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Environmental and economic comparison of waste solvent treatment options

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Abstract: The sustainable development and consumption need more efficient use of natural resources. As a consequence, the use of industrial solvents demands their recovery instead of end-of-pipe treatment. It is not always clear, however, which treatment alternative should be applied. Based on an industrial case study, the environmental and economic evaluation and comparison of the treatment alternatives of a non-ideal solvent mixture containing azeotropes is investigated for determining the preferable option. For the recovery of the industrial solvent mixture, two different separation alternatives are evaluated: a less effective alternative and a novel design based on hybrid separation tools. An end-of-pipe treatment alternative, incineration, is also considered and the split of the solvent mixtures between recovery and incineration is investigated. The environmental evaluation of the alternatives is carried out using 'Eco-indicator 99 life-cycle impact assessment methodology'. Economic investigation is also accomplished. The economic features clearly favour the total recovery, however, the environmental evaluation detects that if a recovery process of low efficiency is applied, its environmental burden can be similar or even higher than that of the incineration. This motivates engineers to design more effective recovery processes and reconsider the evaluation of process alternatives at environmental decision making.

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1 Introduction

Industrial growth on a global scale has shifted environmental concerns towards daily levels of pollutants. The scale of industrial production is now so great that local problems, such as point-source emissions, even of formerly tolerable emissions, such as carbon dioxide, cause global environmental problems, like ozone layer depletion, global warming, acidification, etc. Recent and future investments have and are being made to meet the requirements of sustainable development. This will result in both the qualitative, reduction of pollutions and emissions, and quantitative, reduction of consumption, protection of resources on Earth [1].

"Green chemistry" aims at the pollution prevention in industrial processes. Great efforts are made in order to reach these aims [2, 3]. Among these efforts, US Environmental Protection Agency (EPA) established the Presidential Green Chemistry Challenge Awards Program to 'recognize and support fundamental and innovative chemical methodologies that are useful to industry and that accomplish pollution prevention through source reduction' [4–6]. The basis of the environmental politics of the European Union is published in the Environment Action Programmes, its latest release 'Environment 2010: Our future, our choice – The Sixth Environment Action Programme' was published in 2002. The waste management hierarchy defined by EPA can be considered as a general directive. It ranks pollution prevention options in the following way: source reduction; recycling; waste separation and concentration; energy and material recovery; end-of-pipe waste treatment; disposal. The recycling of internal wastes is more supported than endof-pipe treatment alternatives. Switching the emphasis from waste treatment to waste minimization requires technological changes in the processing industry. Technological changes can be categorized into two areas: retrofitting on existing industrial activities and developing new cleaner processes. It is a heuristic rule that incorporating waste minimization during process design is less complicated than modifying operations at an existing plant [7].

A typical environmental dilemma is the problem of the used solvents forming waste streams. In different industries, usually chemical ones, organic solvents are used in large amounts for synthesis processes as well as for work-up and purification of products. Consequently, huge amount of waste solvent is produced every year. Since many solvents demonstrate high volatility, considerable environmental persistence, and high toxicity, the handling of solvents in the chemical industry represents a high priority environmental issue [8]. Although experts make major efforts to consider environmental impact by process optimization and the selection of an optimal solvent [9–11], the treatment of waste solvents coming from existing technologies is still a problem of high priority.

As far as treatment alternatives for waste solvent streams, two methods are considered; recovery or the end-of-pipe treatment (e.g. incineration). Each treatment option has its own advantage and disadvantage. In the case of the incineration, thermal energy is recovered but new solvents are needed consuming natural resources. In the case of recovery by a separation process such as distillation, membrane separation or other alternatives

can be applied and the recovered solvents can be reused. The selection between solvent treatment alternatives has been usually made on the basis of economic analysis, however, the problem might become more complicated since sometimes the re-use of the solvent is strictly prescribed (e.g. in pharmaceutical industry) and environmental consideration may also complicate the problem.

From an environmental point of view, there is little data in literature about whether waste solvent incineration or regeneration is the preferable treatment option. Hofstetter et al. [12] have made a comparison between these two treatment options for a waste solvent mixture containing toluene with different scenarios for energy supply. It has been found that the results depend on the impact assessment methodology chosen and some pertinent properties of the waste solvent mixture such as the high enthalpy of combustion. If the evaluation is based on Eco-indicator 99 or primary energy demand, distillation is the preferable treatment option due to high credits for recovered non-renewable resources. In contrast, if emissions to air and water are considered more important, such as in the Swiss Ecopoints method, incineration is scored due to higher credits calculated for the avoided energy production. Chen and Shonnard presented a systematic framework for environmentally conscious chemical process design, which means the integration of environmental aspects into the process synthesis [13].

