued

STREAM	**12**		**13**		**14**		**15**		**16**	
FLUID	Bottom Product of the 1st Column		Top Product of the 1st Column		Feed to the Solid Removal Tank		Top Product of the Solid Removal Tank		Thinfilm Evaporator Feed	
STATE	liquid		vapor		mixed		vapor		liquid	
FLOW RATE kg/h	104300.00		22760.60		13850.00		13600.00		250.00	
COMPONENTS	kg/h	%	kg/h	%	kg/h	%	kg/h	%	kg/h	%
CHEMICAL E	4.3	0.0	46.5	0.2		0.0		0.0		0.0
WATER	199.0	0.2	22704.4	99.8	700.1	5.1	691.1	5.1	9.0	3.6
SOLVENT	103905	99.6	9.7	0.0	13144.2	94.9	12903.3	94.9	240.9	96.4
CHEMICAL D	191.7	0.2	0.1	0.0	5.8	0.0	5.7	0.0	0.1	0.0
MASS BALANCE	**104300**	**100**	**27760.7**	**100**	**13850.1**	**100**	**13600.1**	**100**	**250**	**100**

Inputs

- 99.857 ton/h solvent (dimethylacetamide) and 0.143ton/h acetic acid, initially.
- 140 ton/h water by the solution.
- 59.89 MWh/h steam for heating in the system.
- 2.153 MW/h (7551 MJ/h) electricity
- 0.86 ton/h water (cleaning)

Products During Process

- HYDROLYSIS

  (0.160 ton/h Acetic Acid)

  (0.120 ton/h Dimethylamine)

Outputs

- 97.264 ton/h solvent and 0.093 ton/h acetic acid, finally).
- 139,65 ton/h RW
- 0.86 ton/h wastewater due to cleaning (emission to water).
- 0.083 ton/h sludge/solid waste (it is sent to the waste disposal facility for incineration)
- 0.03 ton/h Dimethylamine is lost/wasted. (emission to air)

Avoided Products

- 2 ton/h solvent and 0.21 ton/h acetic acid.
- 0.21 ton/h RW and 0.09 ton/h

Figure 8: Inputs, outputs and avoided products of the SRU for DMAc

For DMSO

Other than analysing the general environmental performance of the SRU for DMAc, alternative solvent, DMSO was also analysed since DMSO is less toxic than dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone and hexamethylphosphoramide. DMSO is a colorless, organosulfur liquid. Because it is aprotic solvent, it can dissolve both polar and nonpolar compoounds. Also, it is weakly acidic, therefore, it tolerates strong bases and extensively used in the study of carbonions [27].

It was assumed that DMSO will not be separated into its components due to hydrolysis at high temperatures as DMAc does. The boiling point of DMAc is 163-165 ^{o}C whereas it is 189 ^{O}C for DMSO [28,29]. In addition to that molecules with higher molecular weights decompose its components easier than molecules with lower molecular weights [30]. The molecular weight of the DMAc is 87.12 g/mol whereas it is 78.13 g/mol for DMSO. Therefore, it is expected that DMAc separates into its components easier [28,29].

The lost amount was taken as ~0.5%. It was assumed that all remaining operational conditions are the same.

The screenshot of data entry in terms of inputs and outputs for DMSO can be depicted from Figure B.8 in Appendix B.

Database Characteristics of Recovering DMSO

Impact Assessment Method: Eco-Indicator 99.

Input/Output: Dimethyl Sulfoxide, at plant/GLO U

Functional Unit: 1 kg DMSO recovered.

Data treatment extrapolations: energy consumptions, emissions, infrastructure and transports are calculated with standard values.

Included processes: Production of dimethylsulfoxide including materials, energy uses, infrastructure and emissions.

Remark: The process "dimethylsulfoxide, at plant, RER/U" is modelled for the production of dimethylsulfoxide from methanol and hydrogen sulfide in Europe. Raw materials are modelled with a stoechiometric calculation, Energy consumptions, emissions, infrastructure and transports are calculated with standard values.

CAS number: 000067-68-5; *Formula:* C2H6SO; *Geography:* The inventory is modelled for Europe.

Technology: Sulfoxidation of methanol

Database Name: “Ecoinvent unit processes”

4.2.2.2 For the End-of Pipe Treatment of Solvent

For this part of the LCA study, it was assumed that a conventional WWTP will serve for the treatment of solvent waste generated in the factory. To this purpose, ‘Treatment, sewage, to wastewater treatment, class 2/CH U’ option which reflects a moderately large WWTP was selected from the Simapro database. About 2,400 ton/d solvent is being recovered via the SRU and 6,500 ton/d wastewater is being produced by the company in general. So, while determining the overall wastewater flowrate to the WWTP, it was considered that the water consumed within the whole factory (i.e. 6,500 ton/d) will be directed to the WWTP. This is named as a “end-of-pipe wastewater treatment - base line” study. If the solvent is not recovered in the SRU and hence directed to the WWTP, the waste solvent flowrate (i.e. 2,400 ton/d) should be additionally considered. This case is named as “end-of pipe treatment of solvent”. In this respect, the flowrate of the wastewater that will be introduced to the WWTP was taken as 6,500 ton/d for the base line study whereas it was taken as 8,900 ton/d (2,400 + 6,500 ton/d) for the end-of-pipe treatment of solvent cases. In the latter cases, it was estimated that the wastewater flow will contain 269 kg solvent/ton wastewater which corresponds to 254 kg DMAc/ton wastewater and 296 kg DMSO/ton wastewater for the DMAc and DMSO cases, respectively. Note that the density of DMAc (d_{DMAc}) = 942.9 kg/ton [28] and the density of DMSO (d_{DMSO}) = 1100 kg/ton [29].

Database Characteristics of End-of Pipe Treatment

- *Functional Unit:* 1 kg waste solvent treated with and without solvent contamination.
- *Impact Assessment Method:* Eco-Indicator 99
- *System boundary:* “cradle to gate”.
- *Method:* ‘Treatment, sewage, to wastewater treatment, class 2/CH U’ Method
- *Data treatment extrapolations:* wastewater compositions from literature and/or estimates
- *Included processes:* Infrastructure materials for municipal wastewater treatment plant, transports, dismantling. Land use burdens.
- *Remark:* Wastewater purified in a moderately large municipal wastewater treatment plant (capacity class 2), with an average capacity size of 71100 per-captia-equivalents PCE.
- *Technology:* Three stage wastewater treatment (mechanical, biological, chemical) including sludge digestion (fermentation) according to the average technology in Switzerland.
- *Database Name:* “Ecoinvent unit processes”

4.2.2.3 For the Incineration of Waste Solvent

As another alternative for handling of the waste solvent, incineration was taken into consideration. For this part of the LCA study, an incineration plant available in the database of SimaPro software was used. Database characteristics for this unit is summarized below.

Database Characteristics for the Incineration of Waste Solvent

- *Functional Unit:* 1 kg solvent incinerated.
- *Impact Assessment Method:* Eco-Indicator 99
- *Method:* “Disposal, solvents mixture, 16.5% water, to hazardous waste incineration/CH U”
- *System boundary:* “cradle to gate”.

- *Included processes:* waste-specific air and water emissions from incineration, auxiliary material consumption for flue gas cleaning. Short-term emissions to river and long-term emissions to groundwater from residual material landfill (from solidified fly ashes and scrubber slugde). Process energy demands for HWI.
- *Remark:* Inventoried waste contains 100% waste solvents mixture.
- *Waste composition (wet, in ppm):* upper heating value 23.68 MJ/kg; lower heating value 21.7 MJ/kg.
- Share of carbon in waste that is biogenic 0%.
- *Net energy produced in HWI:* 17.11MJ/kg electric energy and 1.27MJ/kg thermal energy.
- *Allocation of energy production:* no substitution or expansion. 100% of burden allocated to waste disposal function of HWI.
- One kg of this waste produces 0.07563 kg of residues, which are landfilled. Additional solidification with 0.03025 kg of cement; geography: specific to the technology encountered in Switzerland in 2000. Well applicable to modern incineration practices in Europe or North America or Japan.
- *Technology:* Swiss HWI plant in 2000 with wet flue gas scrubber and low-dust SCR DeNOx facility. Gross thermal efficiency 74.4% and gross electric efficiency 10%.
- *Database name:* “Ecoinvent unit processes”

4.2.3 Impact Assessments

The method has to be selected to be able to perform an impact assessment. The Eco-Indicator 99 method was chosen for all scenarios considered in the thesis study. The reasons/advantages to choose the ‘Eco-Indicator 99’ method can be summarized as; making damage assessment including human health, ecosystem quality and resources, making weighting between damage categories with a high quality, involving fate dispersion and degradation of emissions in the environment, having a wide range of emissions and impacts as depletion, land use, nuclear radiation and having specifications of the uncertainities and assumptions. Additionally, Eco-Indicator 99 arrives at one single score for the entire life cycle.

At this point, it should be mentioned that impact assessment method of IMPACT 2002+ could be considered as appropriate as well since its superiority over Eco-Indicator 99 due to more impact categories covered. Indeed, in this study, IMPACT 2002+ was also tested and it was seen that the resulting total impact score was 200 times lower than that obtained with Eco-Indicator 99 (Appendix A). One of the intentions of this study was to compare the alternative solvent handling methods. So, comparison would be easier and more clear with less impact categories having greater single scores. Moreover, the additional impact categories (non-carcinogens, terrestrial ecotoxicity, photochemical oxidation) covered in Impact 2002+ as compared to Eco-Indicator 99, were not essential for the system studied. Because, the main focus in the SRU is raw material consumption, hence fossil fuel impact category. Therefore, Eco-Indicator 99 method was preferred.

The steps of The Eco-Indicator 99 Methodology can be seen from Figure 9.

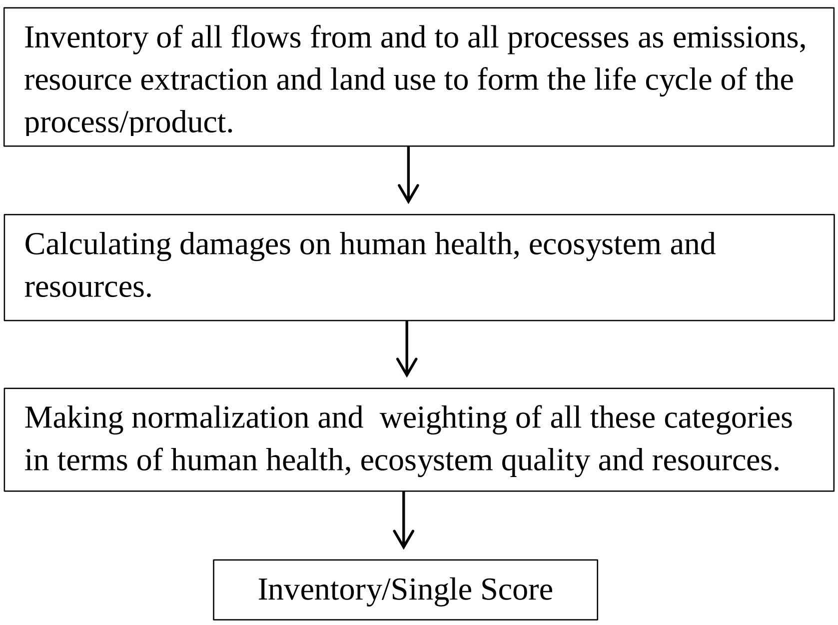


Figure 9: The general procedure of the Eco-indicator 99 methodology [31]

Normalization by Eco-Indicator 99 depends on the damage caused in the environment per inhabitant in a specific area, per year to make the impact scores of the environmental profile comparable. Units are converted into fractions by normalization. For Eco-Indicator 99, factors in terms of deteriorations of human health, ecosystem quality and resources and ecotoxicity are 65.1, 1.95×10^{-4} and 1.19×10^{-4} respectively. Only, ecotoxicity is multiplied by 0.1 before it is normalized, additionally [32].

Making comparison between different impact categories to understand their seriousness is made by use of weighting factors. Weighting is performed by multiplication of a normalized environmental profile with weighting factors. In Eco-Indicator 99, the weighting factors of human health, ecosystem quality and resources are 300, 400 and 300, respectively. Multiplication of normalization factors by weighting factors results in single scores for each category [32].

The unit of both the single score and weighting is mPt (millipoints). The absolute values of points is not necessary for making evaluation because the aim is to compare the relative differences between two cases. Characterization and damage assessment are based on percentages. The unit of normalization reflects the fractions of all emissions and resource usage in the world during one year per impact category.

4.2.4 Sensitivity Analysis

A complete uncertainty analysis could not be performed due to limited data as well as time constraint in the study. However, a sample sensitivity analysis was performed for DMAc recovery case. During this analysis, input and output values were changed by 5% and the changes in the impact scores were observed.

4.2.5 Economic Analysis

Economic analysis is essential in engineering since all engineering practices require large amounts of capitals and owners expect maximum return on capital investments. Two major components of budgets are revenues and costs.

Thus, comparison of the economic analysis of the solvent recovery to end-of-pipe treatment of the waste solvent was made. The cost figures for the SRU and end-of-pipe treatment were readily available from the Plant studied as these units are present in the Plant. The economical comparison was not made for the incineration option since the cost figures were not readily available as this unit is not present in the Plant studied. As known, revenues and costs of an incineration plant depend on type of the waste used, technology and capacity of the plant, directly. So, because of this variability, literature cost figures, even if were available, would not be suitable for the purpose targeted in this thesis. Moreover, there is a coal fired power plant in the company in which electricity and steam are already being produced.

The net profit of recovering the solvent was calculated based on 20 years operational time period using Equation 1, the future value formula (FV) [32]. Net present values (NPV) were also calculated using Equation 2. The main idea in the economic analysis is time value of the money.

$$\mathrm{FV} = \mathrm{PV}\,(1+r)^n \qquad \text{Equation 1 [33]}$$

FV = Future value

r = interest rate

n = time period, year

PV = Present value

$$NPV = \sum_{n=0}^{n} (\mathrm{R(n)} - \mathrm{C(n)})/(1+i)^n \qquad \text{Equation 2 [15]}$$

NPV = Net Present Value

N = time period, year

i = discount rate

R(n) = Revenues in time period (n)

C(n) = Costs in time period (n)

NPV method is about expressing the future cash flows in terms of their present value. If the NPV is greater than zero, the investment is acceptable. If the NPV is less than zero, the investment should be rejected [15].

It was assumed that the costs and revenues will increase by 5% each year considering the time value of money within 20 years time period for the FV. The discount rate for the calculation of NPV was taken as 5%.

The following basic expressions were considered to calculate the net profit.

Total cost = capital cost + O&M cost

Net Profit = (revenue – total cost)

Economical Analysis for Recovering the Solvent

The total indexed capital investment of all 3 subunits by 2016 is 108,230,000 $.

The O&M cost of the SRU by 2016 is ~1,315,000 $/month (~15,780,000 $/y).

By assuming, purchasing cost of DMAc is 900$/ton [34].

The solvent recovery revenue will be 788,400,000 $ in 2016 based on 100 ton/hr = 876,000 ton/y solvent will be recovered, not wasted).

For;

1 ton= 269 gallon [35],

Cost of water production by RO/deionization is about 0.05$ per gallon [36].

Revenue from 1 ton water recovery= 13.5 $. Thus, revenue from water recovery by the SRU can be ignored as compared to the solvent recovery (900$/ton).

Economic Analysis of the End-of-Pipe Treatment of Solvent (Base-line)

Based on the capital cost of the WWTP as 17,000,000 $ with 15,000 ton/d wastewater treatment capacity, the capital cost of end-of-pipe treatment for 2400 ton/d solvent will be 2,720,000 $ [37].

The cost of O&M for current WWTP for 8,000 ton/d wastewater is ~350,000 TL/month = 4,200,000 TL/y = 1,433,448 $/y (1$=2.93 TL, avg value of $, January-June 2016) [38].

It was assumed that the O&M cost will be proportional with the flowrate of the wastewater. Therefore, additional cost of the end-of pipe treatment of solvent will be 430,035 $/y if solvent is not recovered. The summarized revenue and cost values can be seen from Table 7.

Table 7: Revenue and cost values of the solvent recovery and end-of pipe treatment

	Revenue ($/y)	Capital Cost ($)	O&M Cost ($/y)
Solvent Recovery	788,400,000	108,230,000	15,780,000
End of Pipe Treatment	_	2,720,000	430,035

4.2.6 Assumptions

- The data used for the SRU is almost certain since it reflects the system in practice.
- The used data reflects the average amounts.
- The amount of recovered solvent reflects also make-up amount due to losses within the system which equals 7 ton/d whereas the amount of solvent recovery is 2400 ton/d. Also, the make-up amount can be ignored in the economic analysis.

- There will be uncertainities for end-of pipe treatment and incineration analysis since data was taken from the database in SimaPro, data may not reflect the practice exactly.
- The parameters mentioned for a single subunit during the mass and energy balance analysis were assumed to be valid for the entire unit due to the same operational mechanism prevailing.
- The impact of the wastewater sent for the cleaning of the subunits and heat exchangers is very small amount (0.86 ton/h) compared to the amount of wastewater produced (6,500 ton/d) by the company. So, it can be ignored in terms of impact on the WWTP. The vapor loss in the SRU is only due to the ejectors and the amount is nearly 10 kg/h which can be ignored in comparison with the used amount of vapor in total.
- DMSO and DMAc distillation operational conditions (temperature, pressure, steam amount, electricity) are assumed as same.
- Electricity (hard coal) and process steam (from heavy fuel oil) used during the recovery of DMAc in the SRU (2153 Kwh and 59.89 Kwh per kg of waste solvent recovered, respectively) are assumed to be same in case of DMSO recovery.
- DMSO will not be separated into its components due to hydrolysis at applied temperatures in the SRU unlike for DMAc since the boiling point of DMSO is 189 ^{o}C whereas it is 165 ^{o}C for DMAc.
- ‘Treatment, sewage, to wastewater treatment, class 2/CH U’ Method of SimaPro is similar to the current WWTP in the company in terms of capacity.
- “Disposal, solvents mixture, 16.5% water, to hazardous waste incineration/CH U” Method of SimaPro is suitable for the incineration of DMAc and DMSO.
- The O&M cost will be proportional with the flowrate of the wastewater regardless of solvent contamination.

CHAPTER 5

RESULTS AND DISCUSSION

LCA study was performed using SimaPro software for the recovery of the solvent by distilation via the SRU of the chemical factory. During this analysis, recovery operations for the currently used solvent, DMAc and for the possible substitutive solvent, DMSO, were considered in a comparative manner. Then, two different scenarios simulating the alternative solvent handling operations, namely, end-of-pipe treatment and incineration of the solvents were analysed and compared with each other as well as with the solvent recovery option via distilation. The following sections present the results obtained from the corresponding LCA studies.

As stated in Section 4.2.3, environmental impacts are calculated via Eco-Indicator 99 method. Normalisation, weighting and single score graphs are considered during the evaluation of results. However, single score results have been ultimately used for interpretation. Score of single score step is simply obtained by summing up weighting scores under the same end-point impact category. So, comparison is made based on single score results. Unit of these scores are 1 mPt (millipoint) which is equal to 0.001 Pt.

A financial evaluation is also presented in this chapter of the thesis, to analyze profitability of the solvent recovery option in comparison to end-of pipe treatment.

5.1 Impact Assessment of the SRU

5.1.1 Impact Assessment of the SRU for the Case of DMAc

Single score results obtained regarding the impact assessment of the SRU for the case of DMAc are presented in Table 8. Graphical representation of these impact scores is shown in Figure 10. As seen from these presentations, there are some negative scores. This is due to the fact that solvent acts as both input and avoided product for the system studied. It should be mentioned here that a positive score indicates a negative impact and vice versa. As stated earlier, the solvent DMAc and deionized water are recovered within the SRU. As seen from Table 8, single score of the impact due to DMAc came out to be +0.0772 Pt. As a result of the DMAc recovery, the majority of this impact is replaced as indicated by the negative single score of the recovered DMAc, i.e. -0.0767 Pt. In other words, recovering the solvent neutralizes the impact of the solvent to a great extent. The difference between these single score values is due to the solvent loss within the SRU and the decomposition of DMAc into its dimethylamine and acetic acid components during the entire recovery process. On the other hand, the single scores belonging to the deionised water used (0.000166 Pt) and the deionised water recovered (-0.000166 Pt) were equal by magnitude since there is no loss of deionised water within the system.

Table 8 also presents that acetic acid and dimethylamine which are the decomposition products of DMAc, had positive impacts (-0.000178 and -0.000044 Pt, respectively) since they occur within the system sponteneously by hydrolysis and they act as avoided products as they are used as raw materials in the solvent production unit of the factory. So, these components are directed to the solvent production unit of the factory. However, acetic acid had also negative impact (0.000841 Pt) because incoming solution to the SRU from the spinning unit includes acetic acid, initially. Therefore, the negative and positive scores of acetic acid were not equal to each other. Additionally, for operating the SRU, use of process steam and electricity had negative impacts, as expected.

The total single scores of DMAc, process steam, electricity, deionised water, acetic acid and dimethylamine for recovering DMAC for all impact categories in terms of Pt, were; -0.0767, +0.00394, +0.000315, -0.000166, -0.000094 and -0.000044 Pt, respectively. The impact of recovering DMAc was 20 times higher than the impact of process steam usage which is the second most important ingredient of the SRU. The related scores can be seen from Table 8.

The major impact categories of recovering the DMAc appeared as fossil fuels, respiratory inorganics and climate change with the scores; -0.0622, -0.00611 and -0.00354 Pt, respectively (Table 8 and Figure 10). Recovering the DMAc by distillation reduces the fossil fuel use since it could be used as a raw material in the process again. In a way, it can be inferred that recovering the waste solvent instead of burning helps reducing the emissions of particulate matters as sulphate and nitrate aerosols and carbon dioxide (CO_2) and methane (CH_4) to the atmosphere.

However, use of process steam had a negative impact on fossil fuel use, climate change and respiratory inorganics categories with scores of +0.00309, +0.000378 and +0.000363, respectively.