In this paper, environmental and economic evaluation and comparison of the treatment options of a highly non-ideal quaternary waste solvent mixture originating from a printing company is prepared for choosing the preferable option: recovery or incineration. Moreover, the split of the solvent mixtures between the recovery and incineration alternatives is also investigated. The cradle-to-grave Life Cycle Assessment (LCA) study for the solvent mixture is expanded for our investigation with the different kinds of the waste treatment alternatives. A model is built up for quantifying the environmental risk of treatment options. The LCA is evaluated by the Eco-indicator 99 Life Cycle Impact Assessment (LCIA) methodology which enables us to assign one single score to the total environmental impact of the different solvent treatment alternatives [14].

2 Methods

2.1 LCA and Eco-indicator 99

The definition of the Life Cycle Assessment by the International Organization for Standardization (ISO) is: 'a systematic set of procedures for compiling and examining the inputs and outputs of materials and energy and the associated environmental impacts directly attributable to the functioning of a product or service system throughout its life cycle' [15]. The method is developed to evaluate the mass balance of inputs and outputs of systems and to organize and convert those inputs and outputs into environmental themes or categories relative to resource use, human health, and ecological areas. LCA is an environmental decision-making tool that can help an organization estimate the environmental performance of its product or service from cradle to grave. The environmental

impacts addressed by LCA include the depletion of resources as well as the release of polluting and harmful substances and their impacts, both on a local and global scale. The outcome of an LCA is the quantification of the environmental impacts associated with a product throughout the entire production life cycle which makes the identification of a more environmental friendly product, service or process possible. ISO 14040-43 standards give the frames of LCA preparation.

The following steps give the basis for the LCA: 1) Scope and goal definition 2) Life cycle inventory analysis 3) Life cycle impact assessment 4) Life cycle interpretation. After setting up the boundaries of the life cycle assessment, all relevant material and energy flows are collected in the life cycle inventory (LCI). After that, the material and energy flows are converted into environmental impacts referring to several impact categories, i.e. resources, global warming, ozone depletion, acidification, eutrophication, smog formation, human toxicity, land use, noise etc. [16]. This step is called life cycle impact assessment. The last step of the LCA is the interpretation of the calculated environmental impacts in the different impact categories. The ISO standards do not allow the aggregation of the environmental impacts expressed in the different impact categories, the discussion of the separated impact categories is suggested. If the LCA study is used for the comparison of two (or more) processes, the selection of the more environmental friendly process might be difficult if too many environmental impact categories have to be compared.

There are several methods available which make the comparison and the ranking of the environmental impacts easier. One of these methods is the Eco-indicator 99 life-cycle impact assessment methodology, which is specially developed for product design and which is probably the most relevant to European industrial pollutions [14, 17]. The method contains a damage model (fate-, exposure-, effect- and damage analysis), normalization and weighting step, which make it possible to express the environmental impact with a single score, the Eco-indicator point. Eco-indicator scores are used to calculate potential damage caused in the categories of 'Human Health', 'Ecosystem Quality' and 'Resource Depletion'. Environmental impacts calculated according to the three damage categories are converted into dimensionless figures by the normalization step; the weighting step makes it possible to evaluate damage from several aspects (i.e. long term impacts get as high priority as short term impacts or vice versa). There is no absolute value of the indicators; they have only a relative value: similar processes might be compared based on the Eco-indicator scores. The scale of Eco-indicators is chosen in such a way that the value of 1 pt is representative for one thousandth of the yearly environmental load of one average European inhabitant [14]. The Eco-indicator 99 is acknowledged as a standard investigation tool of LCA and applied in 45 countries. The application of the Eco-indicator 99 is supported by the software Sima Pro 5.1 [18].

3 Discussion

An industrial case study on waste solvent treatment alternatives of a printing company has called to attention the necessity of an environmental investigation where the economics environmental impacts of the treatment alternatives are also investigated. In earlier studies, the separation of the waste solvent stream from a highly non-ideal quaternary mixture has already been solved and published [19–21]. The waste solvent mixture contains ethanol (ETOH), isopropyl acetate (IPAC), ethyl acetate (ETAC), and water ($\rm H_2O$). The main physical properties of the components and the composition are shown in Table 1. The quantity of the waste stream is about 40.000 tons/year. Considering the flow rate, continuous operations should be applied for the waste solvent treatment.

The following treatment alternatives are considered:

- (1) Recovery alternatives of the solvents with separation
 - (a) Ternary cut separation scheme,
 - (b) EHAD scheme.
- (2) End-of-pipe treatment with incineration.
- (3) Split of the waste solvent stream between the end-of-pipe and the recovery alternatives

These three groups of alternatives of the waste solvent treatment are evaluated and compared on environmental and economic basis.

	Ethanol	Ethyl acetate	i-propyl-acetate	Water
Weight fraction Formula	0.309 C_2H_6O	0.261 $C_4H_8O_2$	0.221 $C_5H_{10}O_2$	0.209 H ₂ O
Mol. weight, used for calculation [g/mol]	46	88	102	18
Heat of combustion, ΔH_i^{comb} [MJ/kg]	32.33	24.35	20.16	-5^{a}

 $^{^{}a}\Delta H_{H_{2}O}^{vap.}$ (1200 °C) = 5 MJ/kg

Table 1 The physical properties of waste solvent mixture components.

3.1 Recovery of the solvents

The recovery of the solvent components is possible with several techniques. In this study, two possible alternatives published recently in the literature [20, 21] are investigated. Both processes fulfils the purity requirement, which is 95wt % for the solvent components, and the water leaving the system must not contain any solvent components. In these procedures, water is used as the separating or extractive agent corresponding with the international environmental politics. Green chemistry [22] proposes to avoid the use of new materials as separating agents. An assessment of the environmental impacts of the solvent recovery needs the engineering modelling of the two processes that is carried out with ASPEN PLUS 12.1. in order to obtain operational (steam and cooling water demand) and investment (sizing of the unit operations) data.

In an earlier design [19, 21] of a quite complicated separation process, the so called 'ternary cut scheme' has been elaborated for the recovery of the studied solvent mixture.

The process consists of seven distillation columns (C1-C7) and two liquid-liquid extractors (E1-E2), see Figure 1. First the quaternary mixture is separated into two ternary ones. The top product contains no IPAC and the bottom product contains no ETAC. The two ternary mixtures can be processed simultaneously in a similar way.

This separation scheme can be simplified significantly, if the so called extractive heterogeneous-azeotropic distillation (EHAD) [20] is applied and used as a basis for this separation problem (Figure 2). In this novel design, ordinary distillations and internal recycles are also applied. This separation scheme consists of four distillation columns (C1-C4) and a phase separator (S), so this scheme is much simpler than the previous one.

A great advantage of the recovery is that no considerable amount of make-up solvents is needed, however, a huge amount of steam is consumed.

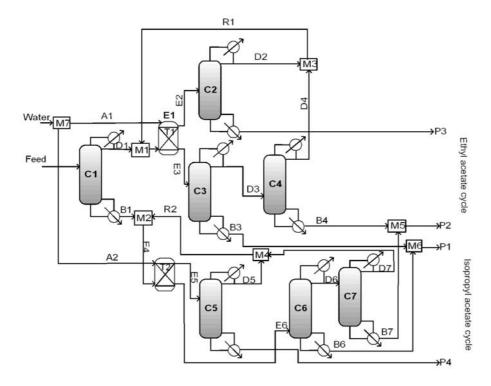


Fig. 1 Ternary cut scheme for the separation of the waste solvent stream [21].

3.2 Incineration of the solvents

The other treatment alternative of the waste solvents is the end-of-pipe treatment. Incineration is considered as a typical end-of-pipe treatment. Such a special waste solvent incinerator is shown in Figure 3 [23]. The combustion takes place in the furnace, the flue gas goes to a washer then to a catalytic flue gas cleaner. Slag and ash are collected during the cleaning of the furnace and its wastes should also be treated. Electricity and steam are produced during the incineration process but the extent of the obtained energy depends on the heat of combustion of the inflow waste solvent stream. If the waste solvents are incinerated, the heat of combustion is recovered, however, fresh solvents should be

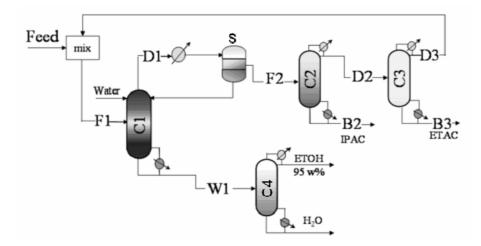


Fig. 2 EHAD scheme for the separation of the waste solvent stream [20].

used as a make-up. This means the more extensive use of natural resources in this case.

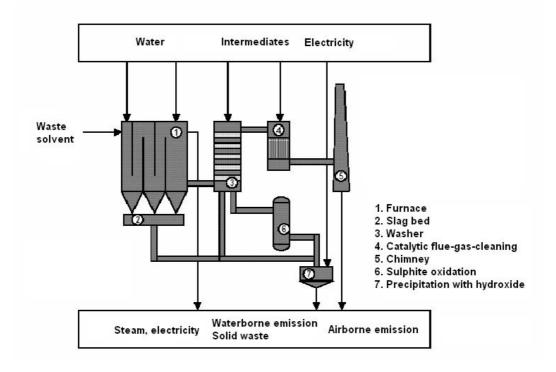


Fig. 3 Structure of a typical waste solvent incinerator [23].