Table 8: Single scores of the SRU for DMAc (Screenshot from SimaPro)

Impact category	Unit	Dimethylacetamide, at plant/GLO U	De-ionised water, reverse osmosis,	Dimethylacetamide, at plant/GLO U	De-ionised water, reverse osmosis,
Carcinogens	Pt	0,00242	3,58E-7	-0,0024	-3,57E-7
Respiratory organics	Pt	2,58E-5	1,42E-8	-2,56E-5	-1,42E-8
Respiratory inorganics	Pt	0,00615	3,05E-5	-0,00611	-3,05E-5
Climate change	Pt	0,00356	2,02E-5	-0,00354	-2,02E-5
Radiation	Pt	0,000112	2,23E-7	-0,000111	-2,22E-7
Ozone layer	Pt	2,57E-6	9,85E-9	-2,56E-6	-9,84E-9
Ecotoxicity	Pt	0,00106	6E-7	-0,00105	-6E-7
Acidification/ Eutrophication	Pt	0,00115	6E-6	-0,00114	-5,99E-6
Land use	Pt	8,87E-5	0	-8,82E-5	0
Minerals	Pt	5,17E-5	2,01E-7	-5,14E-5	-2E-7
Fossil fuels	Pt	0,0626	0,000108	-0,0622	-0,000108
Total	Pt	0,0772	0,000166	-0,0767	-0,000166

Table 8: Single scores of the SRU for DMAc (Screenshot from SimaPro) - continued

Impact category	Unit	Acetic acid, 98% in H2O, at plant/RER	Electricity, hard coal, at power	Process steam from heavy fuel oil, heat	Dimethylamine, at plant/RER U	Acetic acid, 98% in H2O, at plant/RER
Carcinogens	Pt	2,74E-6	1,43E-5	2,67E-5	-8,67E-7	-5,81E-6
Respiratory organics	Pt	3,37E-8	1,65E-8	4,29E-7	-8,57E-9	-7,13E-8
Respiratory inorganics	Pt	6,45E-6	2,13E-5	0,000363	-2,97E-6	-1,37E-5
Climate change	Pt	3,39E-6	3,51E-5	0,000378	-1,8E-6	-7,18E-6
Radiation	Pt	1,31E-7	6,9E-8	2,6E-8	-3,22E-8	-2,77E-7
Ozone layer	Pt	3,09E-9	4,73E-10	1,07E-9	-1,26E-9	-6,55E-9
Ecotoxicity	Pt	1,03E-6	3,8E-6	3,53E-5	-5,87E-7	-2,19E-6
Acidification/ Eutrophication	Pt	9,3E-7	4,2E-6	3,83E-5	-8,37E-7	-1,97E-6
Land use	Pt	1,03E-7	2,8E-6	0	-2,84E-8	-2,19E-7
Minerals	Pt	4,19E-8	6,63E-9	3,62E-7	-4,93E-8	-8,88E-8
Fossil fuels	Pt	6,92E-5	0,000233	0,00309	-3,68E-5	-0,000147
Total	Pt	8,41E-5	0,000315	0,00394	-4,4E-5	-0,000178

The related graphs of characterization and damage assessment, normalization and weighting results can be seen through Figures B5-B7 in Appendix B.

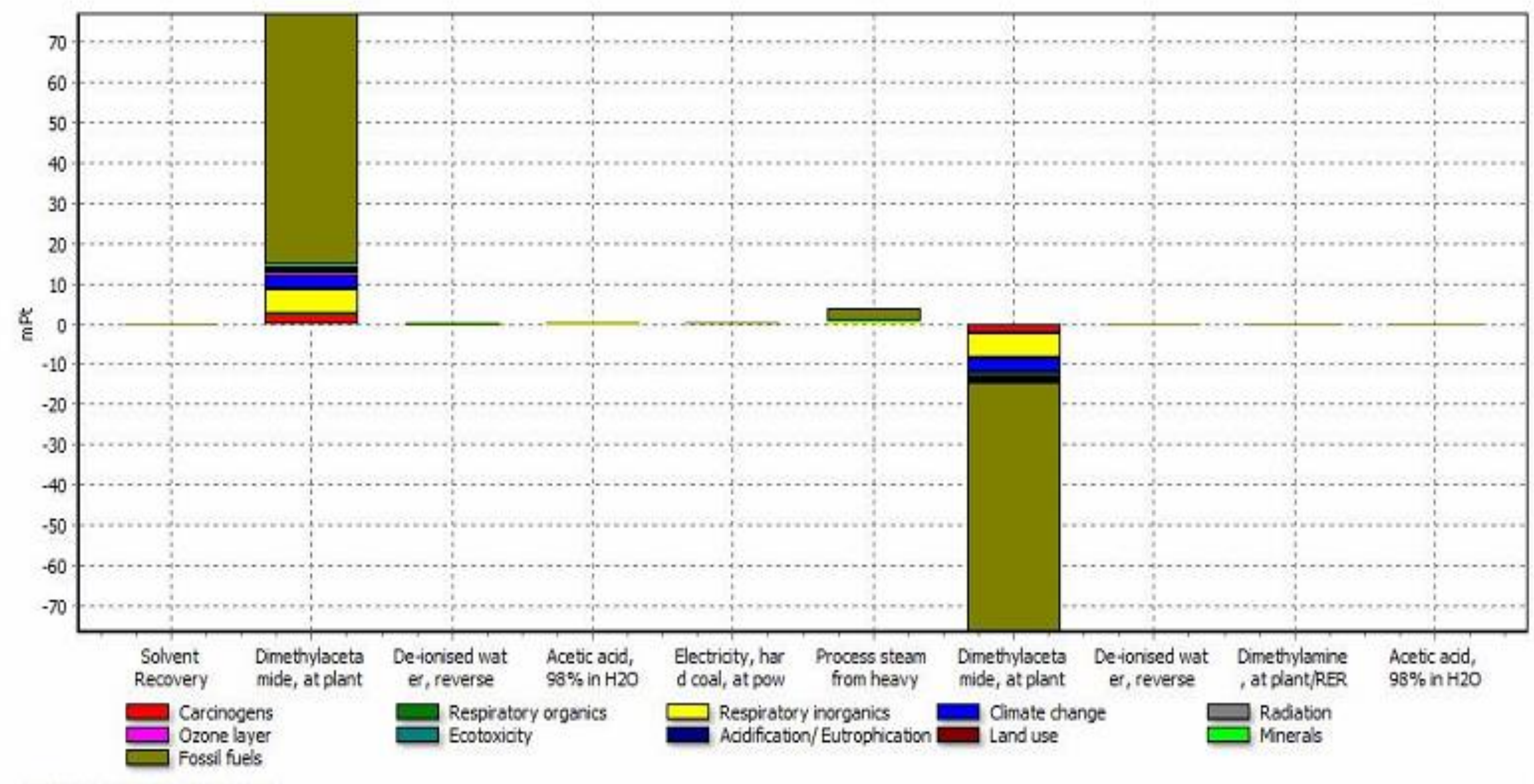


Figure 10: Single score of the SRU for DMAc

Sensitivity Analysis

Due to gathering some of the data from the SimaPro databases, also having some conditions in some of the unit processes not reflecting plant conditions (such as geographical location), some uncertainities may be of concern. To see how much the results will change if the data used is not certain, sensitivity analysis was performed for DMAc. During this analysis, results obtained when the input and output amounts were changed by 5% can be seen from Table 9. The related inputs/outputs can be seen from Figures E1-E2 in Appendix E.

Table 9: Sensitivity analysis of DMAc recovery

Impact category	Unit	Total	Total
Total	Pt	0,00457	0,00457
Carcinogens	Pt	5,14E-5	5,13E-5
Respiratory organics	Pt	5,52E-7	5,51E-7
Respiratory inorganics	Pt	0,000411	0,00041
Climate change	Pt	0,000429	0,000428
Radiation	Pt	5,79E-7	5,74E-7
Ozone layer	Pt	1,21E-8	1,2E-8
Ecotoxicity	Pt	4,37E-5	4,36E-5
Acidification/ Eutrophication	Pt	4,75E-5	4,74E-5
Land use	Pt	3,19E-6	3,18E-6
Minerals	Pt	5,79E-7	5,77E-7
Fossil fuels	Pt	0,00359	0,00358

DMAc

Sensitivity (DMAc)

As seen from Table 9, the difference on results of impact categories were found ignorable as the amounts of all input and outputs decreased by 5% only.

5.1.2 Impact Assessment of the SRU for the Case of DMSO

In addition to the impact assessment study for DMAc, impact assessment of an alternative solvent DMSO, was also sought to see the effect of solvent substitution on the environmental performance of the SRU.

Single score results regarding the impact assessment of the SRU for the case of DMSO are presented in Table 10. Graphical representation of these impact scores is shown in Figure 11. As seen, similar to the DMAc case, both positive and negative scores for the DMSO and the deionised water were obtained since they act as both input and output. Single score of DMSO use was found to be +0.0516 Pt. This negative impact is almost compensated by the single score impact amount of -0.0514 Pt as a result of DMSO recovery (Table 10 and Figure 11). The difference is due to the uncompansated amount which reflects the solvent loss (5%) within the SRU. However, the single scores of the deionised water use and its recovery were exactly equal since there is no loss of deionised water within the system boundary.

As in the case of DMAc, the impacts due to process steam and electricity use during the operation of the SRU were of concern for DMSO case as well. Unlike for DMAc case, there were no components other than DMSO, deionised water, process steam and electricity to exert an impact since it was assumed that no DMSO decomposition would occur.

The total single scores of DMSO, process steam, electricity and deionised water for recovering DMSO for all impact categories in terms of Pt, were; -0.0514, +0.00394, +0.000315 and -0.000166 Pt, respectively. The impact of recovering DMSO was 13 times higher than the impact of process steam use which is the second most important ingredient of the SRU. The related scores can be seen from Table 10.

The major impact categories of recovering the DMSO appeared as fossil fuels, respiratory inorganics and climate change with the scores of -0.0449, -0.00252 and -0.00198 Pt, respectively (Table 10 and Figure 11). Like for the DMAc case, recovering the DMSO by distillation is expected to reduce the fossil fuel use since it could be used as a raw material in the process again.

The single scores belonging to the impact of process steam use in terms of “fossil fuel consumption”, “climate change” and “release of respiratory inorganics” categories appeared as +0.00309, +0.000378 and +0.000363 Pt, respectively, as same with DMAc case since it was assumed that the process steam input is same as with DMAc recovery case.

Table 10: Single scores of the SRU for DMSO (Screenshot from SimaPro)

Impact category	Unit	Dimethyl sulfoxide, at plant/RER U	De-ionised water, reverse osmosis,	Dimethyl sulfoxide, at plant/RER U	De-ionised water, reverse osmosis,
Carcinogens	Pt	0,00103	3,58E-7	-0,00103	-3,57E-7
Respiratory organics	Pt	7,07E-6	1,42E-8	-7,04E-6	-1,42E-8
Respiratory inorganics	Pt	0,00253	3,05E-5	-0,00252	-3,05E-5
Climate change	Pt	0,00199	2,02E-5	-0,00198	-2,02E-5
Radiation	Pt	4,38E-5	2,23E-7	-4,36E-5	-2,22E-7
Ozone layer	Pt	1,33E-6	9,85E-9	-1,32E-6	-9,84E-9
Ecotoxicity	Pt	0,00034	6E-7	-0,000338	-6E-7
Acidification/ Eutrophication	Pt	0,000449	6E-6	-0,000447	-5,99E-6
Land use	Pt	3,36E-5	0	-3,34E-5	0
Minerals	Pt	4,85E-5	2,01E-7	-4,83E-5	-2E-7
Fossil fuels	Pt	0,0451	0,000108	-0,0449	-0,000108
Total	Pt	0,0516	0,000166	-0,0514	-0,000166

Table 10: Single scores of the SRU for DMSO (Screenshot from SimaPro) - continued

Impact category	Unit	Electricity, hard coal, at power	Process steam from heavy fuel oil, heat
Carcinogens	Pt	1,43E-5	2,67E-5
Respiratory organics	Pt	1,65E-8	4,29E-7
Respiratory inorganics	Pt	2,13E-5	0,000363
Climate change	Pt	3,51E-5	0,000378
Radiation	Pt	6,9E-8	2,6E-8
Ozone layer	Pt	4,73E-10	1,07E-9
Ecotoxicity	Pt	3,8E-6	3,53E-5
Acidification/ Eutrophication	Pt	4,2E-6	3,83E-5
Land use	Pt	2,8E-6	0
Minerals	Pt	6,63E-9	3,62E-7
Fossil fuels	Pt	0,000233	0,00309
Total	Pt	0,000315	0,00394

The related graphs of characterisation and damage assessment, normalisation and weighting results can be seen through Figures B9-B11 in Appendix B.

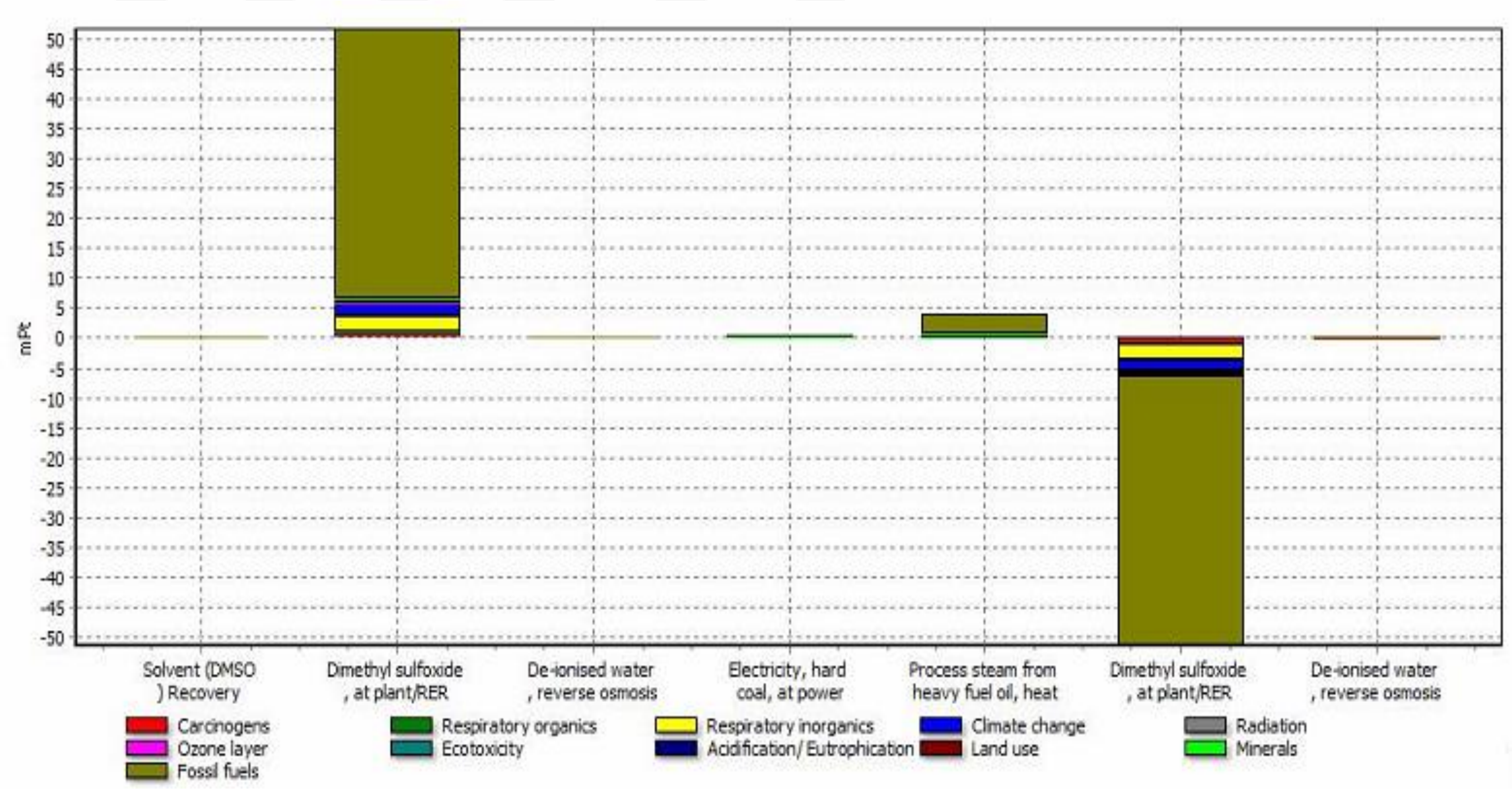


Figure 11: Single score of the SRU for DMSO

5.1.3 Comparison of Impact Assessments for Recovering DMAC and DMSO

In this section, the impact assessment results obtained for the DMAc and DMSO recovery cases were compared.

The total single scores pertaining to the DMAc and DMSO cases were 0.00457 Pt and 0.00451 Pt, respectively, as indicated in Table 11. These two scores are very close to each other, being the one for DMAc slightly higher. This shows the impacts of dimethylamine and acetic acid production within the system can be neglected within the total performance of the SRU. As stated earlier, DMAc is expected to decompose into its components, namely dimethylamine and acetic acid, within the system whereas DMSO is not.

When the single scores belonging to the individual impact categories are concerned, it is seen that the recovery of DMAc has higher impact as compared to DMSO, in all impact categories except for the "minerals" (Table 11). The reason for this exception could be possibly due to higher amount of raw material (i.e mineral) requirement during the production of DMSO than that of DMAc.

Table 11: Comparison of total single scores of SRU for DMAc and DMSO (Screenshots from SimaPro)

DMAc

Impact category	Unit	Total
Total	Pt	0,00457
Carcinogens	Pt	5,14E-5
Respiratory organics	Pt	5,52E-7
Respiratory inorganics	Pt	0,000411
Climate change	Pt	0,000429
Radiation	Pt	5,79E-7
Ozone layer	Pt	1,21E-8
Ecotoxicity	Pt	4,37E-5
Acidification/ Eutrophication	Pt	4,75E-5
Land use	Pt	3,19E-6
Minerals	Pt	5,79E-7
Fossil fuels	Pt	0,00359

DMSO

Impact category	Unit	Total
Total	Pt	0,00451
Carcinogens	Pt	4,62E-5
Respiratory organics	Pt	4,81E-7
Respiratory inorganics	Pt	0,000397
Climate change	Pt	0,000423
Radiation	Pt	3,14E-7
Ozone layer	Pt	8,18E-9
Ecotoxicity	Pt	4,08E-5
Acidification/ Eutrophication	Pt	4,48E-5
Land use	Pt	2,97E-6
Minerals	Pt	6,11E-7
Fossil fuels	Pt	0,00355

Visualised version pertaining to the comparison of total single scores for DMAc and DMSO cases is presented in Figure 12.

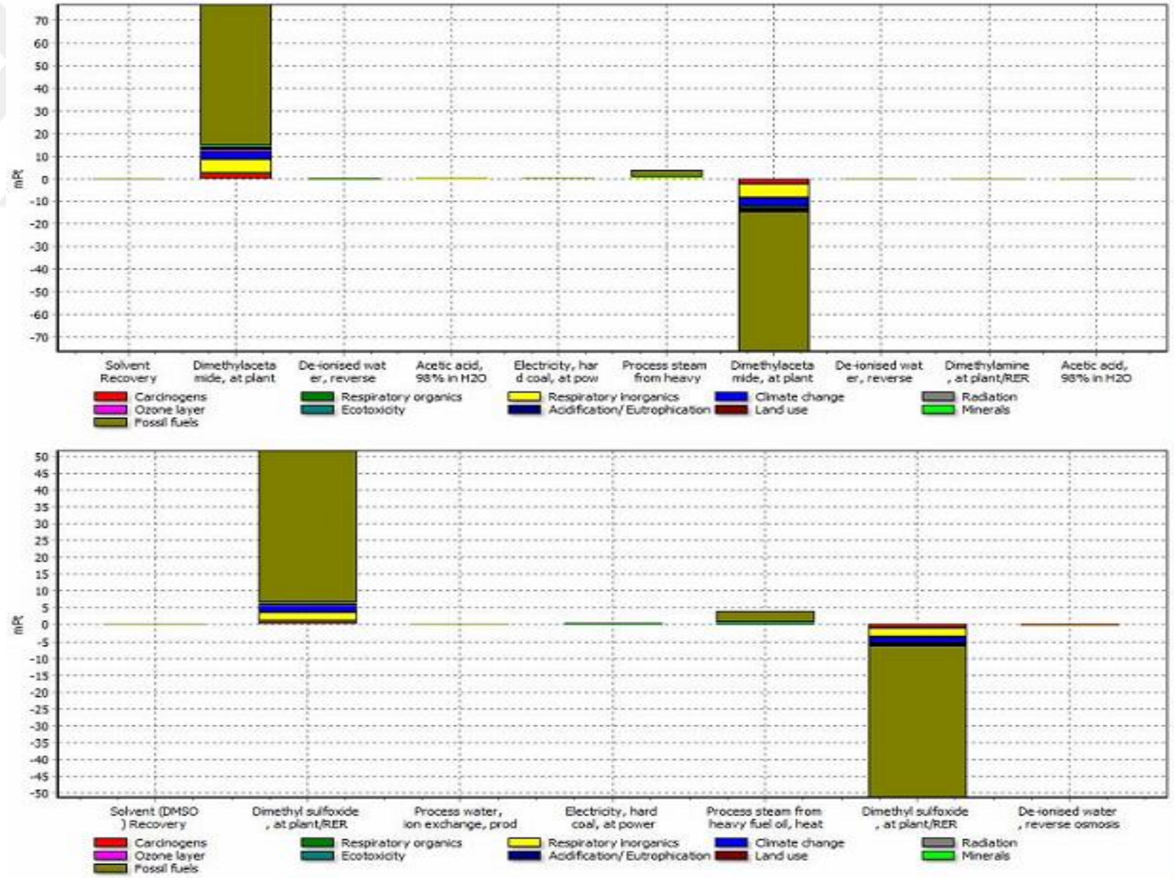


Figure 12: Comparison of single scores of the SRU for DMAc and DMSO cases, respectively

5.2 Impact Assessment of the End-of-Pipe Solvent Treatment

As an alternative solvent handling method, the end-of-pipe solvent treatment was assesssed and the results obtained are presented in this section. As stated earlier (Sec. 4.2.2.2), 'Treatment, sewage, to wastewater treatment, class 2/CH U' option was selected from the Simapro database. This unit was taken as a baseline treatment plant. For the assessment of solvent waste treatment, DMAc and DMSO (254 kg DMAc/ton wastewater and 296 kg DMSO/ton wastewater) was additionally introduced as input to the treatment plant. Functional unit was set as 1 kg solvent treated.

The single scores for the impacts can be seen through Tables 12-14. Graphical representation of the impacts is provided in Figure 13. As seen from Table 12 and Figure 13, for the baseline end-of-pipe treatment, the highest score was for the "carcinogens" category which was followed by the impact categories of "respiratory inorganics", "fossil fuels", "acidification/eutrophication", "ecotoxicity" and "climate change" in decreasing order. However, a new order of the impact categories was realized when solvent(s) was introduced to the treatment plant, as "fossil fuels", "respiratory organics", "climate change", "carcinogens", "acidification/ eutrophication" and "ecotoxicity" in decreasing order (Table 13-14 and Figure 13). So, if solvent is not recovered and sent to the treatment plant, "fossil fuel" and "respiratory inorganics" categories override the "carcinogen" category. Carcinogenic effects arising from the conventional wastewater treatment could be attributed to the fact that volatile organics in wastewater may be air-stripped during treatment. Many of the compounds are carcinogens and/or mutagens [38]. However, if the treatment plant receives the solvent, negative impacts on "fossil fuels" and "climate change" impact categories become more pronouncable as compared to baseline (Table 12-14). This can be considered as expected since solvent production requires fossil fuel consumption and in turn causes a climate change due to air emissions.

The total single scores of end-of pipe treatment without solvent, with DMAc and with DMSO were found to be 1.17E-5 Pt, 0.0471 Pt and 0.0367 Pt, respectively, (Table 12-14). It is clearly seen from these impact values that DMAc and DMSO increased the overall impact of the baseline end-of-pipe treatment by 4,125 and 3,137 times, respectively. So, very high negative effect of end-of-pipe treatment of solvent is evident, being much higher in case of DMAc.