3.3 Treatment with simultaneous incineration and recovery

If the waste solvent incinerator operates next to the recovery plant, the energy demand of the recovery can be covered by on-site produced steam. The incinerator can be fueled either by waste solvent or by light fuel oil in order to get a sufficient amount of steam that covers the energy demand of the recovery. Therewith a connection between the two

systems is possible: a fraction of the waste solvent stream can be fed into the incinerator in order to produce energy that can be utilized at the recovery and the rest of the solvents can be recovered. If energy obtained by the incineration of the waste solvent fraction getting to incineration exceeds the energy demand of the recovery surplus energy can be utilized in the grid. If waste solvent-based energy production is not sufficient, the missing steam can be produced by the incineration of light fuel oil.

4 System modelling

For the correct comparison of the recovery and recycling of the solvents and their end-ofpipe treatment, it is necessary to carry out the LCA of the solvents used. The functional unit of the study is the environmental impact caused during a one hour operation of the waste solvent treatment plant. The symbolic flowsheet for the LCA of the two waste solvent treatment alternatives, that is recovery and incineration, and the possible connection between them are shown in Figure 4. The two alternative systems are defined and represented with dotted lines which are considered as system boundaries. Fresh solvent production, the use of the solvents in the company and the disposal are within the system boundary. The environmental impacts of the treatment processes are assessed by the Eco-indicator 99 method. The realisation of such an assessment needs the comprehensive knowledge of the three alternatives and the preparation of life-cycle inventories, each individual step is analysed and considered before its evaluation. Eco-indicator 99 delivers points to each individual step and these points are summarised. However, these points can be applied only for a relative comparison of the different alternatives. The proper application of the Eco-indicator 99 needs the evaluation of an accurate calculation model for each functional unit of the waste solvent treatment alternatives.

The environmental impact of the functional unit ($I_{treatment\ option}$) can be calculated on a standard basis represented by Equation (1), the dimension is EI-99 points/h.

$$I_{treatment\ option} = I_{solv.\ prod.} + I_{ws\ treatment} \tag{1}$$

 $I_{solv. prod.}$ represents the environmental impacts caused by the industrial production of the components in the waste solvent mixture. This is the product of the massflow of the i^{th} solvent component (\dot{m}_i) in the waste solvent stream and the specific impact indicator $(i_{i,prod})$ referring to the petrochemical production of the i^{th} component, as shown in Equation (2).

$$I_{solv. prod} = \sum \left(\dot{m}_i \cdot i_{i,prod} \right) \tag{2}$$

 $I_{ws\ treatment}$ represents the environmental impacts during one hour operation of the investigated treatment plant. To determine the accurate Eco-points referring to the different treatment options a detailed model of each processing unit of the solvent treatment alternatives (recovery and/or incineration) should be elaborated. The preparation of the LCA needs the detailed life-cycle inventories of the treatment alternatives.

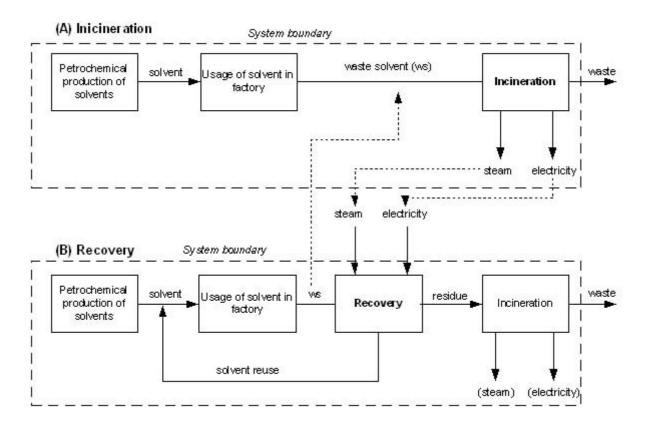


Fig. 4 Model of the waste solvent treatment options.

4.1 Assessment procedure of the recovery

Assessment of the environmental impacts of the solvent recovery needs the engineering modelling of the two processes that is carried out with ASPEN PLUS 12.1. Simulation and modelling deliver data for the determination of construction material, heat and cooling water demand in the case of each unit operation. The operation of the recovery with ternary cut scheme requires 19.68 MJ heat energy and 235 kg cooling water per 1 kilogram of waste solvent. Recovery with EHAD scheme consumes 8.79 MJ heat energy and 105 kg cooling water per 1 kilogram of waste solvent. The components of the waste solvent mixture are recovered with 95 % efficiency, the residue that contains mainly water is disposed of in a municipal waste incinerator.