As can be depicted from the comparison of Table 13 and 14, DMSO is more eco-friendly than DMAC in all impact categories, except for the “minerals” category. Nevertheless, the mineral consumption by DMSO seems slightly higher (only 1.09 times higher) than by DMAc. The reason for the lower impact scores of DMSO as compared to DMAc can be attributed to the less toxicity of DMSO [27].

Here, it should be mentioned that uncertainity of the results should not be disregarded since the data used for the end-of pipe treatment was selected from the library of Simapro, so, it may not reflect the practice as the SRU does. However, one should also notice that the comparative results will still remain valid since the end-of-pipe treatment operational conditions are all same for the three cases compared.

The normalization and weighting graphs obtained during the LCA runs are provided through Figures C1-C6 in Appendix C.

Table 12: Single scores of the end-of-pipe wastewater treatment without solvent - baseline (Screenshot from SimaPro)

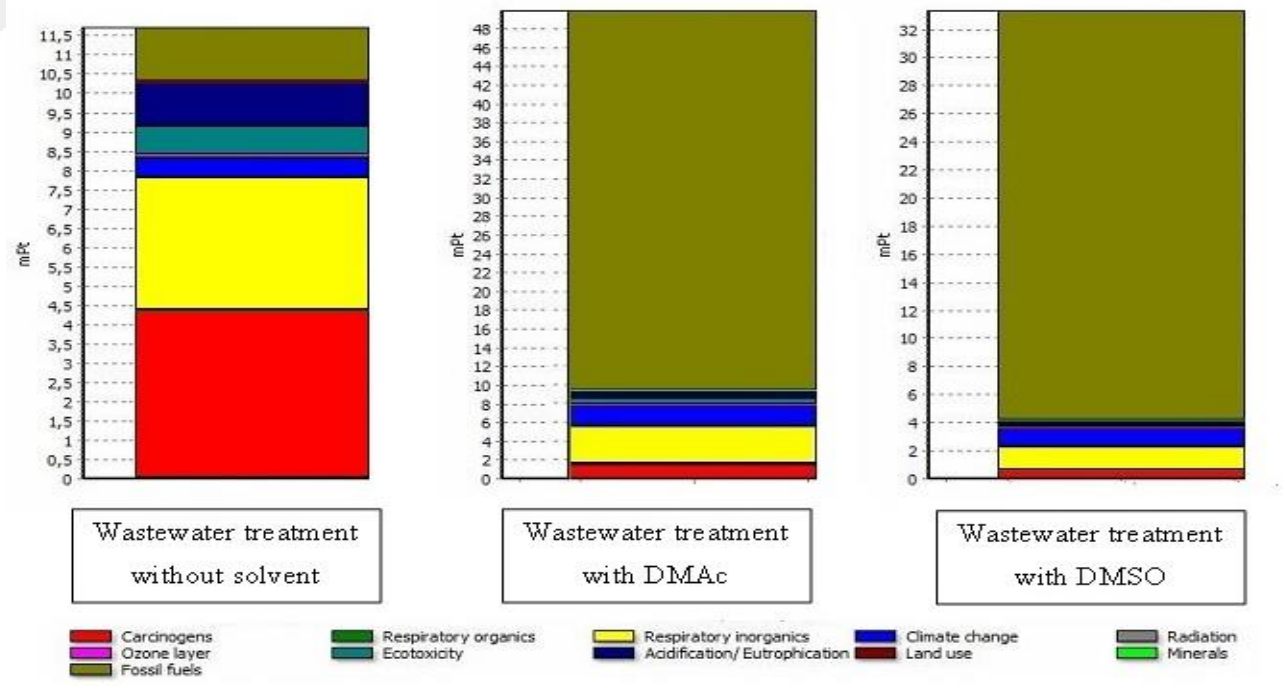
Impact category	Unit	Total
Total	Pt	1,17E-5
Carcinogens	Pt	4,38E-6
Respiratory organics	Pt	7,6E-10
Respiratory inorganics	Pt	3,43E-6
Climate change	Pt	5,15E-7
Radiation	Pt	6,91E-8
Ozone layer	Pt	6,37E-10
Ecotoxicity	Pt	7,47E-7
Acidification/ Eutrophication	Pt	1,13E-6
Land use	Pt	1,45E-8
Minerals	Pt	2,69E-8
Fossil fuels	Pt	1,4E-6

Table 13: Single scores of the end-of-pipe solvent treatment for DMAc (Screenshot from SimaPro)

Impact category	Unit	Total
Total	Pt	0,0471
Carcinogens	Pt	0,00148
Respiratory organics	Pt	1,57E-5
Respiratory inorganics	Pt	0,00376
Climate change	Pt	0,00217
Radiation	Pt	6,81E-5
Ozone layer	Pt	1,57E-6
Ecotoxicity	Pt	0,000645
Acidification/ Eutrophication	Pt	0,000702
Land use	Pt	5,42E-5
Minerals	Pt	3,16E-5
Fossil fuels	Pt	0,0382

Table 14: Single scores of the end-of-pipe treatment for DMSO (Screenshot from SimaPro)

Impact category	Unit	Total
Total	Pt	0,0367
Carcinogens	Pt	0,000739
Respiratory organics	Pt	5,02E-6
Respiratory inorganics	Pt	0,0018
Climate change	Pt	0,00142
Radiation	Pt	3,12E-5
Ozone layer	Pt	9,42E-7
Ecotoxicity	Pt	0,000242
Acidification/ Eutrophication	Pt	0,00032
Land use	Pt	2,39E-5
Minerals	Pt	3,45E-5
Fossil fuels	Pt	0,0321



(a) **(b)** **(c)**

Figure 13: Comparison of single scores of the end-of pire treatments; a) without solvent, b) with DMAc, c) with DMSO

5.3 Impact Assesment of the Solvent Incineration

Incineration of the waste solvent, as an alternative solvent handling method, was assesssed for both DMAc and DMSO, and the results obtained are presented in this section. As stated earlier (Sec. 4.2.2.3), method was selected from the Simapro database. Functional unit was 1 kg solvent incinerated.

The single scores for the impacts of the incineration can be seen in Table 15 in a comparative way for DMAc and DMSO incineration. Graphical representations of the impacts for DMAC and DMSO cases are provided in Figure 14 and 15, respectively. As seen from Table 15, major three impact categories came out to be "climate change", "fossil fuels" and "respiratory inorganics", in decreasing order, for both DMAc and DMSO incineration. It shows that emissions into the air and due to the combustion have priority, as expected. Total single score of the impacts of the DMAc incineration (0.0195 Pt) equals ~2.4 times that of DMSO (0.00814 Pt). The single scores of "climate change", "fossil fuels" and "respiratory inorganics" impact categories for DMAc were 0.00802 Pt, 0.00751 Pt and 0.00256 Pt while they were 0.00334 Pt, 0.00313 Pt and 0.00107 Pt for DMSO. As seen from these values, incineration of the waste solvent DMSO results in less impact in all impact categories. This could be attributed to the less toxicity of DMSO than of DMAc [27].

Table 15: Comparison of the single scores of the DMAc and DMSO incinerations (Combination of screenshots from SimaPro)

Impact category	Unit	Solvent Incineration (DMAc)	Solvent Incineration (DMSO)
Total	Pt	0,0195	0,00814
Carcinogens	Pt	0,000699	0,000291
Respiratory organics	Pt	2,25E-6	9,38E-7
Respiratory inorganics	Pt	0,00256	0,00107
Climate change	Pt	0,00802	0,00334
Radiation	Pt	1,79E-5	7,46E-6
Ozone layer	Pt	5,13E-7	2,14E-7
Ecotoxicity	Pt	0,000202	8,43E-5
Acidification/ Eutrophication	Pt	0,000483	0,000201
Land use	Pt	2,38E-5	9,92E-6
Minerals	Pt	2,55E-6	1,06E-6
Fossil fuels	Pt	0,00751	0,00313

The graphs of characterisation and damage assessment, normalisation and weighting results of the incineration of DMAc and DMSO can be seen through Figures D1-D6 in Appendix D.

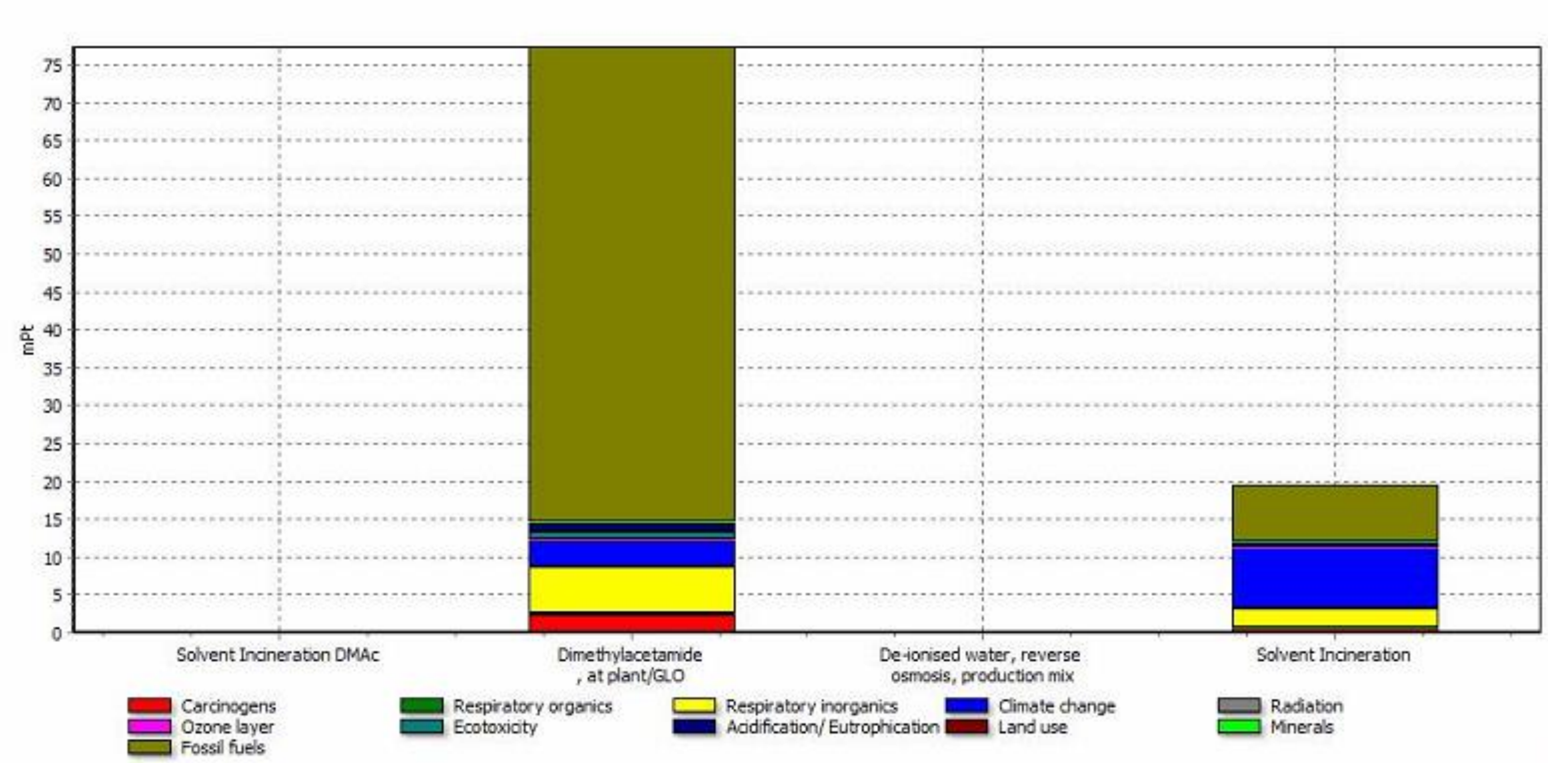


Figure 14: Single score of DMAc incineration

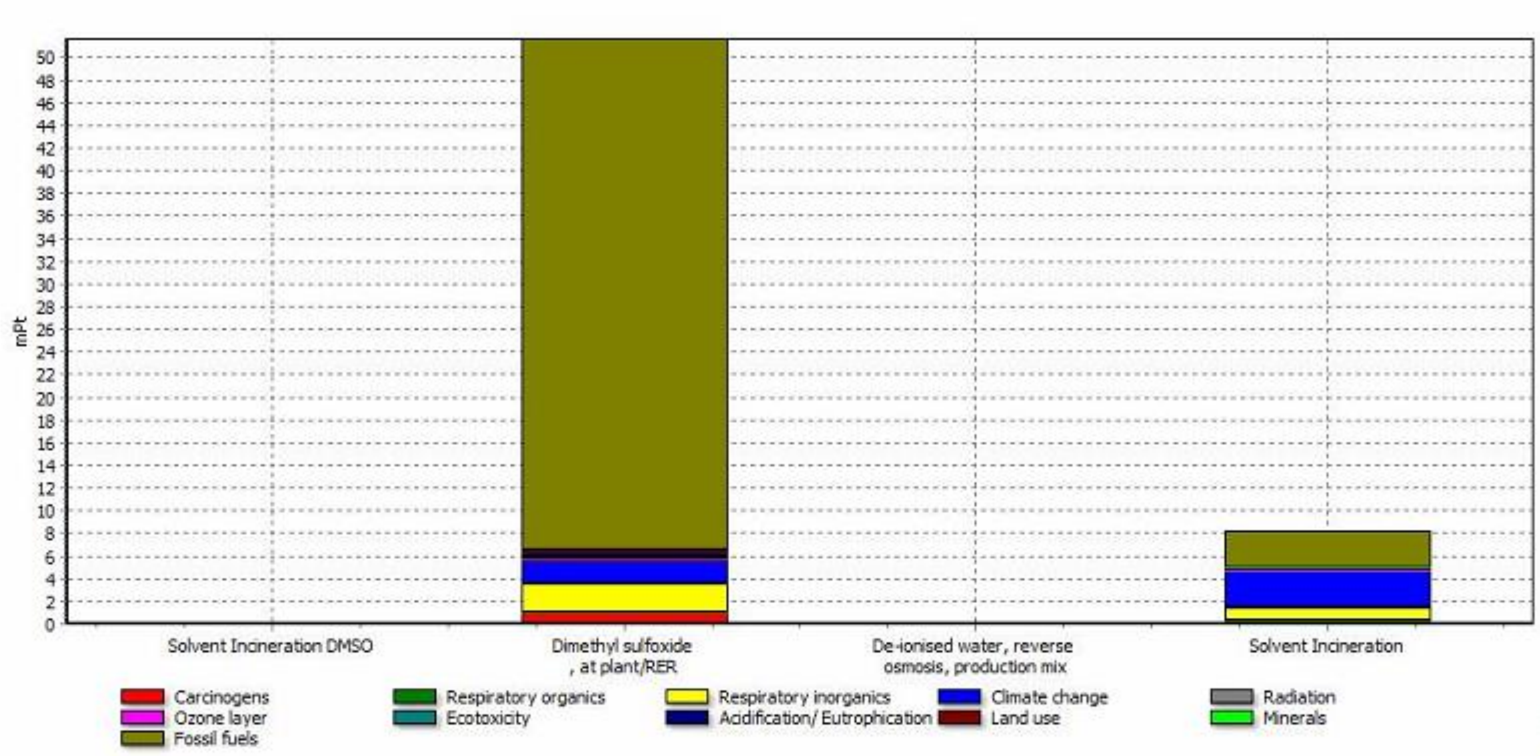


Figure 15: Single score of the DMSO incineration

5.4 Comparison of Waste Solvent Handling Methods Studied

Comparison of waste handling methods from environmental perspective is required to understand which method is preferable handling option. Based on the results obtained through this LCA study, comparison of solvent recovery from the waste solvent by distillation, waste solvent incineration and end-of-pipe waste solvent treatment was performed. Indeed, the former two options are expected to enable a reduction of the demand of fossil fuels (non-renewable resources). Because, the use of fossil fuel is avoided by the use of waste solvent as fuel for steam and electricity production in the incineration whereas solvents from the petrochemical solvent production are saved by the waste solvent recovery. Both types of avoided products will result in the reduction of environmental impacts. Similarly, end-of-pipe treatment of the waste solvent will provide a reduction in the environmental impact since the solvent could be rendered harmless or less harmfull via the treatment. Results obtained from the LCA studies belonging to these three options are summarized in Table 16. As can be depicted from this table, environmental impact score of the solvent recovery by distillation is the smallest whereas that of the end-of-pipe treatment is the highest for both DMAc and DMSO cases.

This finding could be attributed to the fact that the solvent recovery yields a saving the solvent which, in turn, means a saving the non-renewable sources and less emissions to air and less discharge to water as compared to incineration. Not recovering and sending the waste solvent to the WWTP appeared as the least preferable option because waste solvent could not be recovered neither physically nor thermally in this case. Nevertheless, the impact scores of the end-of-pipe treatment are not so different than that of solvent recovery and incineration options. Because, solvents are rendered less harmfull through the treatment to a degree depending on the biodegradability and/or toxicty of them. It is apperant from the comparison of end-of-pipe treatment option scores for DMAc and DMSO cases that the less toxic solvent and/or the higher biodegradable solvent, the lower the impact scores (Table 16). That means, as the solvent is more biodegradable/less toxic, the impact scores will be more comparable to the scores of solvent recovery and incineration. It can be said that distillation is more suitable method for toxic solvents.

The following can be depicted from the values given in Table 16. For DMAc; single score of wastewater treatment equals to 2.4 and 10.3 times of the single scores of incineration and distillation, respectively, whereas it equals to 4.5 and 8.1 times for DMSO.

So, it can be inferred that, in case of incineration, type of solvent makes a difference in terms of environmental impact as compared to other means of solvent handling methods.

Table 16: Comparison of single scores of waste solvent handling methods (Combination of screenshots from SimaPro)

Impact category	Unit	Solvent Incineration	Solvent Incineration	Solvent Recovery	Solvent Recovery	wastewater treatment	wastewater treatment
Total	Pt	0,0195	0,00814	0,00457	0,00451	0,0471	0,0367
Carcinogens	Pt	0,000699	0,000291	5,14E-5	4,62E-5	0,00148	0,000739
Respiratory organics	Pt	2,25E-6	9,38E-7	5,52E-7	4,81E-7	1,57E-5	5,02E-6
Respiratory inorganics	Pt	0,00256	0,00107	0,000411	0,000397	0,00376	0,0018
Climate change	Pt	0,00802	0,00334	0,000429	0,000423	0,00217	0,00142
Radiation	Pt	1,79E-5	7,46E-6	5,79E-7	3,14E-7	6,81E-5	3,12E-5
Ozone layer	Pt	5,13E-7	2,14E-7	1,21E-8	8,18E-9	1,57E-6	9,42E-7
Ecotoxicity	Pt	0,000202	8,43E-5	4,37E-5	4,08E-5	0,000645	0,000242
Acidification/ Eutrophication	Pt	0,000483	0,000201	4,75E-5	4,48E-5	0,000702	0,00032
Land use	Pt	2,38E-5	9,92E-6	3,19E-6	2,97E-6	5,42E-5	2,39E-5
Minerals	Pt	2,55E-6	1,06E-6	5,79E-7	6,11E-7	3,16E-5	3,45E-5
Fossil fuels	Pt	0,00751	0,00313	0,00359	0,00355	0,0382	0,0321
		DMAc	DMSO	DMAc	DMSO	DMAc	DMSO

5.5 Economic Analysis of Solvent Recovery and End-of-Pipe Treatment

In this part, a financial evaluation is performed for the solvent recovery and end-of-pipe treatment options. Incineration option was not included in the analysis since the financial data was not readily available from the practice. Taking 1 ton of solvent handled as a basis and considering the data provided in Sec 4.2.4, investment and oprerational costs as well as revenues, where applicable, were calculated over a 20 years period. Future Values (FV) and Net Present Values (NPV) were calculated applying interest and discount rates of 5% per annum, respectively. Since the solvent recovered in the SRU is reused in the factory, economical value of the solvent recovered is considered as a revenue. All the cost figures were divided by the amount of the solvent handled to find the cost per ton of solvent handled. Results obtained through these economical analysis are presented in Table 17.

Table 17: Results of the Economic Analysis

	Solvent Recovery	**End-of-Pipe Treatment**
INVESTMENT		
FV, $	287,166,411	7,216,970
$/ton	16.4	0.4
NPV, $	103,076,190	2,590,476
$/ton	5.9	0.2
OPERATION AND MAINTENANCE		
FV, $	521,780,756	14,219,518
$/ton	29.8	0.8
NPV	202,317,790	5,513,544
$/ton	11.6	0.3
REVENUE		
FV, $	26,069,198,215	0
$/ton	1488	0
NPV	10,108,196,794	0
$/ton	577	0
NET FV, $	25,260,251,048	-21,436,487
NET UNIT FV, $/ton	**1441.8**	**-1.2**
NET NPV, $	9,802,802,814	-8,104,021
NET UNIT NPV, $/ton	**560**	**-0.5**

As seen from Table 17, unit revenue from solvent recovery is 1488 \$/ton, while unit investment and O&M costs are calculated as 16.4 \$/ton and 29.8 \$/ton, respectively, in terms of FV. Thus, the net profit is 1441.8 \$/ton as FV. When the end-of-pipe treatment is concerned, these cost figures are 0, 0.4 \$, 0.8 \$ and -1.2 \$/ton, respectively.

NPV and FV for the end-of-pipe treatment are both negative while those for solvent recovery are positive. These results clearly indicate that solvent recovery is economically favorable option. Indeed, this is an expected finding, however, the magnitude differences are striking.

CHAPTER 6

CONCLUSION

In this study, the impact assessment of the SRU was performed using LCA for the cases of two solvents, one existingly being recovered in the factory studied and the other being possible subsitituve solvent, DMAc and DMSO, respectively, in comparison to the other solvent handling methods, namely, end-of-pipe solvent treatment and incineration of the solvent.

The following conclusions can be drawn from the study:

For the solvent recovery in the SRU,

- DMAc has more environmental impact than DMSO, +0.0772 Pt and +0.0516 Pt, respectively.
- Environmental impacts of both DMAc and DMSO are almost compensated by their recovery in the SRU, since the recovered portions will be reused as a raw solvent in the factory.
- Overall total impact scores for the recovery of DMAc and DMSO in the SRU are very close to each other (0.00457 Pt and 0.00451 Pt, respectively)
- The three major impact categories for solvent recovery were “fossil fuels”, “respiratory inorganics” and “climate change”. Recovering the solvents by distillation prevents fossil fuels usage since it can be used as a raw material in the process, again.

For the end-of-pipe treatment of waste solvent,

- DMAc and DMSO increased the overall impact of the baseline end-of-pipe treatment by 4,125 and 3,137 times, respectively. So, very high negative effect of end-of-pipe treatment of solvent is evident, being much higher in case of DMAc.

For the solvent incineration,

- Incineration of the waste solvent DMSO results in less impact than DMAc in all impact categories.

Comparison of three solvent handling methods revealed that environmental impact of the solvent recovery by distillation is the smallest whereas that of the end-of-pipe treatment is the highest for both DMAc and DMSO cases. Nevertheless, as the solvent is more biodegradable/less toxic, the impact of end-of-pipe treatment will be more comparable to the scores of solvent recovery and incineration. In case of incineration, effect of solvent type is more pronouncable in terms of environmental impacts as compared to other means of solvent handling methods.

Finally, financial comparison of the solvent handling methods indicated that solvent recovery is economically favorable option.