Environmental impacts of the recovery processes are calculated by the following equation:

$$I_{ws,recovery} = I_{baisc,dist} + I_{investment,dist} + I_{operation} + I_{residue} - I_{rec.ws}, \tag{3}$$

where

$$I_{basic,dist} = \dot{m} \cdot i_{basic,dist} \tag{4}$$

$$I_{investment, dist} = (\dot{m})^{0.6} \cdot i_{investment, dist}$$
 (5)

$$I_{operation} = \dot{m}_{steam, oil} \cdot i_{inc, oil} + r_{cooling water} \cdot \dot{m} \cdot i_{cooling water}$$
 (6)

$$I_{residue} = (1 - \alpha) \cdot \dot{m} \cdot i_{residue} \tag{7}$$

$$I_{rec.ws} = \alpha \cdot I_{solv.prod} \tag{8}$$

 $I_{basic, dist}$ represents the contribution to the total environmental impact of the recovery process caused by solvents and chemicals (methanol and N₂) used for the cleaning and the maintenance of the columns (by breakdown). In Equation (4), $i_{basic, dist}$ represents the environmental impacts of the production of these chemicals and the emissions of the recovery plants to air and water referring to 1 kg waste solvent; \dot{m} is the total massflow of the waste solvent mixture. $I_{investment, dist}$ stands for installed material of the recovery plant. The environmental impact of the installation referring to 1 kilogram of waste solvent mixture is denoted by $i_{investment, dist}$ which has different values for the two recovery alternatives. Project life is 10 years. An interaction between the environmental impact of investment and waste solvent stream with a power of 0.6 is supposed. $I_{operation, dist}$ represents the environmental impacts of the steam and cooling water consumption. Steam has two possible sources: incineration of waste solvents and incineration of light fuel oil. In Equation (6) only the environmental impacts of the extra steam produced by the incineration of oil is considered since the environmental impacts of the solvent combustion is considered at the incinerator. According to this, in Equation (6), $\dot{m}_{steam.oil} [kg/h]$ represents the massflow of the steam obtained from the incineration of light fuel oil and $i_{steam, oil}$ stands for the environmental impacts of the incineration light fuel referring to 1 kilogram of steam obtained. The environmental impacts of the cooling water consumed by the recovery are calculated as the product of the cooling water demand referring to 1 kilogram of waste solvent ($\mathbf{r}_{cooling\ water}$), the massflow (\dot{m}) of the waste solvent stream getting to recovery, and the impact indicator referring to the production and delivery of 1 kilogram of cooling water ($i_{cooling\ water}$). In Equation (7) $I_{residue}$ stands for the environmental impacts of the disposal of the residue in a municipal incinerator. The specific impact of the residue treatment referring to 1 kilogram of waste solvent is denoted by i_{inc} . The yield of the recovery (α) is 0.95. Recovered solvents replace fresh solvents and therewith the environmental impacts of their industrial production. Therefore, the environmental impacts of the recovered solvents $(I_{rec. ws})$ are equal to the environmental impacts of the industrial production of the studied waste solvent mixture $(I_{solv. prod})$ multiplied by the yield and have a negative sign in Equation (3).

4.2 Assessment procedure of the incineration

For the preparation of the life cycle assessment of the incinerator detailed literature data are applied [17] and a complete life cycle inventory is carried out for the selected waste solvent incinerator. The applied literature data describe an existing on-site incinerator. In 1998, the reference year for data used in this study, the incinerator produced 191 GWh thermal energy and 14 GWh electric energy. More than 81 % of the energy produced originated from the incineration of waste solvents (33,500 tons in 1998). The incinerator can be fueled by light fuel oil or by waste solvents; however, in this case some support oil is needed for keeping the desired furnace temperature. Data include material and energy requirements, emissions to air and water and solid emissions sent to landfill. It

is considered that the input and output flow rates are in a linear correlation with the incoming massflow of the waste solvent except $\rm CO_2$ emission and support oil (light fuel oil) requirement. In the furnace, low pressure steam (6 bar, 220 °C; 0.897 MWh/t steam) is produced during the operation with 86 % efficiency. Steam and electricity are so called 'avoided products' as they replace the industrial production of these valuable products, so their 'impact' reduces the total environmental impact with their contribution.