So, it can be safely stated that solvent recovery option is both environmentally and economically desirable method to handle the solvent waste.

Some uncertainty in the results reported should be expected since some of the data used were extracted from the databases of the SimaPro software. So, some of the conditions considered may not reflect the real situation in the plant. However, the uncertanity in the results belonging to the LCA study for the SRU is at minimum as the real plant data were used to a greater extent as compared to end-of-pipe treatment and incineration options. As a matter of fact, sensitivity analysis performed for the DMAc case revealed that 5% variation in the data values did result in negligable differences in the impacts. Additionally, since the scope of the study is the comparison of the several waste solvent handling scenarios, it was thought that this possible uncertainty will not effect the results to a great extent as it will affect all the scenario cases to the same extent.

CHAPTER 7

RECOMMENDATIONS

For Further Study

Uncertanities and assumptions should be taken into cautiously for the end-of pipe treatment and incineration methods because data was taken from the library in SimaPro. Therefore, it may not reflect a plant in practice. LCA analysis should be repeated with actual data and differences in technologies should be elaborated.

To the Plant Manager

LCA results show that DMSO is eco-friendly than DMAc for the three solvent handling methods studied. However, since DMSO has high freezing point (18.5 ^{o}C) and boiling point (189 ^{o}C), its phase is solid at the room temperature. So, it may limit the utility in some chemical processes. Besides the environmental advantage, the advantages/disadvantages of using DMSO instead of DMAc should be evaluated by process engineers by focusing on this technical issue.

Although not basing on a direct result of this thesis study, the author of this thesis would like to make the following recomendation by combining the results of this thesis study with her work experience in the factory. From the mass balance analysis of the SRU, it is seen that dimethylamine loss within the system occurs by the ratio of 1:4. To reduce this loss, the operational conditions in terms of applied pressure, vacuum, temperature and time should be studied, separately. The existing periodic maintenance plan and the efficiency of the mechanical maintenance should be reviewed by the specialists, accordingly. Also, type of the condensers used should be evaluated. Using extra condenser can be another option to mimimize/prevent the escape of dimethylamine to the atmosphere based on its low boiling point, 7 ^{o}C.

Additionally, when DMSO is used, since its hydrolysis, unlike for DMAc, will not be applicable in the SRU, a solvent production unit which is in operation now, would not be required. So, considering this possibility, revenue and the O&M cost of the solvent production unit should be recalculated.

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APPENDIX A

Comparison of Single Scores of the SRU with the Eco-Indicator 99 and Impact 2002+ Methods

The single scores of the SRU with the Eco-Indicator 99 and Impact 2002+ are compared in Figure A.1.

Impact category	Unit	Total
Total	Pt	0,00457
Carcinogens	Pt	5,14E-5
Respiratory organics	Pt	5,52E-7
Respiratory inorganics	Pt	0,000411
Climate change	Pt	0,000429
Radiation	Pt	5,79E-7
Ozone layer	Pt	1,21E-8
Ecotoxicity	Pt	4,37E-5
Acidification/ Eutrophication	Pt	4,75E-5
Land use	Pt	3,19E-6
Minerals	Pt	5,79E-7
Fossil fuels	Pt	0,00359

DMAc

Impact category	Unit	Total
Total	Pt	2,21E-5
Carcinogens	Pt	1,12E-7
Non-carcinogens	Pt	6,01E-8
Respiratory inorganics	Pt	2,86E-6
Ionizing radiation	Pt	4,41E-9
Ozone layer depletion	Pt	9,62E-11
Respiratory organics	Pt	3,92E-9
Aquatic ecotoxicity	Pt	5,94E-10
Terrestrial ecotoxicity	Pt	4,33E-8
Terrestrial acid/nutri	Pt	3,55E-8
Land occupation	Pt	5,41E-10
Aquatic acidification	Pt	-
Aquatic eutrophication	Pt	-
Global warming	Pt	1,03E-5
Non-renewable energy	Pt	8,68E-6
Mineral extraction	Pt	7,77E-11

Impact category	Unit	Total
Total	Pt	0,00451
Carcinogens	Pt	4,62E-5
Respiratory organics	Pt	4,81E-7
Respiratory inorganics	Pt	0,000397
Climate change	Pt	0,000423
Radiation	Pt	3,14E-7
Ozone layer	Pt	8,18E-9
Ecotoxicity	Pt	4,08E-5
Acidification/ Eutrophication	Pt	4,48E-5
Land use	Pt	2,97E-6
Minerals	Pt	6,11E-7
Fossil fuels	Pt	0,00355

DMSO

Impact category	Unit	Total
Total	Pt	2,17E-5
Carcinogens	Pt	1,12E-7
Non-carcinogens	Pt	5,99E-8
Respiratory inorganics	Pt	2,77E-6
Ionizing radiation	Pt	2,39E-9
Ozone layer depletion	Pt	6,78E-11
Respiratory organics	Pt	3,41E-9
Aquatic ecotoxicity	Pt	4,37E-10
Terrestrial ecotoxicity	Pt	3,85E-8
Terrestrial acid/nutri	Pt	3,35E-8
Land occupation	Pt	4,95E-10
Aquatic acidification	Pt	-
Aquatic eutrophication	Pt	-
Global warming	Pt	1,02E-5
Non-renewable energy	Pt	8,56E-6
Mineral extraction	Pt	7,87E-11

ECO-INDICATOR 99

IMPACT 2002

Figure A.1: Comparison of the single scores of the SRU with the Eco-Indicator 99 and Impact 2002+ methods

APPENDIX B

Screenshots of the Solvent Recovery

Goal and scope – DQI requirements – time of the SRU, goal and scope – DQI requirements – type of the SRU , goal and scope – DQI requirements – system boundaries of the SRU, inventory part - processes – inputs/outputs of the SRU for DMAc, characterization and damage assessment result of the SRU for DMAc, normalization result of the SRU for DMAc, weighting result of the SRU for DMAc, inventory part - processes – inputs/outputs of the SRU for DMSO, characterization and damage assessment result of the SRU for DMSO, normalization result of the SRU for DMSO, weighting result of the SRU for DMSO, comparison of characterization and damage assessment results of the SRU for DMAc and DMSO, comparison of normalization results of the SRU for DMAc and DMSO and comparison of weighting results of the SRU for DMAc and DMSO can be seen from Figures B.1-B.14.

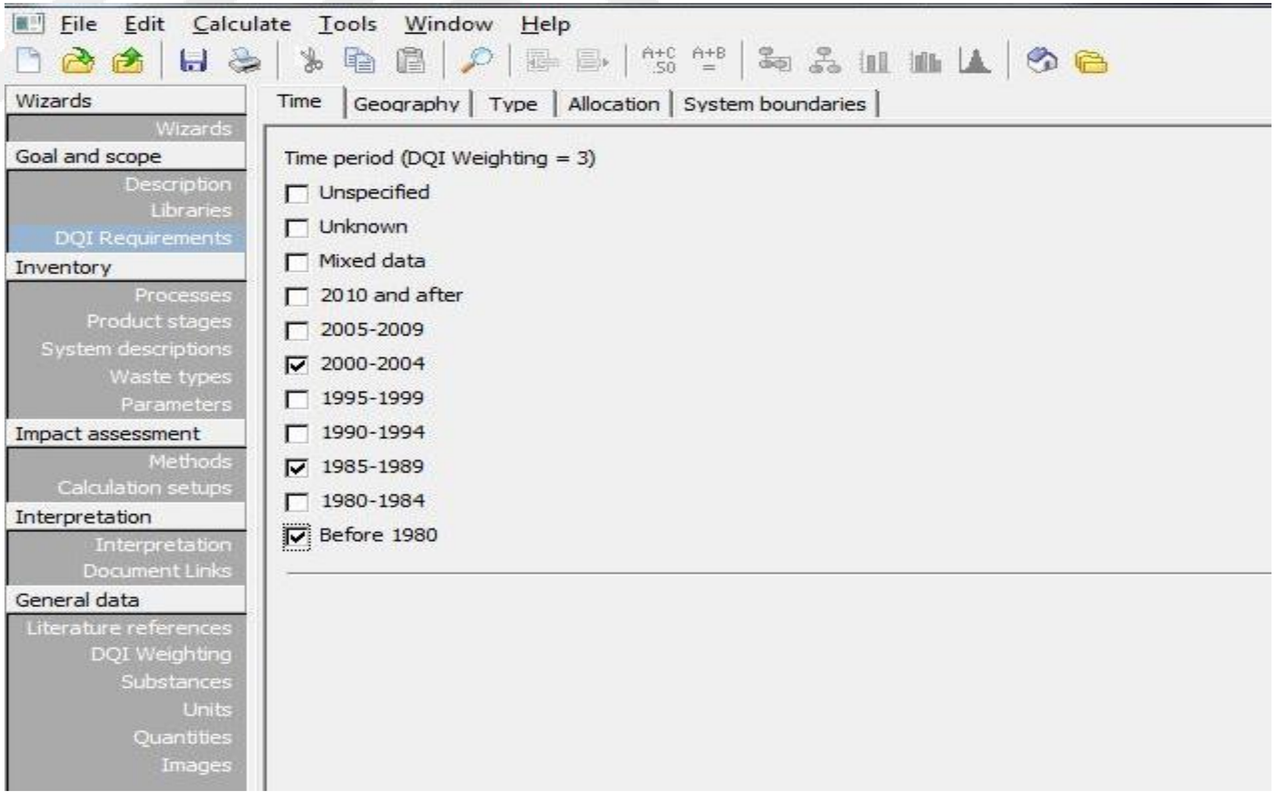


Figure B.1: Goal and scope – DQI requirements – time of the SRU

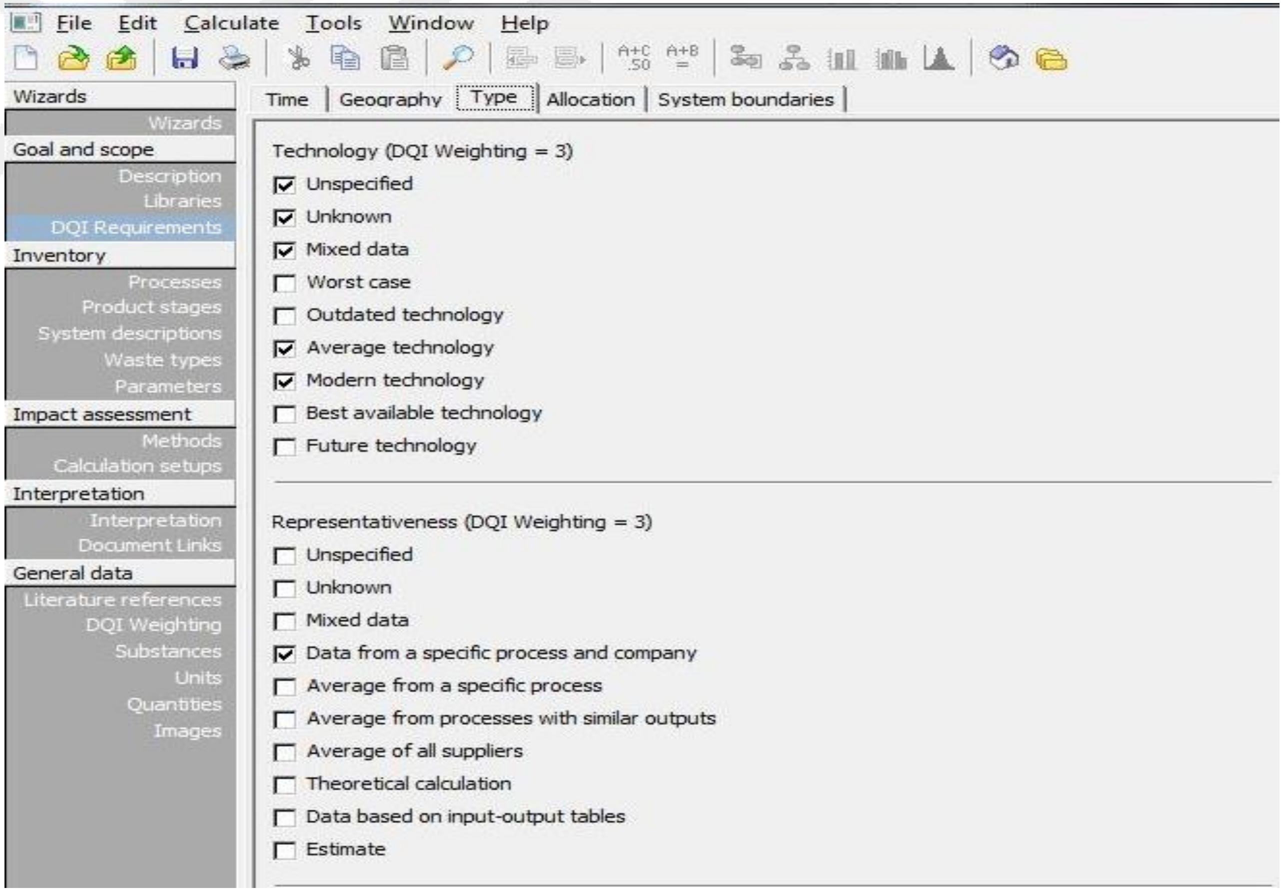


Figure B.2: Goal and scope – DQI requirements – type of the SRU

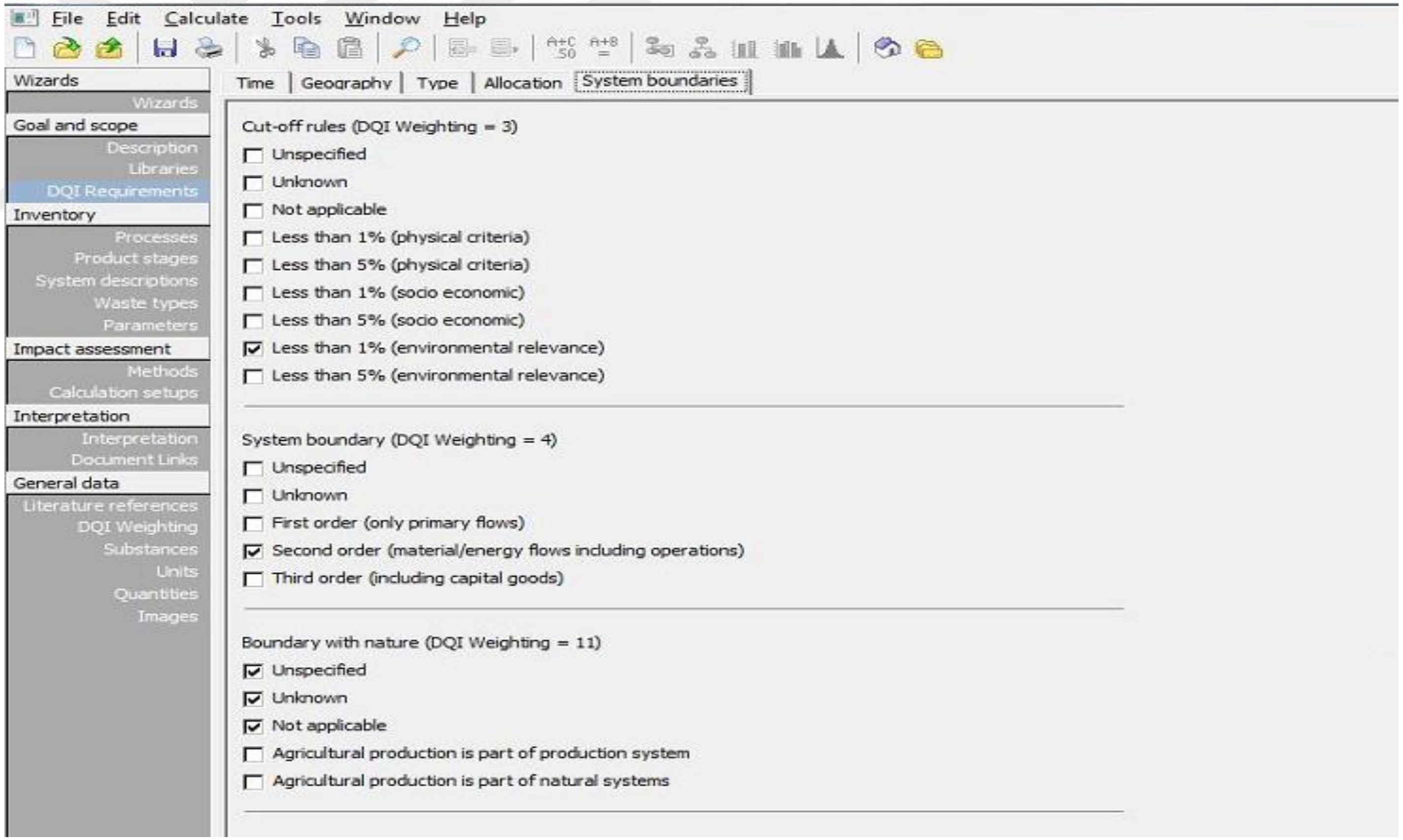
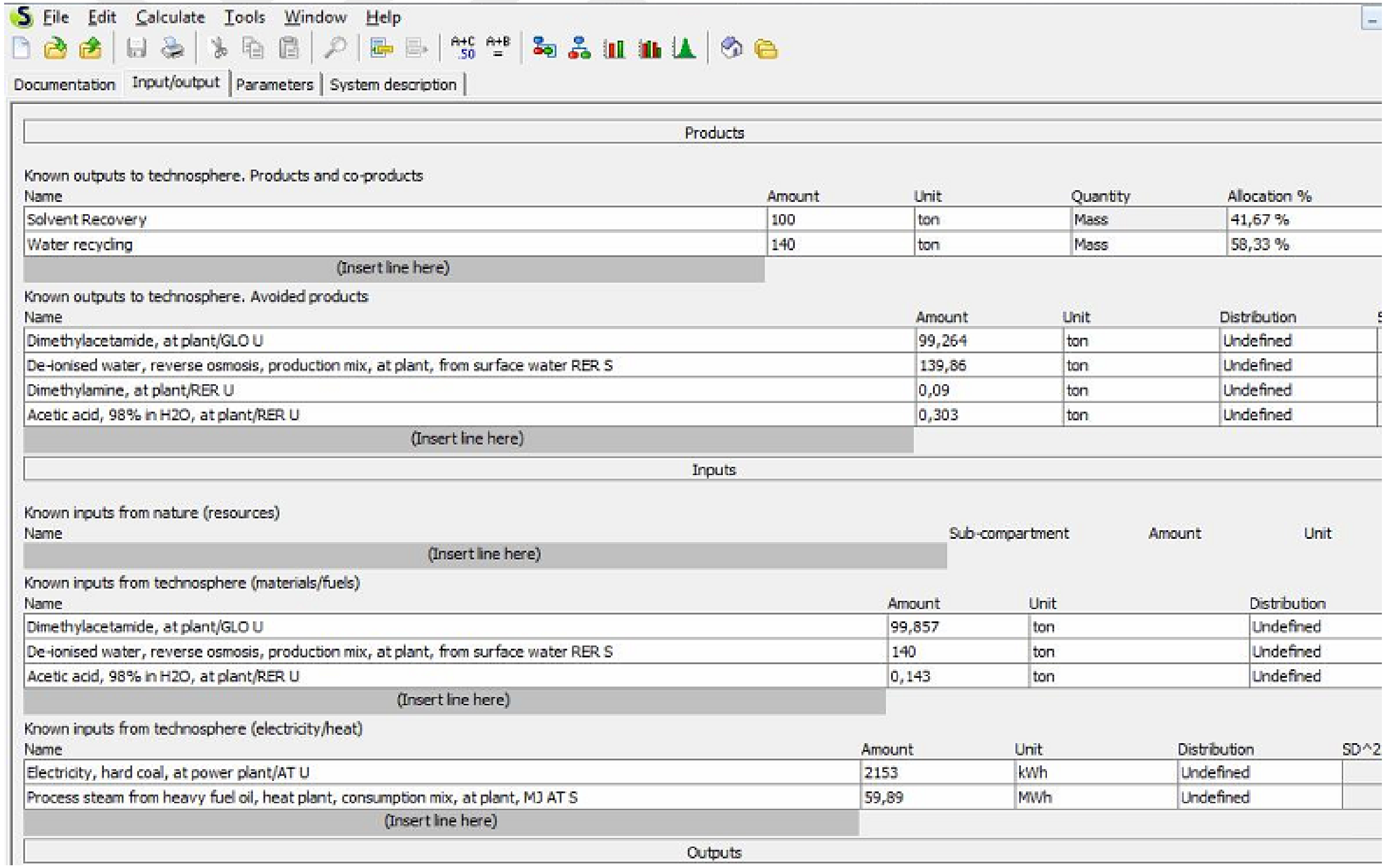


Figure B.3: Goal and scope – DQI requirements – system boundaries of the SRU



File Edit Calculate Tools Window Help

Documentation | Input/output | Parameters | System description

Products

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation %
Solvent Recovery	100	ton	Mass	41,67 %
Water recycling	140	ton	Mass	58,33 %
(Insert line here)				

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution
Dimethylacetamide, at plant/GLO U	99,264	ton	Undefined
De-ionised water, reverse osmosis, production mix, at plant, from surface water RER S	139,86	ton	Undefined
Dimethylamine, at plant/RER U	0,09	ton	Undefined
Acetic acid, 98% in H2O, at plant/RER U	0,303	ton	Undefined
(Insert line here)			

Inputs

Known inputs from nature (resources)

Name	Sub-compartment	Amount	Unit
(Insert line here)			

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution
Dimethylacetamide, at plant/GLO U	99,857	ton	Undefined
De-ionised water, reverse osmosis, production mix, at plant, from surface water RER S	140	ton	Undefined
Acetic acid, 98% in H2O, at plant/RER U	0,143	ton	Undefined
(Insert line here)			

Known inputs from technosphere (electricity/heat)

Name	Amount	Unit	Distribution	SD^2
Electricity, hard coal, at power plant/AT U	2153	kWh	Undefined	
Process steam from heavy fuel oil, heat plant, consumption mix, at plant, MJ AT S	59,89	MWh	Undefined	
(Insert line here)				