The environmental impacts caused during one hour's operation are calculated by Equation (9–14). Equations (10) and (11) stand for material and flows that are considered to be independent from the composition of the waste solvent mixture. Equations (12–14) stand for composition dependent upon material and energy flows.

$$I_{ws,inc} = I_{basic,inc} + I_{investment,inc} + I_{CO_2} + I_{oil} - I_{gain}, \tag{9}$$

where

$$I_{basic,inc} = \dot{m} \cdot i_{basic,inc} \tag{10}$$

$$I_{investmentm, inc} = (\dot{m})^{0.6} \cdot i_{investment, inc}$$
(11)

$$I_{CO_2} = \sum \left(\dot{m}_{C,i} \cdot i_{C-CO_2} \right) + \left(\dot{m}_{C,oil,\text{Support}} + \dot{m}_{C,oil,start-up} \right) \cdot i_{C-CO_2}$$
 (12)

$$I_{oil} = (\dot{m}_{oil, start-up} + r_{oil, ws} \cdot \dot{m}) \cdot i_{oil}$$
(13)

$$I_{gain} = \eta \cdot \left(\dot{m}_{inc} \cdot \Delta H_{Fedd}^{Comb} - \dot{m}_{recovery} \cdot \Delta H_{recovery} \cdot i_{gain} \right)$$
 (14)

 $I_{basic,inc}$ refers to the composition-independent material and energy flows of the incinerator. It includes the environmental impacts of the production of chemicals consumed at the plant, emissions to air and water, and solid emissions. The aggregated environmental indicator of these terms referring to 1 kilogram of waste solvent is denoted by $i_{basic,inc}$. The total massflow of the waste solvent mixture is signed by \dot{m} [kg/h]. $I_{investment,inc}$ stands for the installed material of the incinerator plant; $i_{investment,inc}$ represents the environmental impacts of the construction materials referring to 1 kilogram of waste solvent. An interaction between the environmental impact of investment and waste solvent stream with a power of 0.6 is supposed (according to process design heuristics). Project life is 10 years. Total oxidation of the waste solvent in the furnace is assumed, therefore, CO₂ emission can be calculated from the carbon-mass-balance. The environmental impact of the CO_2 released to air is denoted by I_{CO_2} which includes carbon entering the system from the waste solvent components $(\dot{m}_{C,i} [kgC/\cdot h])$ and the applied light fuel oils: support oil and start-up oil $(\dot{m}_{C,oil,support})$ and $\dot{m}_{C,oil,start-up}[kgC/\cdot h]$. The carbon content of light oil is assumed to be 86wt %. The specific environmental impact indicator of CO₂ emission is denoted by i_{C-CO_2} representing the emission of 1 kg CO₂ per kg carbon input. Total oxidation of the solvent components is ensured if the required high temperature (1,200 °C) in the furnace is guaranteed, too. Therefore, support oil is added to the waste solvents to reach the desired heat input that is 23 MJ/kg. Since the heat of combustion of the waste solvent mixture is only about 20 MJ/kg, therefore, $r_{oil,ws} = 0.177$ kg oil is added to each kilogram of waste solvent mixture. I_{oil} represents the environmental impacts of the industrial production of light fuel oil consumed during operation in form of start-up oil

(829 t/year) and support oil. The environmental impacts of the industrial production of 1 kilogram of light fuel oil is indicated as i_{oil} . I_{gain} stands for the avoided environmental impacts through the production of steam and electricity. In our consideration, the produced energy is either added to the grid or it is consumed by the simultaneously working regenerating plants, therefore, the extent of the valuable products (energy sent to the grid) is the difference between produced energy and energy consumption of the possible simultaneous working recovery plant. Considering the efficiency of the incinerator (η) that is 86 % and the heat of combustion of the waste solvent mixture and of the support oil (together 23 MJ/kg, signed by $\Delta H_{Feed}^{Comb}),$ about 19.8 MJ energy can be obtained by the incineration of one kilogram of waste solvent. The heat energy requirement of the recovery is denoted by $\Delta H_{recovery}$ [MJ/h]. The environmental impacts of the valuable products can be calculated if the massflow of the waste solvent stream sent to recovery $(\dot{m}_{recovery} [kg/h])$ and to incineration $(\dot{m}_{inc} [kg/h])$ are determined. The environmental impacts of the heat energy production that are avoided by the delivery of the surplus heat to the grid are denoted by i_{gain} [EI – 99 points/MJ energy]. If the heat requirement of the recovery plant is higher than the heat energy produced by the incineration of the waste solvent, the value of I_{qain} is zero.

4.3 Assessment procedure of the simultaneous incineration and recovery

A model of the treatment options is prepared in order to estimate the total environmental impact, if the two studied treatment options are working simultaneously. The model equations are direct or indirect functions of the waste solvent massflow entering the treatment options which can be incineration or recovery. The total environmental impact referring to the functional unit is calculated as the superposition of Equations (3) and (9).