Outputs

Figure B.4: Inventory part - processes – inputs/outputs of the SRU for DMAc

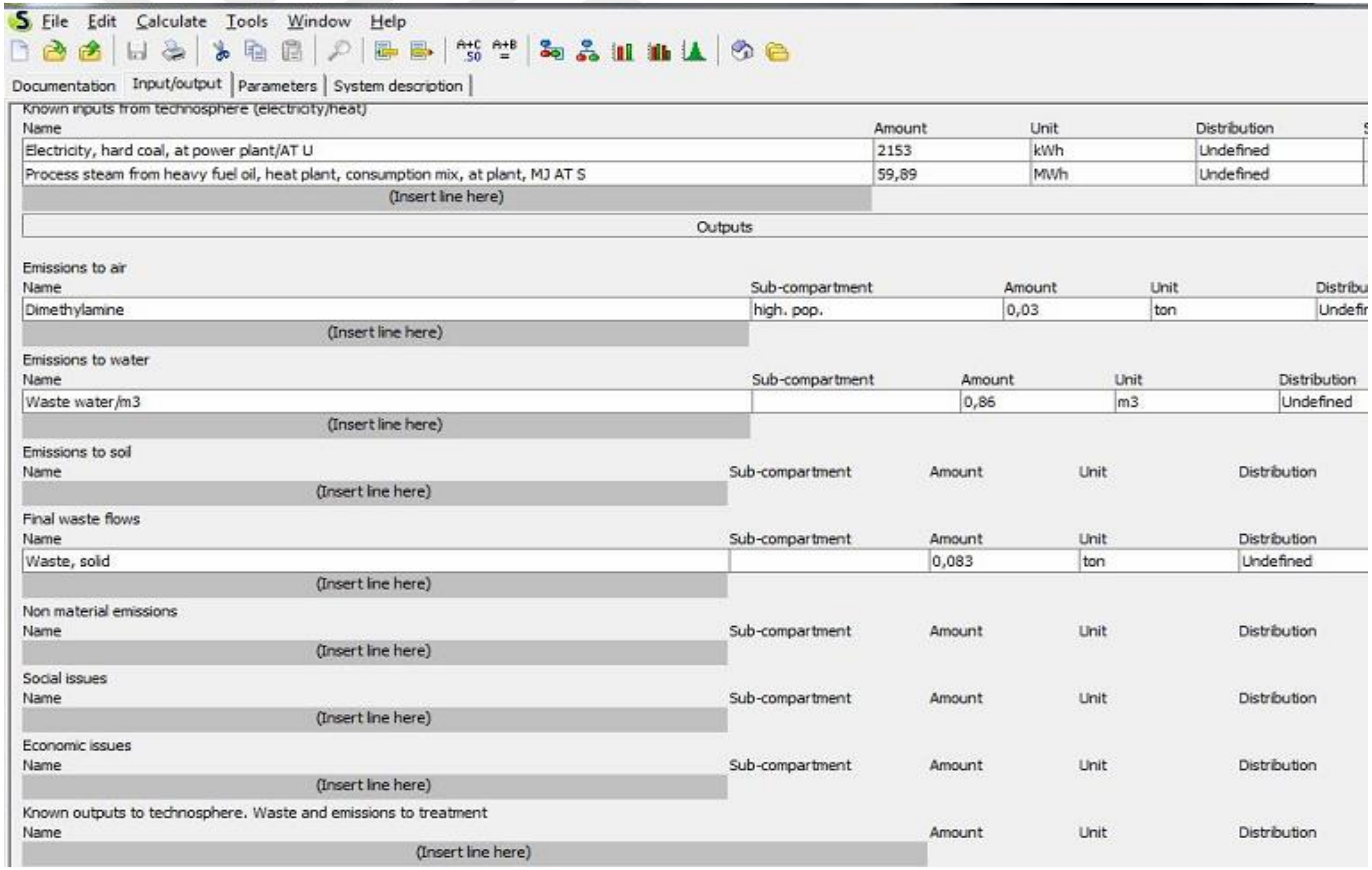


Figure B.4: Inventory part **-** processes – inputs/outputs of the SRU for DMAc - continued

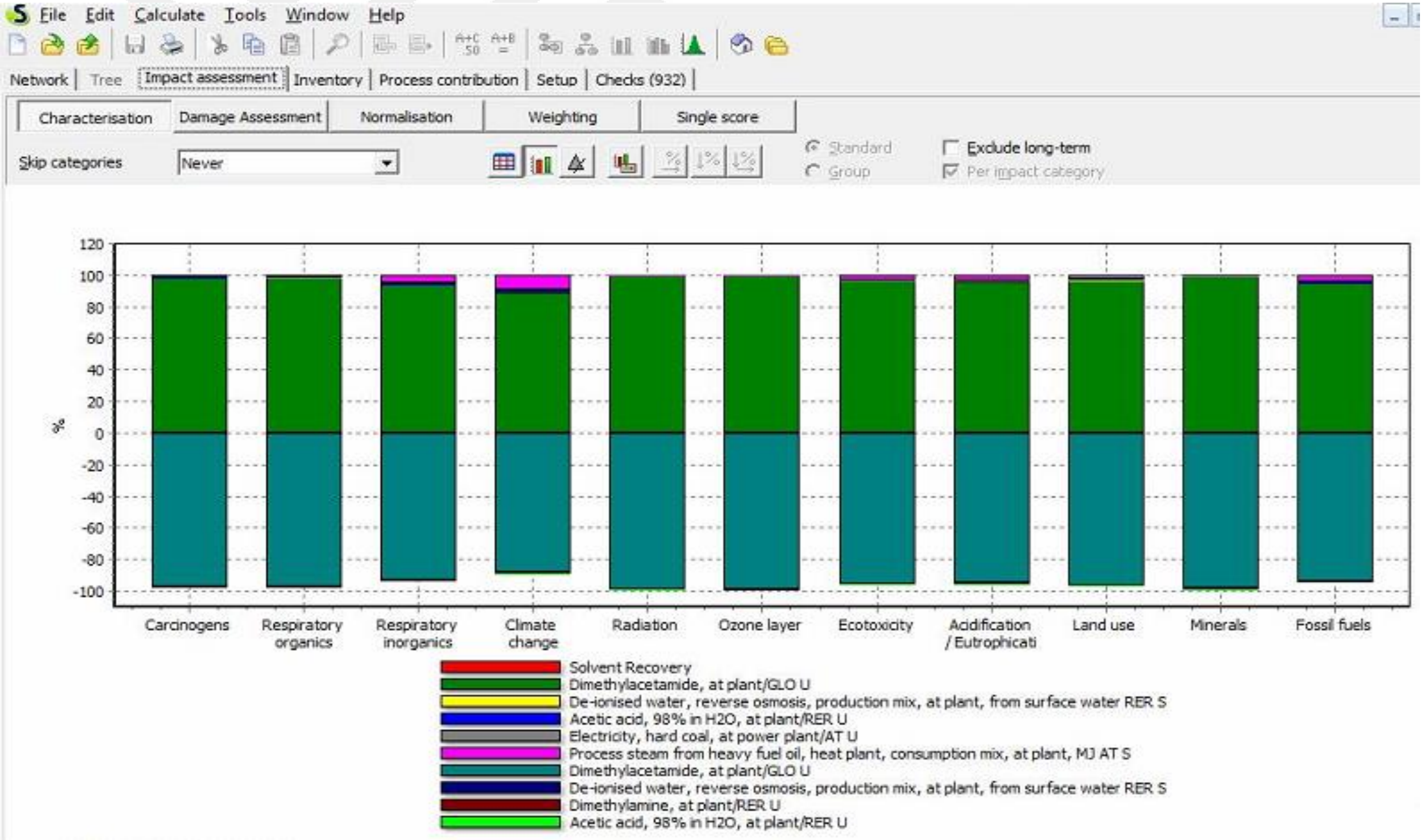


Figure B.5: Characterization and damage assessment result of the SRU for DMAc

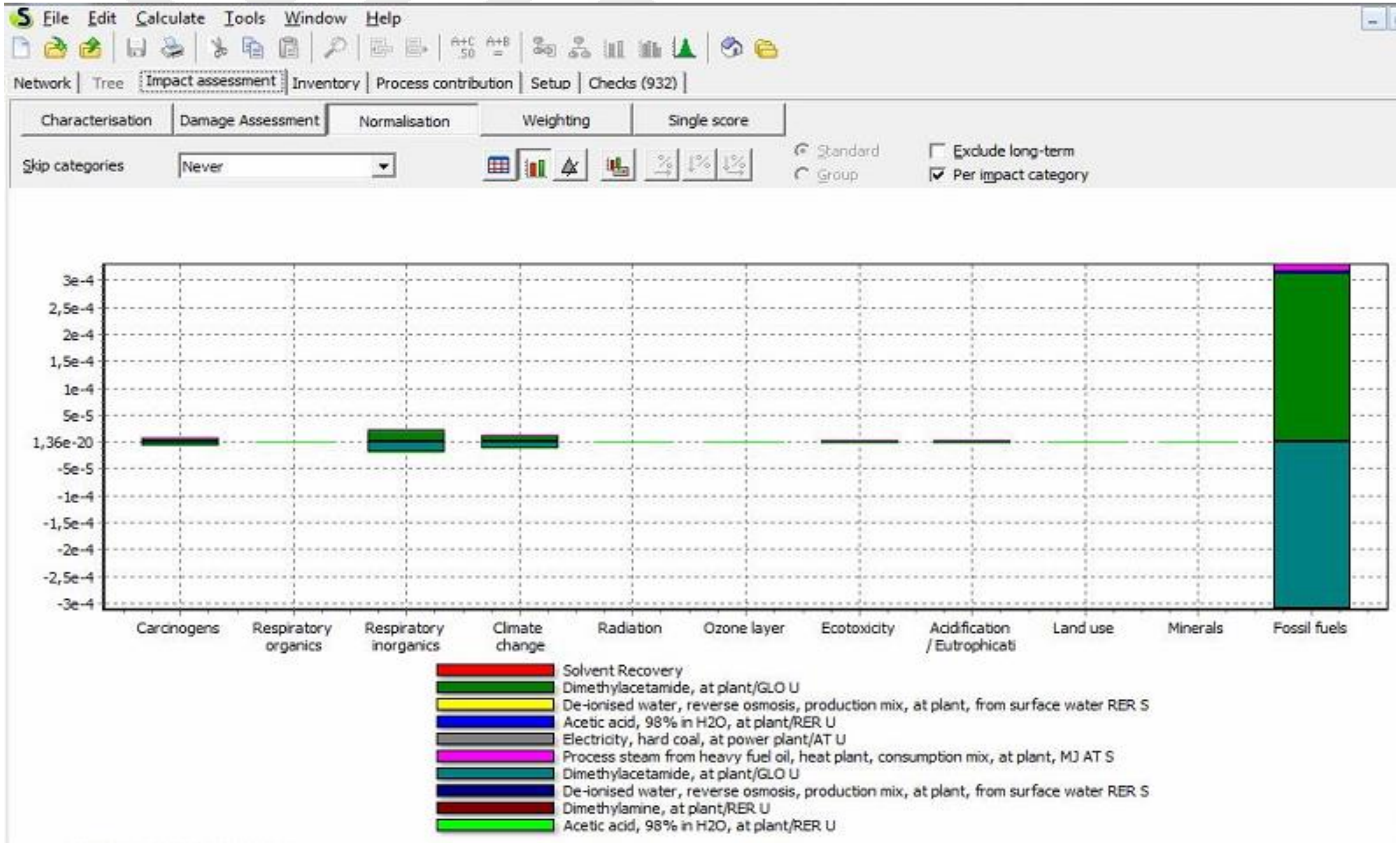


Figure B.6: Normalization result of the SRU for DMAc

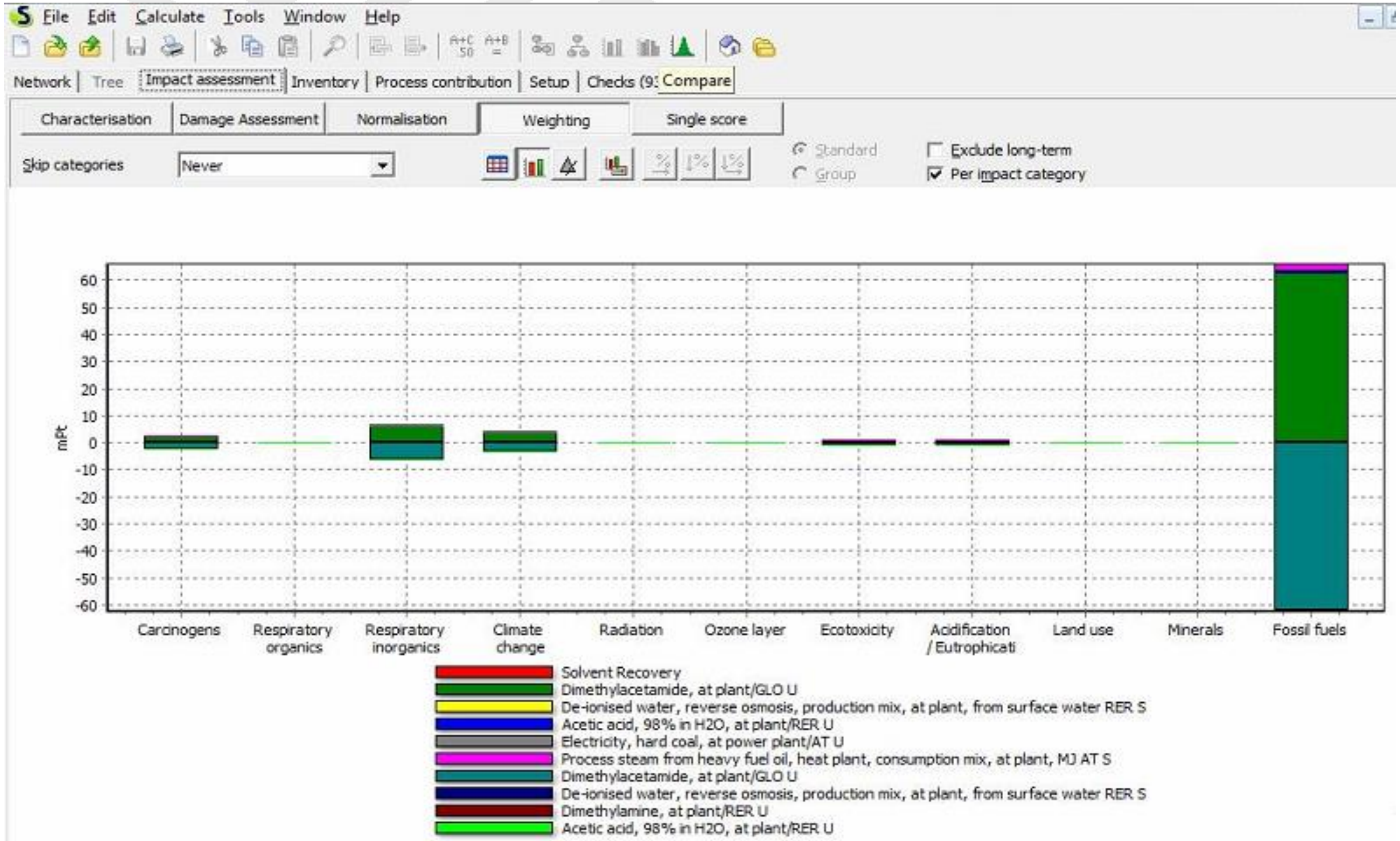
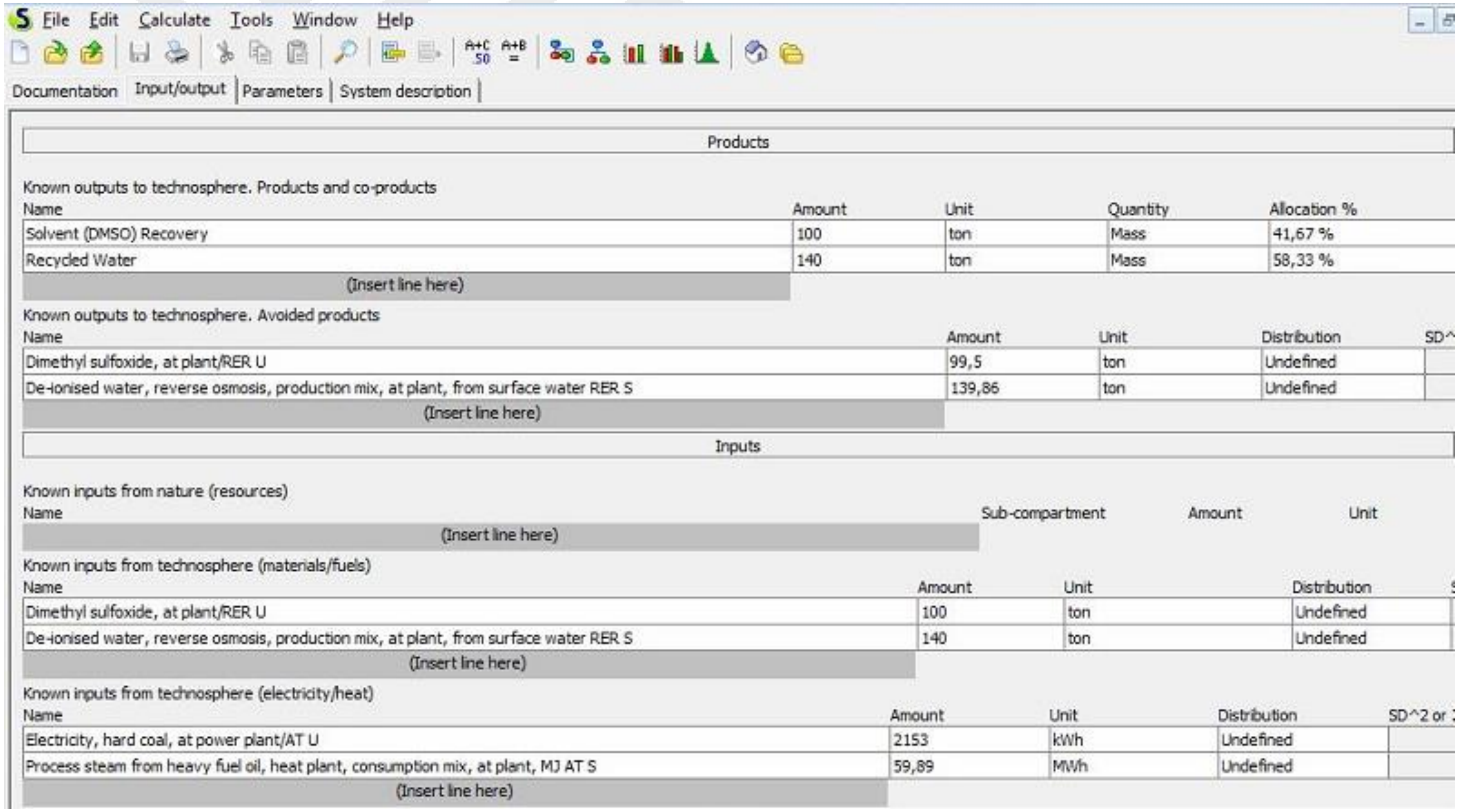


Figure B.7: Weighting result of the SRU for DMAc



File Edit Calculate Tools Window Help

Documentation | Input/output | Parameters | System description

Products

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation %
Solvent (DMSO) Recovery	100	ton	Mass	41,67 %
Recycled Water	140	ton	Mass	58,33 %
(Insert line here)				

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^
Dimethyl sulfoxide, at plant/RER U	99,5	ton	Undefined	
De-ionised water, reverse osmosis, production mix, at plant, from surface water RER S	139,86	ton	Undefined	
(Insert line here)				

Inputs

Known inputs from nature (resources)

Name	Sub-compartment	Amount	Unit
(Insert line here)			

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution
Dimethyl sulfoxide, at plant/RER U	100	ton	Undefined
De-ionised water, reverse osmosis, production mix, at plant, from surface water RER S	140	ton	Undefined
(Insert line here)			

Known inputs from technosphere (electricity/heat)

Name	Amount	Unit	Distribution	SD^2 or
Electricity, hard coal, at power plant/AT U	2153	kWh	Undefined	
Process steam from heavy fuel oil, heat plant, consumption mix, at plant, MJ AT S	59,89	MWh	Undefined	
(Insert line here)				

Figure B.8: Inventory part **-** processes – inputs/outputs of the SRU for DMSO

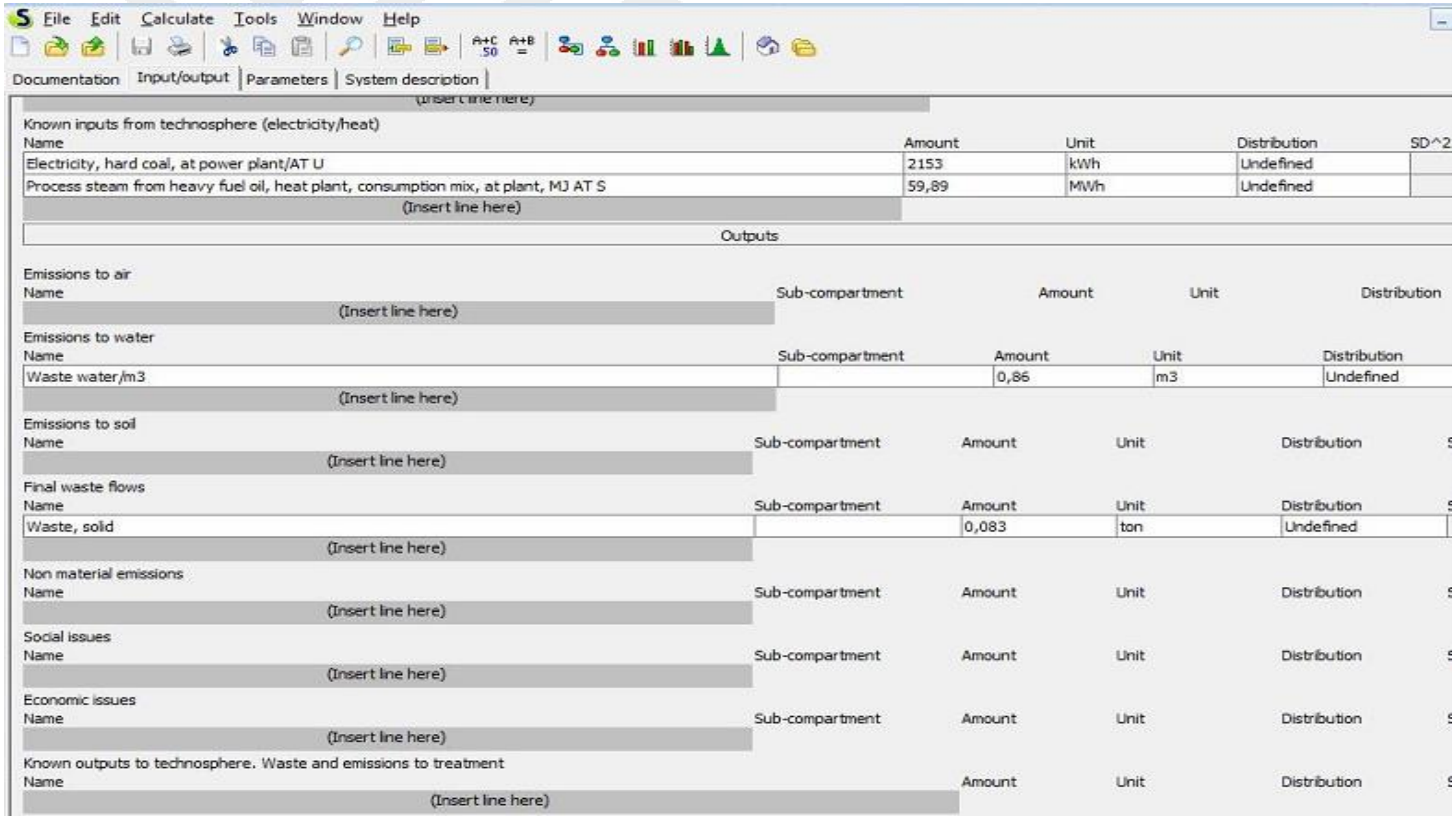


Figure B.8: Inventory part **-** processes – inputs/outputs of the SRU for DMSO – continued