4.4 Economic calculation

The economic calculation needs the complete engineering model of the treatment alternatives to determine their major parameters needed. For the recovery alternatives, these models are made in the ASPEN PLUS environment [20, 21] presenting operational data and the main geometric data for the sizing of the unit operations. Operational costs include steam (low pressure steam) and cooling water consumption. Capital costs include the material demand of the unit operations and installation costs calculated on the basis of geometrical data actualised with the Marshall and Swift index given for each year to consider the inflation [25]. The project life is 10 years.

In the case of the incineration, utility cost is calculated based on the operational datasheet of the incinerator found in the literature [17] that includes energy and material requirements. The quantity and cost of support oil and oil used for steam production is added to the utility cost, too. According to process design heuristics, the capital cost of an incinerator performing the treatment of 40,000 t/yr waste solvent is about 24 million dollars. The project life is 10 years. Prices for calculations are shown in Table 2.

Material cost	
ETOH (USD/kg)	1.23
IPAC (USD/kg)	0.9
ETAC (USD/kg)	1.28
Utility cost	
Steam (USD/t)	18.1
Electricity (USD/MWh)	43
Light fuel oil (USD/t)	600
Water (USD/t)	0.042
Capital cost	
Marshall and Swift index (2003) Project life (years)	1, 123.6 10

Table 2 Data used by the economic assessment.

5 Results

5.1 Results of the life cycle assessment

The specific environmental impact indicators discussed above are detected and related to mass of waste and also to energy (Table 3). The specific environmental impact indicators of solvent production are presented in detail in category 'Incineration', while in category 'Recovery' the impact indicator referring to the production of the waste solvent mixture is presented. The impact indicators of investment of the distillation plants are divided into two groups according to the two separation schemes selected: the first value stands for the EHAD scheme and the second one for the ternary cut scheme.

Incineration	$i_{i,production} \ ext{[pt/kg ws]}$	$i_{basic,inc}$ [pt/kg ws]	$i_{investment,inc}$ [pt/kg ws]	i_{C-CO_2} [pt/kg]	$i_{gain} \ [ext{pt/MJ}]$	i_{oil} [pt/kg oil]
EtOH ETAC	0.241 0.289	0.0253	0.166	0.0054	0.0177	0.129
IPAC water	0.292 0.0000302					
Recovery	$i_{ws\ mix,\ production}$ [pt/kg ws]	$i_{basic, dist}$ [pt/kg ws]	investment, dist [pt/kg ws]	$i_{steam, external}$ [pt/kg steam]	$i_{cooling\ water}$ [pt/kg water]	i_{inc} [pt/kg ws]
EHAD Tern. cut	0.214	1.22×10^{-6}	0.0518 0.1165	0.0184	0.0000332	0.131

Table 3 Impact factors applied by the calculation of the Eco-indicator points.

First the Eco-indicator points for the total incineration and total recovery are determined using equations (2-15). The different elements of the environmental contributions

Incineration	$I_{solvent},$ production	$I_{basic,}$ $inci-eration$	$I_{investment}, inc$	I_{CO_2}	$I_{oil,support}$	I_{gain}	Total
	913	108	25	11	51	-477	632
Regeneration	$I_{solvent}$	I_{basic}	$I_{investment}$,	$I_{residue}$	$I_{operation}$	$I_{recovered}$	Total
	ws mix	distillation	dist			ws	
Tern. cut scheme	ws mix 913	distillation 0.01	dist 17	29	568		661

and the total impacts are shown in Table 4.

Table 4 LCA results of the total recovery and total incineration of the waste solvents expressed with Eco-indicator points.

The environmental impacts of the total incineration expressed with Eco-indicator points reach 632 points. The highest contribution to this value is made by the solvent make-up production (913 points). Avoided products (-477 points) partially balance these impacts, however, it is clearly shown that the reduction is only 52 %. The incineration process including also support oil consumption increases the total environmental impact of the waste solvent treatment with incineration by 25 %. The environmental impacts of CO₂ production and investment referring to the functional unit are relatively low (11 and 25 points, respectively). The LCA shows that the loss of the solvent components has the highest contribution to the total environmental impact of the end-of-pipe waste solvent treatment.

Treatments with recovery reduce significantly the loss of the solvents; however, in this case a considerable amount of heat energy is required. Table 4 shows that environmental impacts of the solvent production (913 points) are almost totally preceded by the recovered solvent components (-868 points). Basic emissions, treatment of distillation residues and investment materials do not increase the total impact significantly. However, environmental impacts of the steam and cooling water used by the recovery have huge influence on the total impact. In the ternary cut scheme $I_{operation}$ gives 86 % of the total impact (661 points) of the recovery exceeding therewith the impacts (632 points) of the incineration. The LCA of the ternary cut scheme shows that environmental impacts can be significantly reduced with lower heat energy and cooling water demand. In the case of the more effective recovery alternative (EHAD scheme), $I_{operation}$ is much lower, with 256 points. As a result, the recovery with EHAD scheme (338 points) is significantly better than the end-of-pipe treatment.