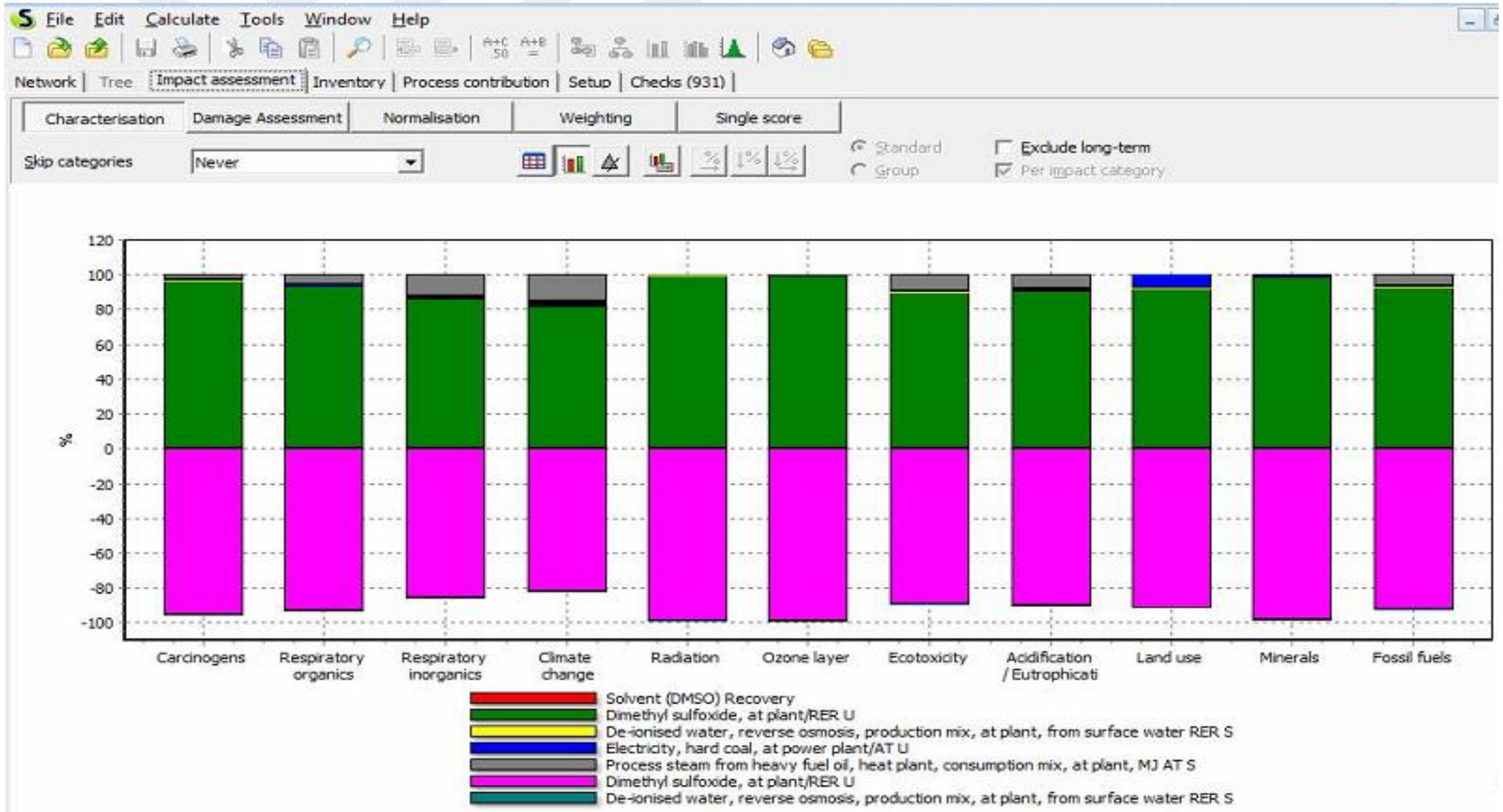


Figure B.9: Characterization and damage assessment result of the SRU for DMSO

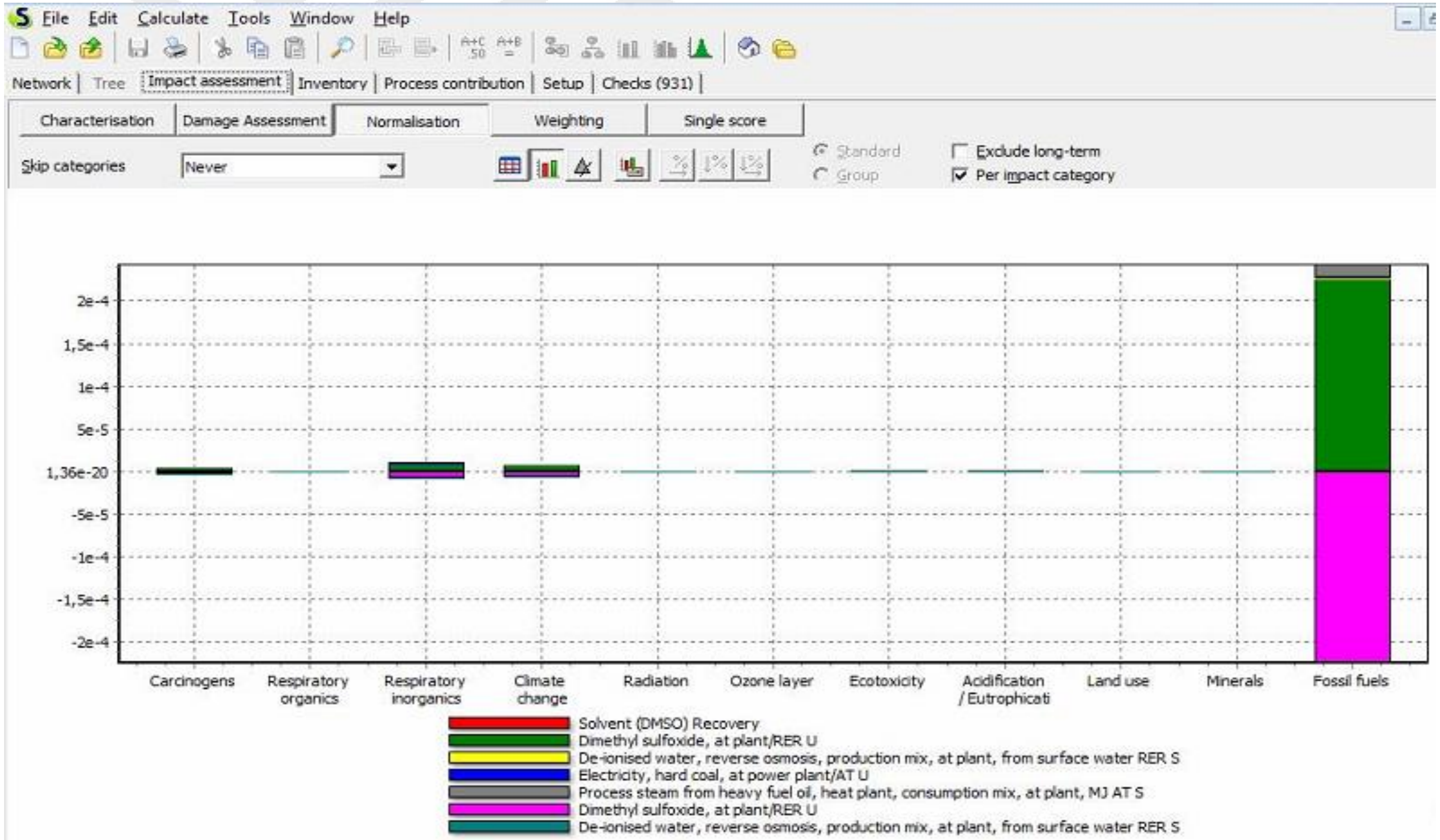


Figure B.10: Normalization result of the SRU for DMSO

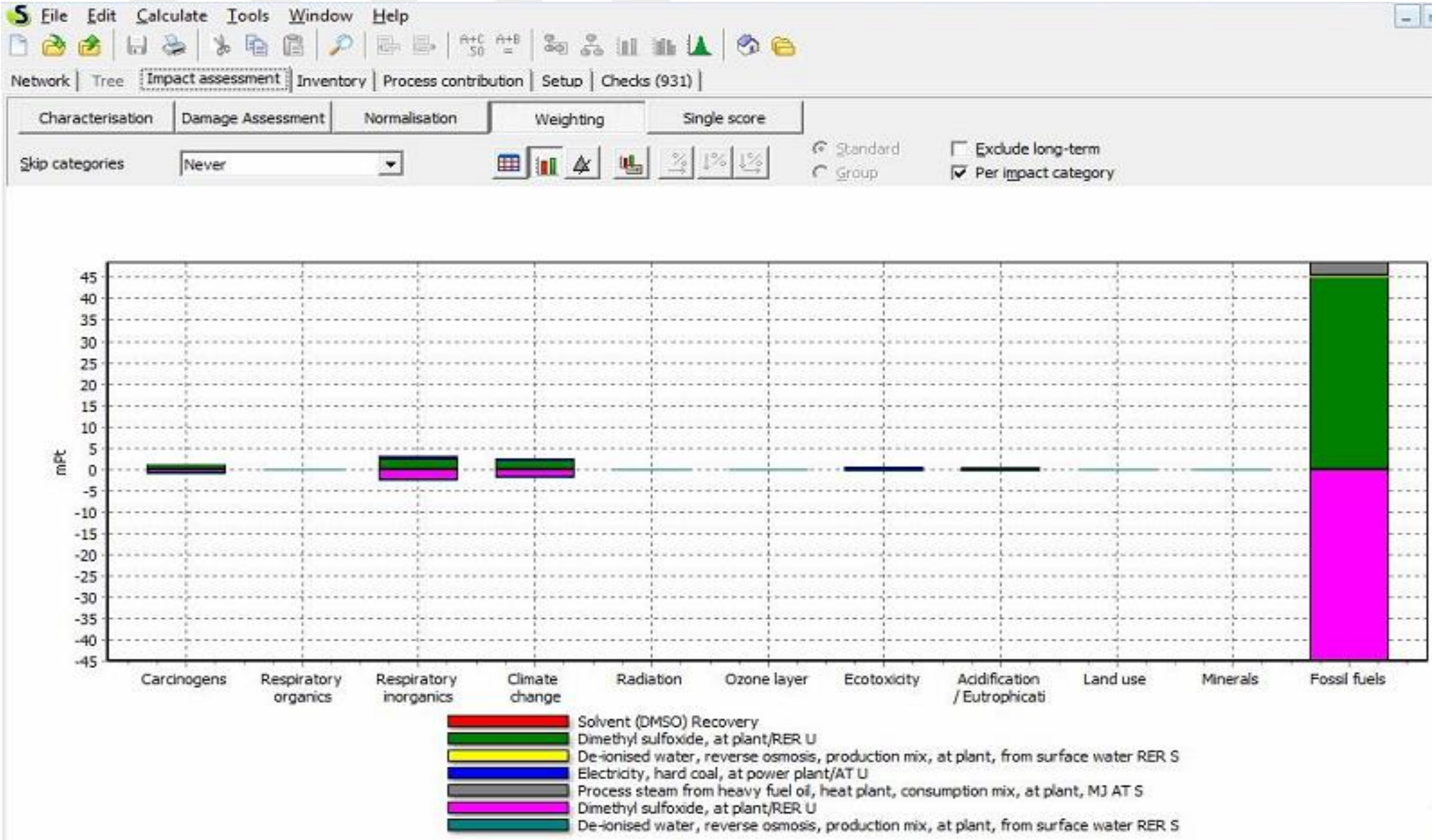


Figure B.11: Weighting result of the SRU for DMSO

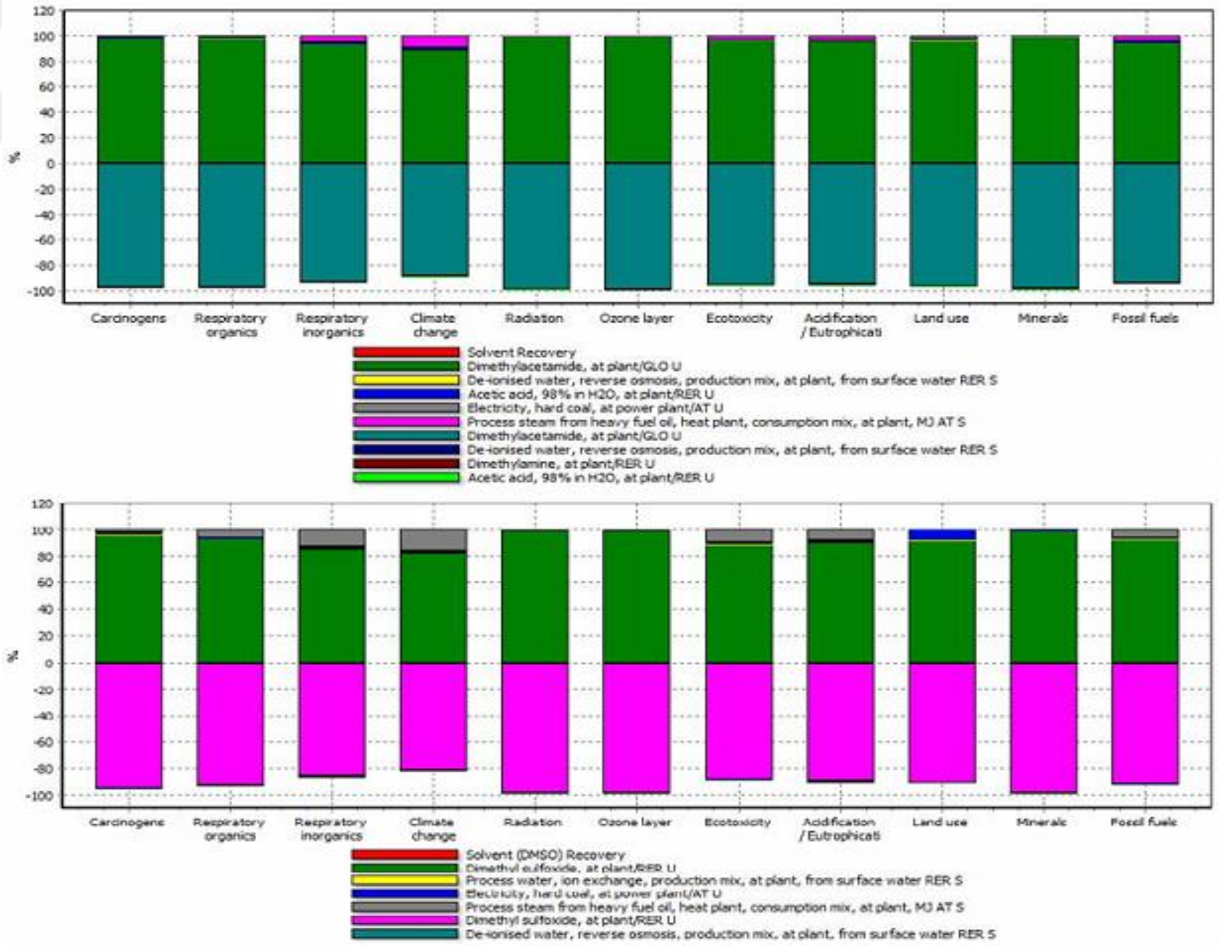


Figure B.12: Comparison of characterization and damage assessment results of the SRU for DMAc and DMSO

Figure B.13: Comparison of normalization results of the SRU for DMAc and DMSO

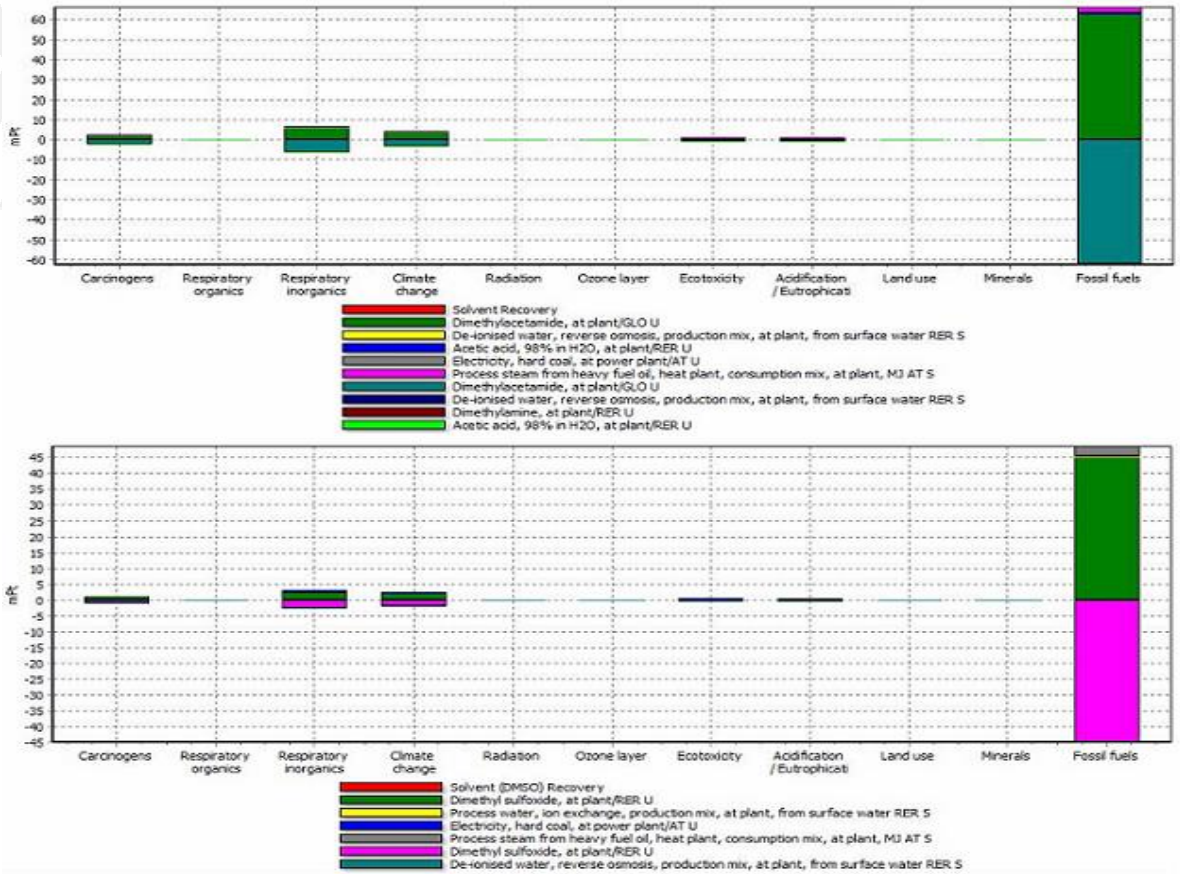


Figure B.14: Comparison of weighting results of the SRU for DMAc and DMSO

APPENDIX C

Screenshots of the End-of Pipe Treatment

Normalization result of the end-of pipe treatment (baseline), weighting result of the end-of pipe treatment (baseline), normalization result of the end-of pipe treatment with DMAc, weighting result of the end-of pipe treatment with DMAc, normalization result of the end-of pipe treatment with DMSO and weighting result of the end-of pipe treatment with DMSO can be seen from Figures C.1-C.6.

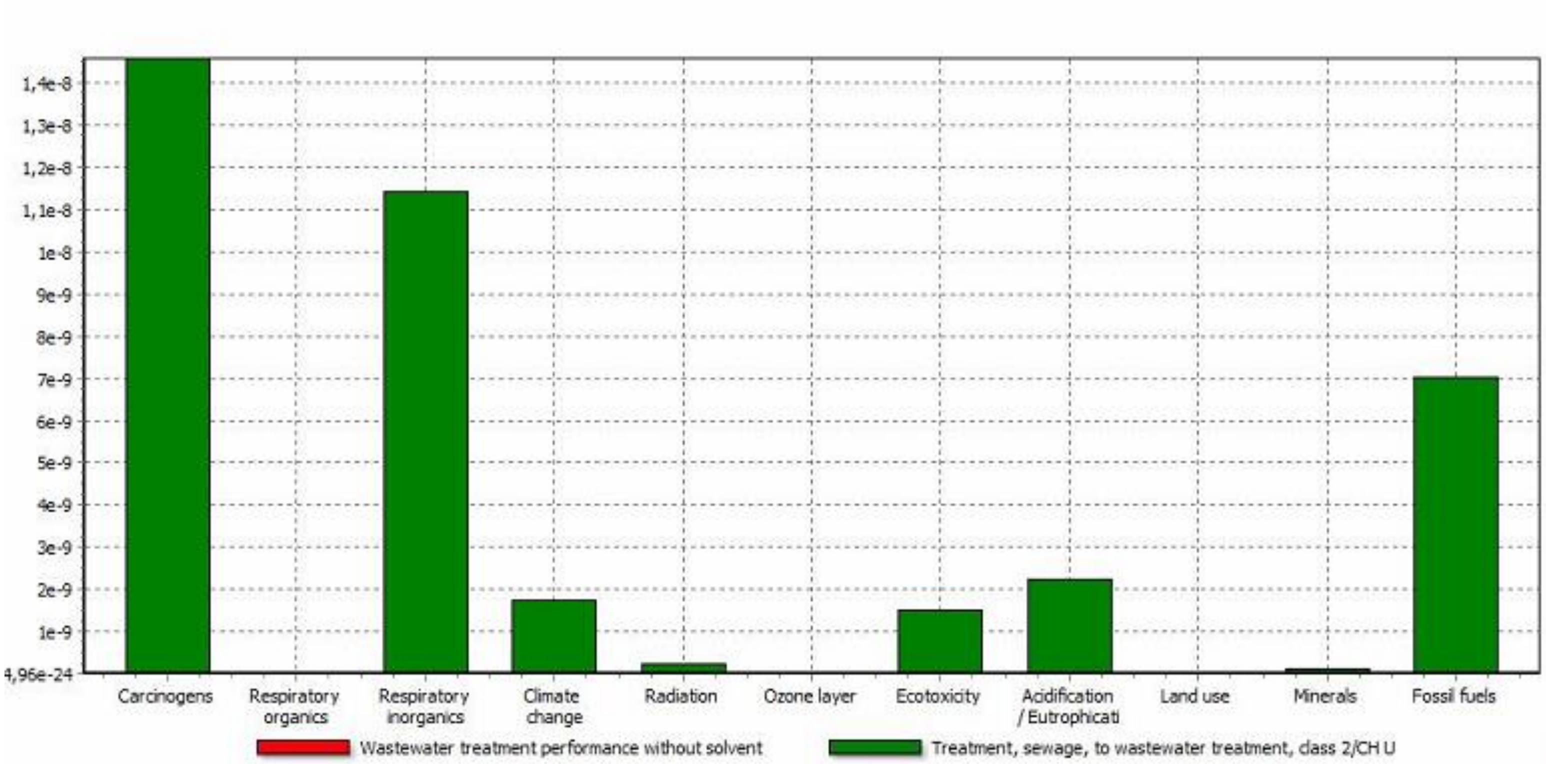


Figure C.1: Normalization result of the end-of pipe treatment (baseline)

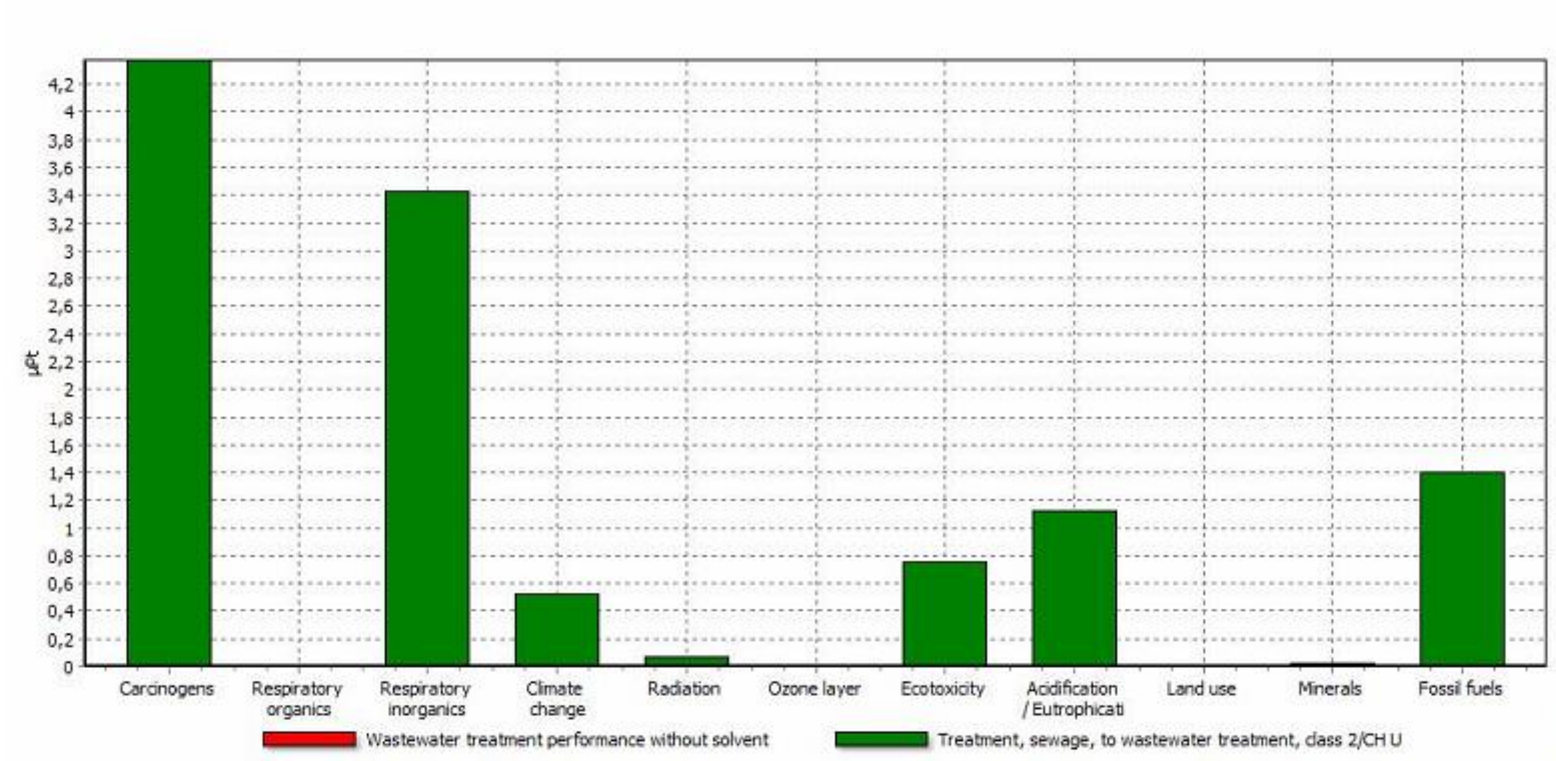


Figure C.2: Weighting result of the end-of pipe treatment (baseline)

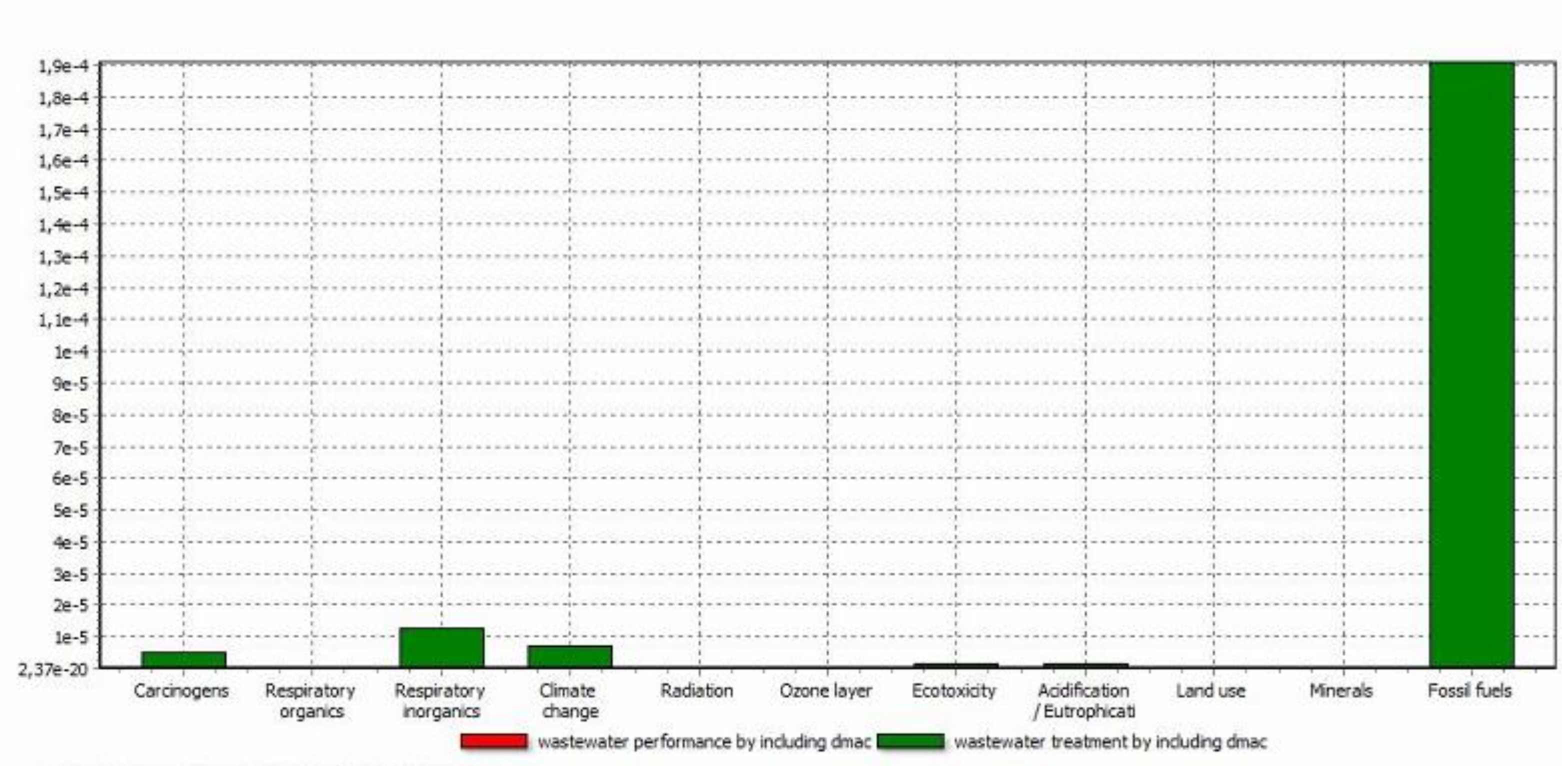


Figure C.3: Normalization result of the end-of pipe treatment with DMAc

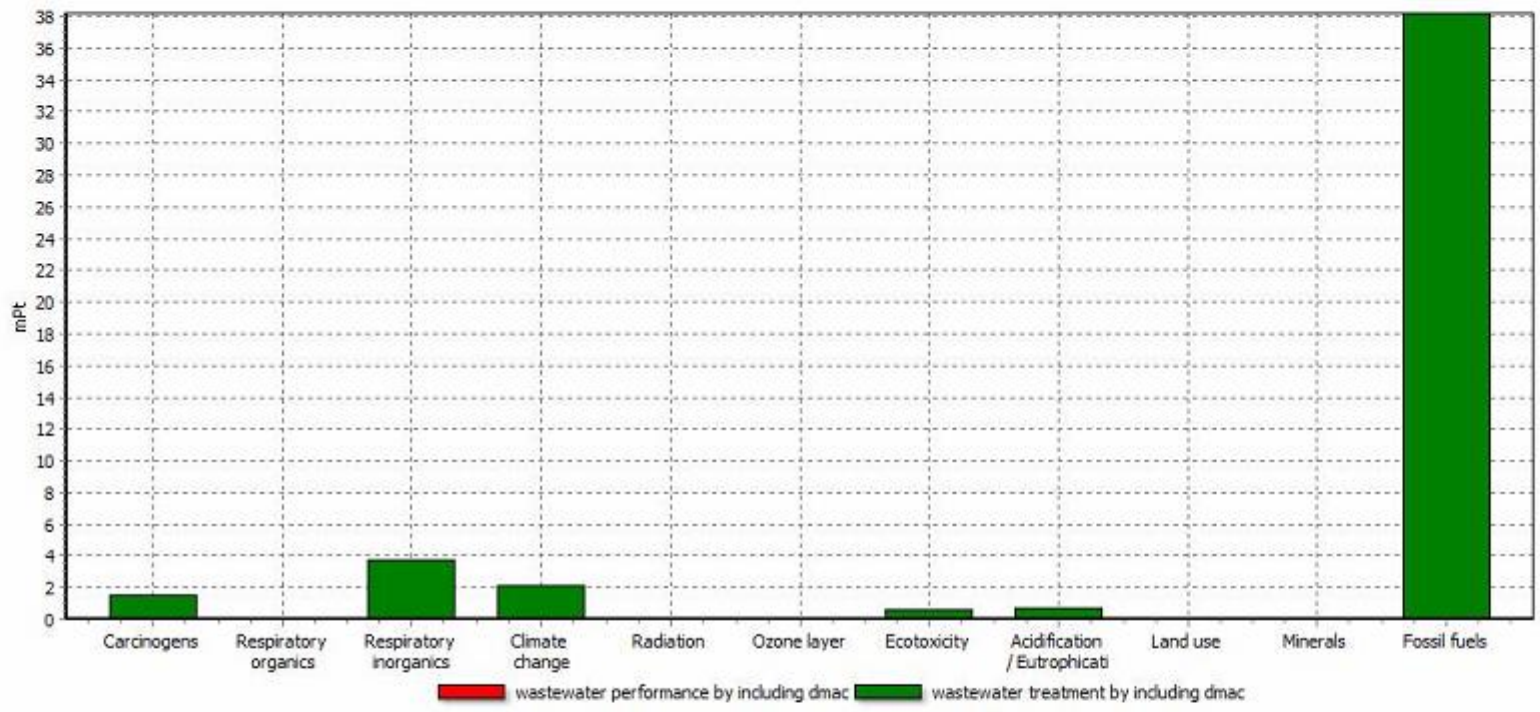


Figure C.4: Weighting result of the end-of pipe treatment with DMAc

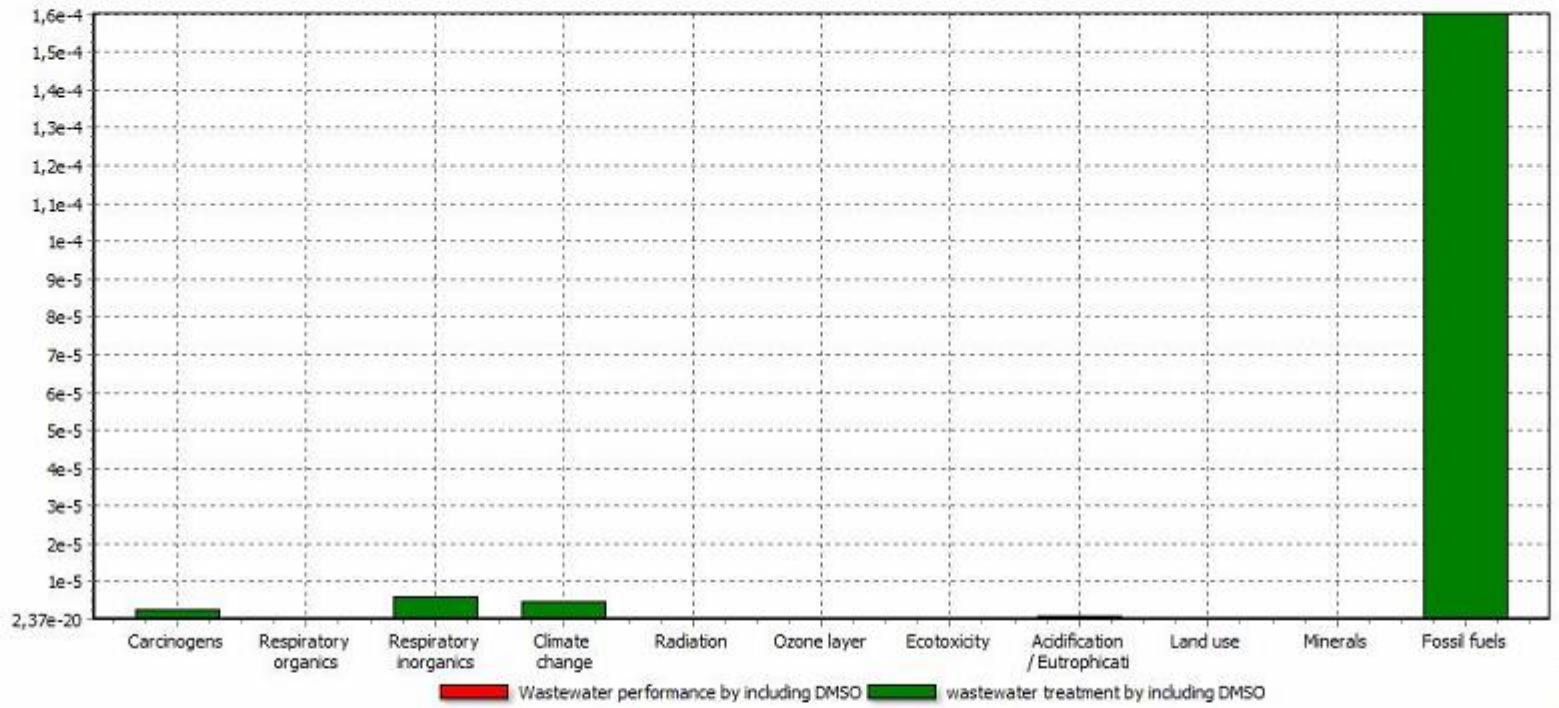


Figure C.5: Normalization result of the end-of pipe treatment with DMSO

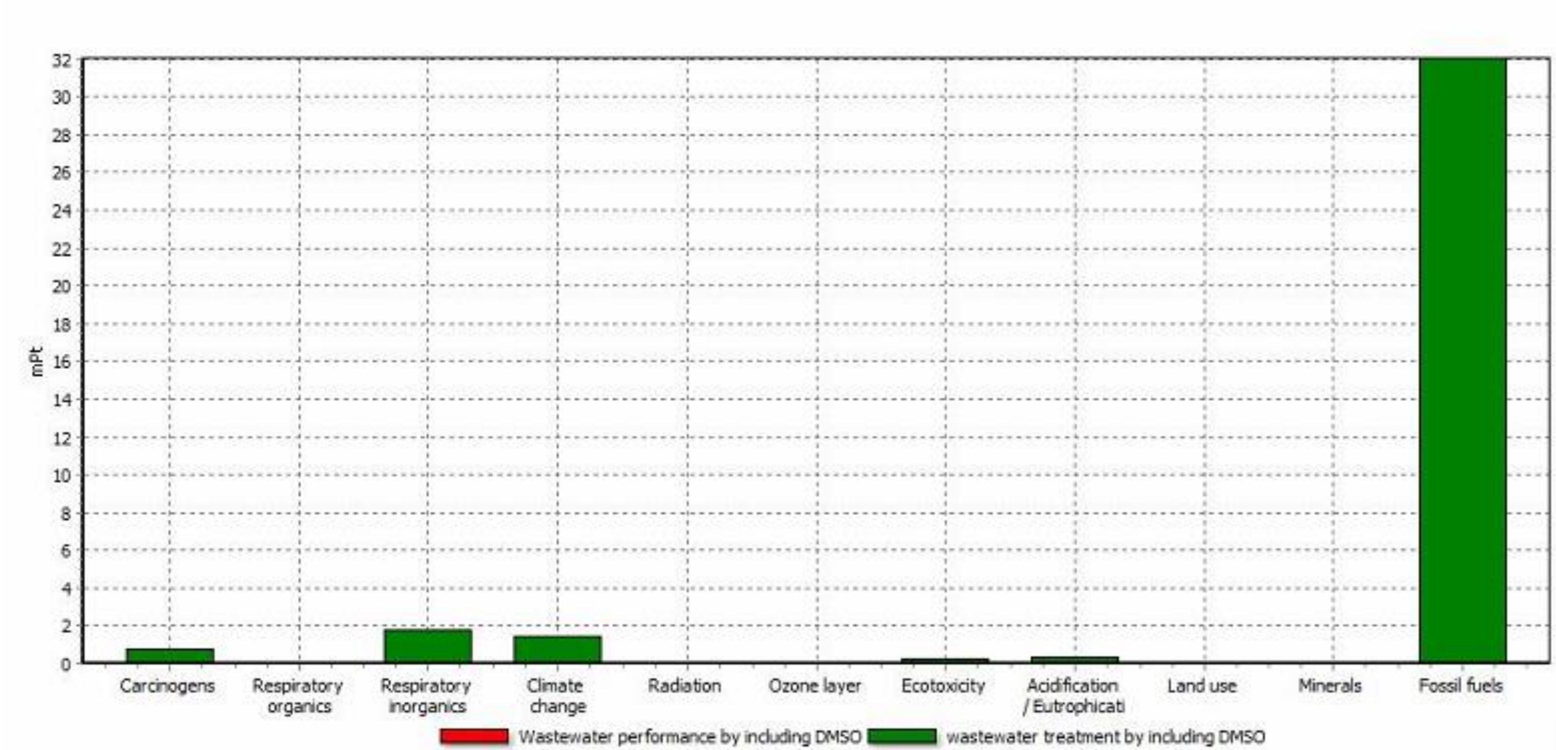


Figure C.6: Weighting result of the end-of pipe treatment with DMSO

APPENDIX D

Screenshots of the Incineration

Characterization and damage assessment result of the DMAC incineration, normalization result of the DMAC incineration, weighting result of the DMAC incineration, characterization and damage assessment result of the DMSO incineration, normalization result of the DMSO incineration and weighting result of the DMSO incineration can be seen from Figures D.1-D.6.

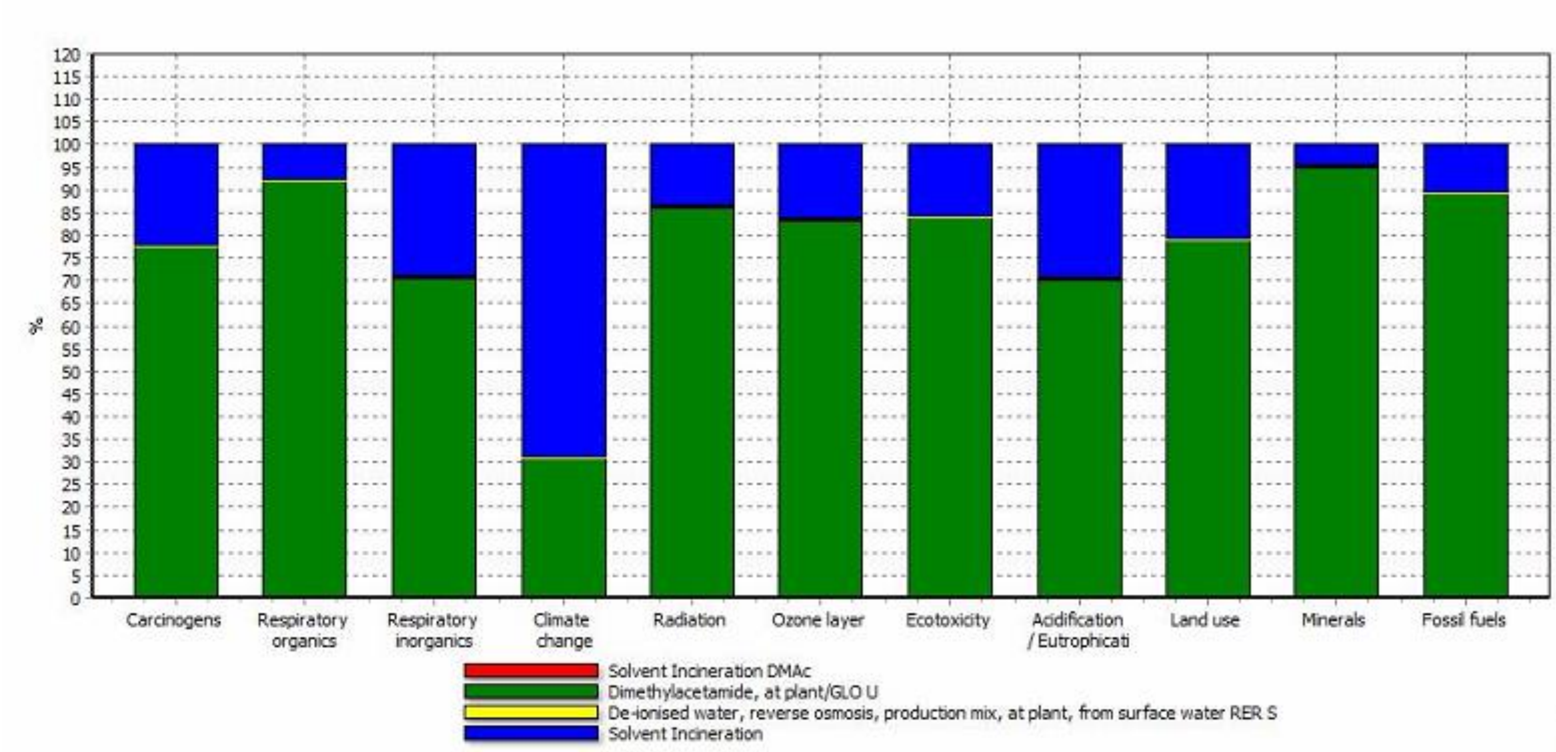


Figure D.1: Characterization and damage assessment result of the DMAC incineration

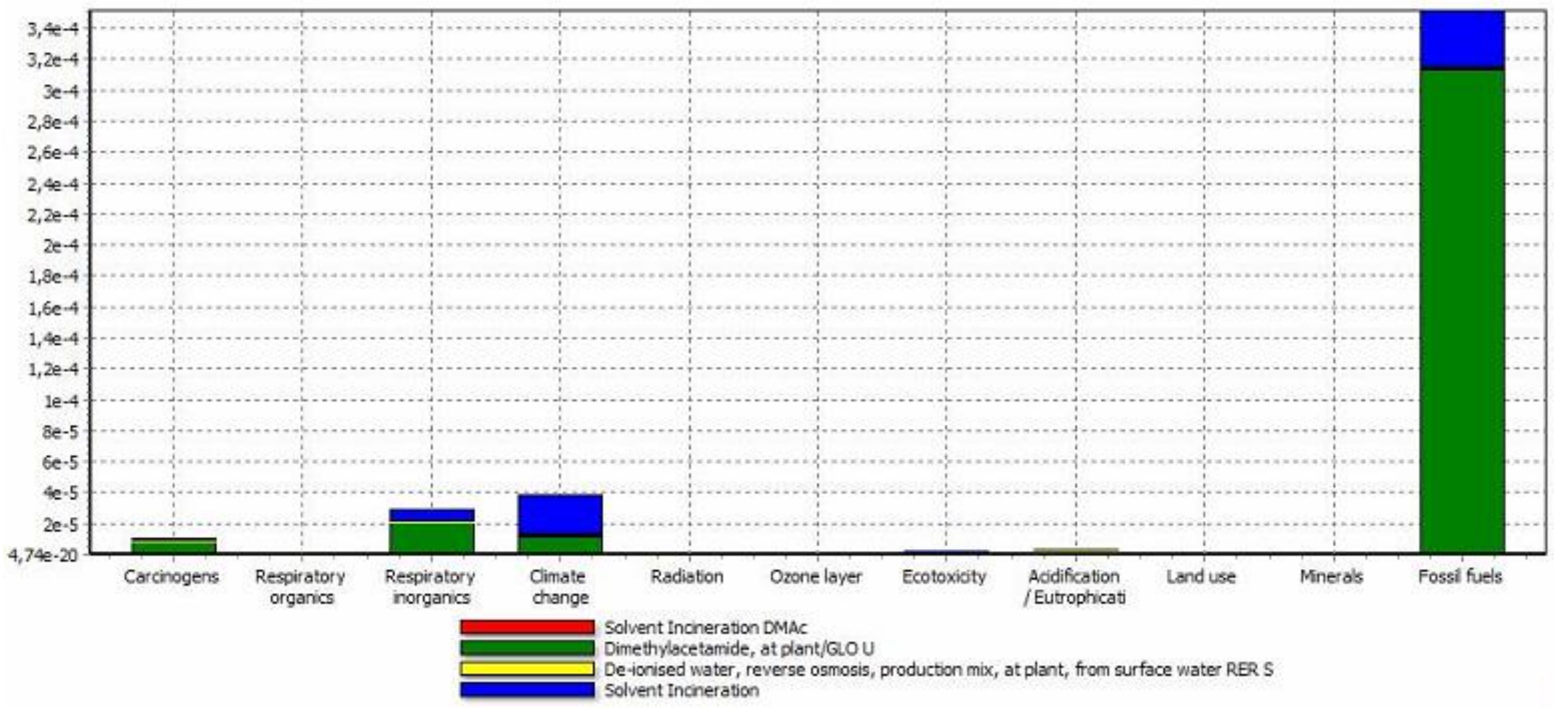


Figure D.2: Normalization result of the DMAC incineration

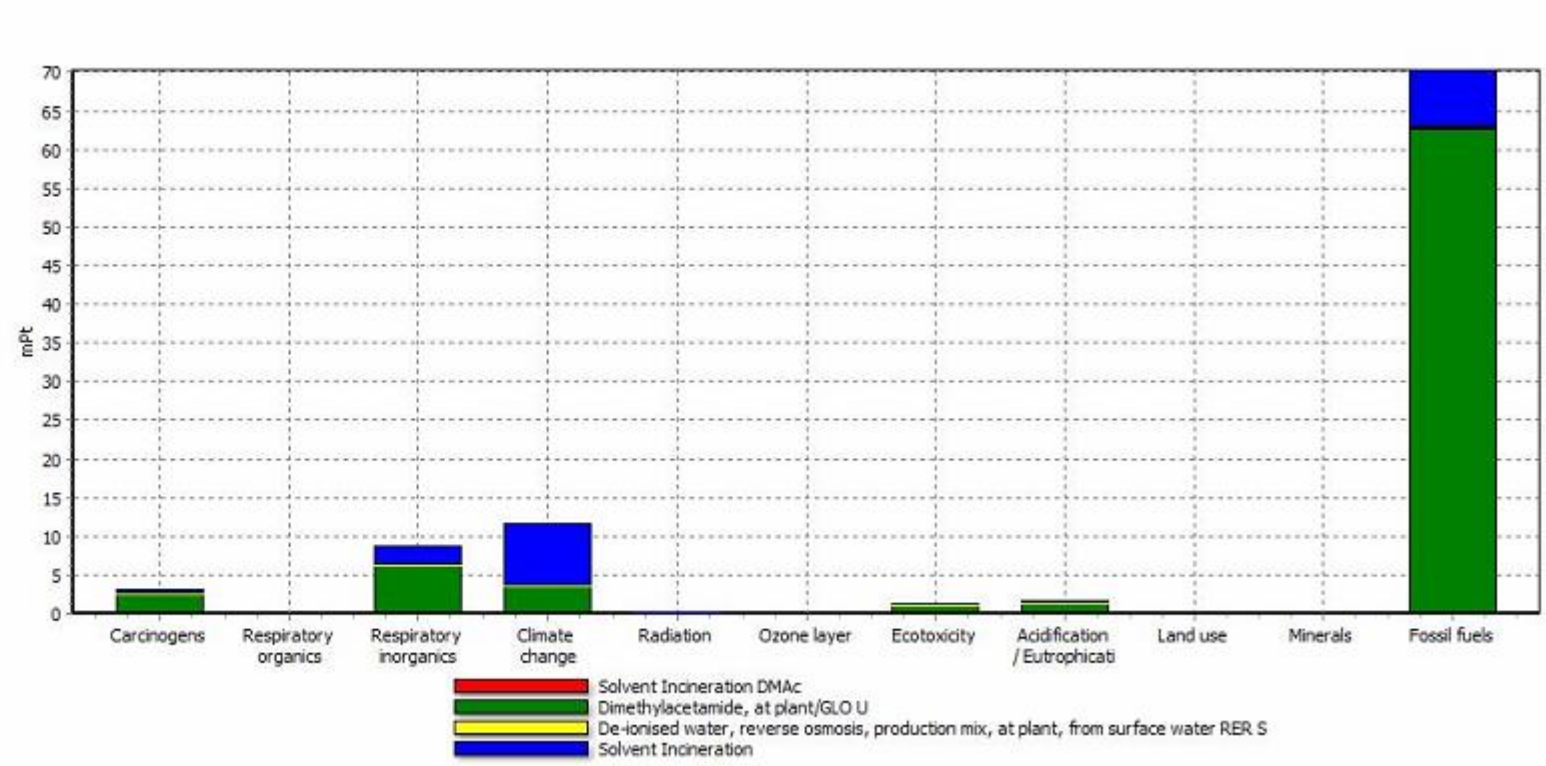


Figure D.3: Weighting result of the DMAC incineration

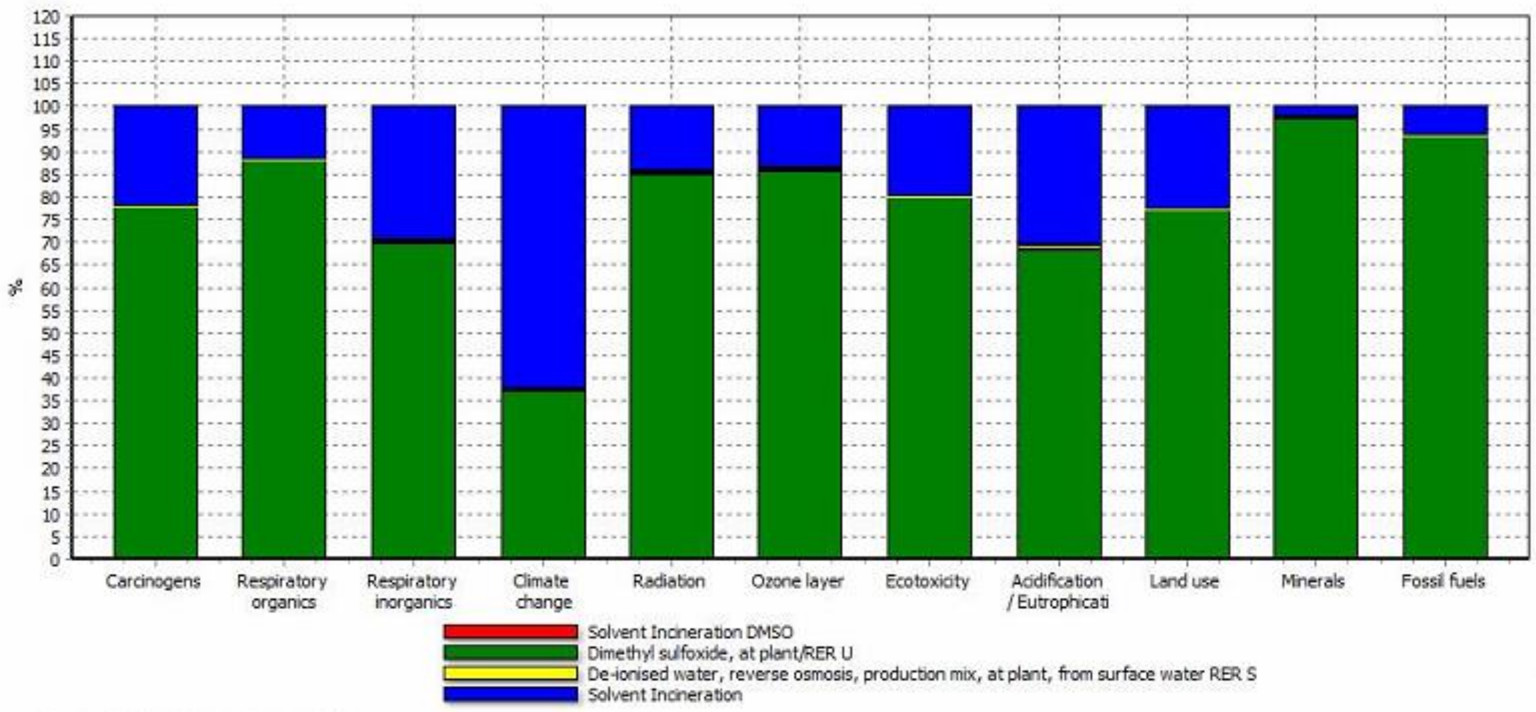


Figure D.4: Characterization and damage assessment result of the DMSO incineration

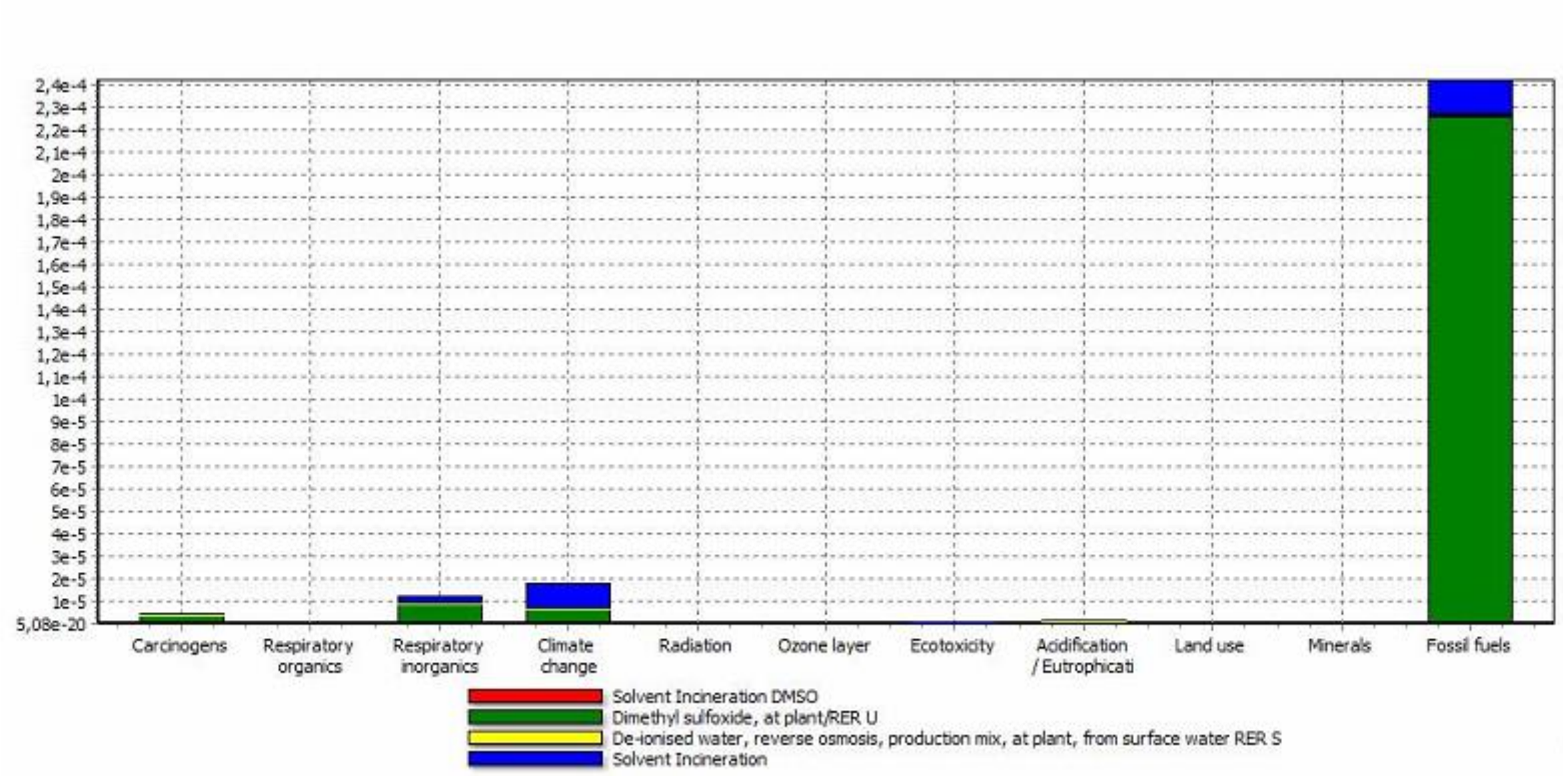


Figure D.5: Normalization result of the DMSO incineration

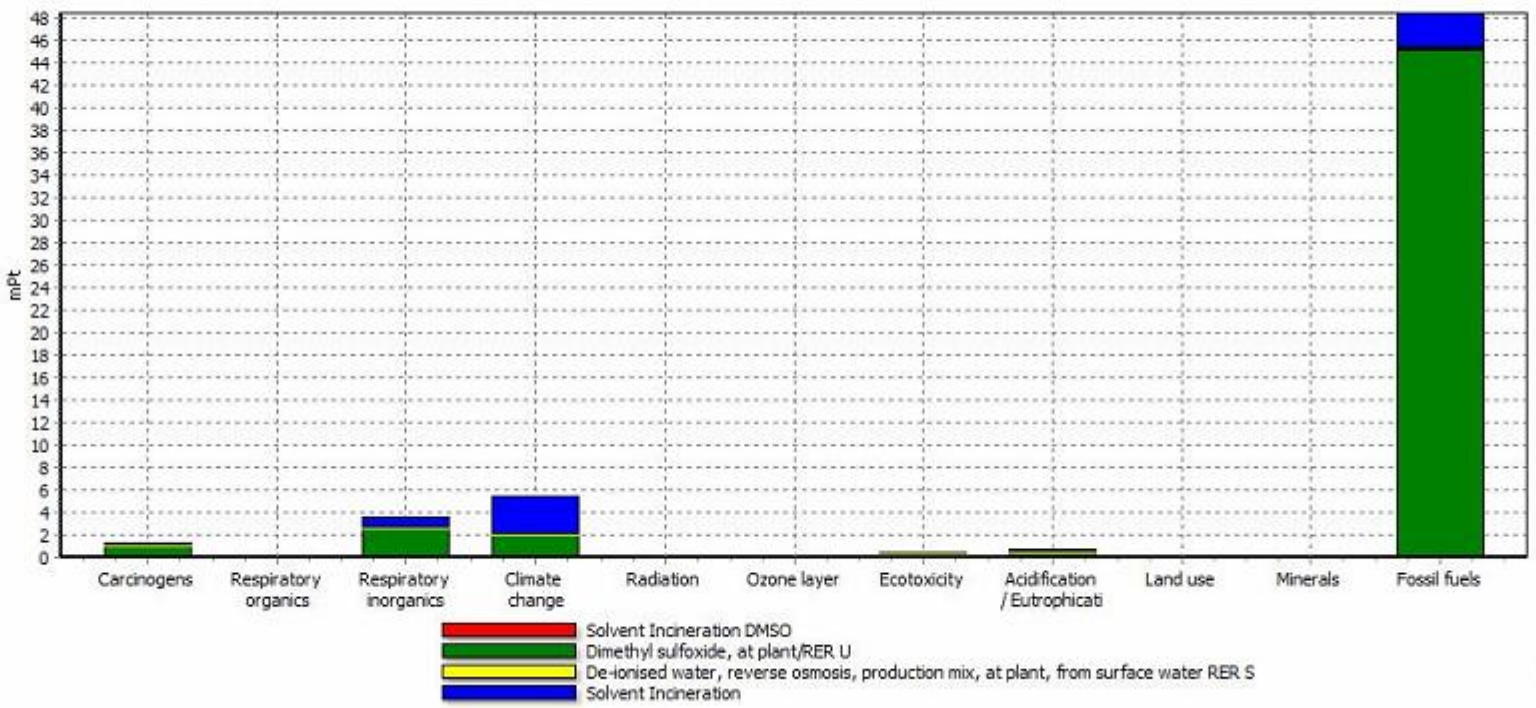


Figure D.6: Weighting result of the DMSO incineration

APPENDIX E

Screenshots of the Sensitivity Analysis of DMAc

Sensitivity analysis-inputs/outputs of the SRU for DMAc can be seen from Figures E1.E-2.

Documentation | Input/output | Parameters | System description

Products

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation %
Solvent Recovery-Sensitivity	95	ton	Mass	41,67 %
Water recycling-Sensitivity	133	ton	Mass	58,33 %
(Insert line here)				

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution
Dimethylacetamide, at plant/GLO U	94,3	ton	Undefined
De-ionised water, reverse osmosis, production mix, at plant, from surface water RER S	132,86	ton	Undefined
Dimethylamine, at plant/RER U	0,085	ton	Undefined
Acetic acid, 98% in H2O, at plant/RER U	0,29	ton	Undefined
(Insert line here)			

Inputs

Known inputs from nature (resources)

Name	Sub-compartment	Amount	Unit
(Insert line here)			

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution
Dimethylacetamide, at plant/GLO U	94,86	ton	Undefined
De-ionised water, reverse osmosis, production mix, at plant, from surface water RER S	133	ton	Undefined
Acetic acid, 98% in H2O, at plant/RER U	0,136	ton	Undefined
(Insert line here)			

Known inputs from technosphere (electricity/heat)

Name	Amount	Unit	Distribution	SD^2
Electricity, hard coal, at power plant/AT U	2045	kWh	Undefined	
Process steam from heavy fuel oil, heat plant, consumption mix, at plant, MJ AT S	56,9	MWh	Undefined	
(Insert line here)				

Figure E.1: Sensitivity analysis-inputs/outputs of the SRU for DMAc

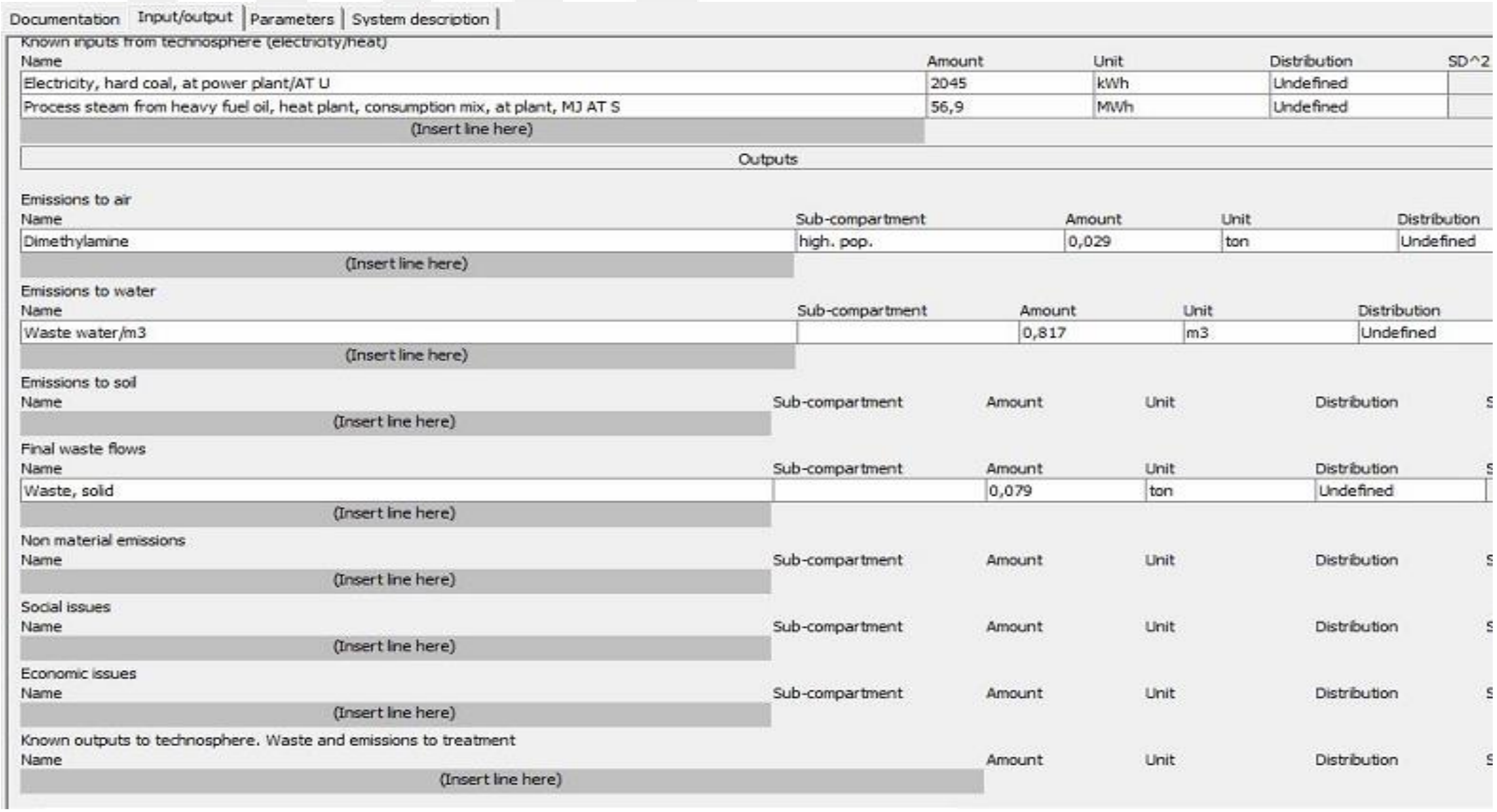


Figure E.2: Sensitivity analysis-inputs/outputs of the SRU for DMAc – continued