The simultaneous treatment of the waste solvent mixture with both recovery and incineration is also considered. The total environmental impact referring to the treatment of the waste solvent mixture during one hour is the superposition of the impacts caused by the two processes: incineration and recovery. Figure 5 shows the total impact and the contributions of the different treatment options to the total value if simultaneous incineration and recovery with ternary cut scheme are assumed. It is clearly shown that at low fraction of solvent recovery the incineration covers the steam demand of the

recovery, therefore the environmental impacts referring to recovery are low. Meanwhile, the environmental impacts of the incineration are mainly determined by the solvent make-up production that is balanced with the surplus avoided products (steam sent to the grid). If the fraction of solvent recovery exceeds 0.5, steam production of the incineration does not cover the steam demand of the recovery. The missing steam is produced by the incineration of light fuel oil. The environmental impacts of the combustion of fuel oil are considered for the regeneration since the steam is used there. Therefore, if the fraction of solvent recovery exceeds 0.5 the environmental impacts of the recovery increase rapidly since it includes the impacts of light fuel oil combustion. The total impact of the waste solvent treatment with simultaneously working recovery with ternary cut scheme and incineration is minimal if total incineration is applied.

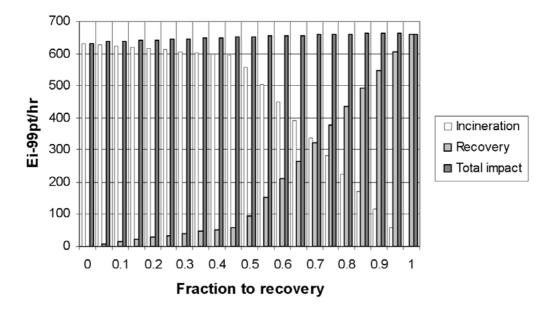


Fig. 5 Environmental impacts of the simultaneously working recovery applying ternary cut scheme and incineration.

Figure 6 shows the environmental impacts caused by simultaneously working incineration and recovery with EHAD scheme. The incineration covers the steam demand of the recovery if at least 30 % of the waste solvent mixture is sent to incineration and the rest is recovered. If more fractions are sent to recovery than the 70 % of the waste solvent mixture, the combustion of light fuel oil is required which increases the environmental impacts of the recovery. EHAD scheme is a more effective recovery alternative and has lower heat energy demand. According to this, total environmental impacts show that the most attractive solution is the total recovery of the waste solvent mixture with distillation applying EHAD. Moreover, the results show that environmental impacts cannot be reduced by the division of the waste solvent mixture between the two treatment plants.

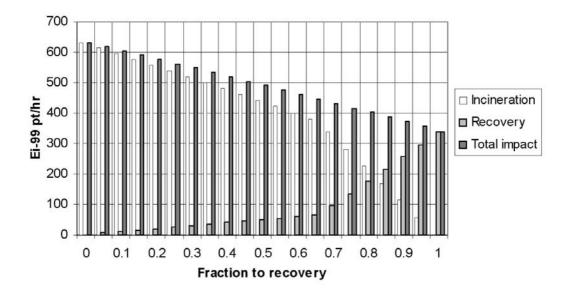


Fig. 6 Environmental impacts of the simultaneously working recovery applying EHAD scheme and incineration.

5.2 Economic analysis

Selection between the waste treatment options is generally carried out on the basis of economic evaluation. Therefore, the environmental evaluation presented above is completed with an economic analysis. Table 5 shows the results of the economic evaluation. Recovery is significantly better from economic viewpoint than the end-of-pipe treatment due to the high solvent make-up costs. If the waste solvent treatment is carried out by recovery with the EHAD scheme the total cost can be reduced by almost 90 % compared to the end-of-pipe treatment. Based on the economic evaluation, the recommended waste solvent treatment option is the total recovery with the EHAD scheme followed by the recovery with ternary cut scheme and the less attractive option is the end-of-pipe treatment with incineration.

	Total annual cost [1,000 USD/year]	Relative value [%]
Incineration	26,400	100
Recovery with tern. cut	6,430	24
Recovery with EHAD	2,860	11

Table 5 Total annual costs of the waste solvent treatment options.

5.3 Comparison of the LCIA and economic results

In this paper, economic evaluation and environmental impact assessment are compared. Environmental impact assessment shows that the most preferable solution for the treatment of the investigated waste solvent mixture is the recovery with EHAD scheme that is followed by the incineration and the less attractive solution from environmental point of view is the recovery with the ternary cut scheme. Economic assessment does not give the same result, since from economic point of view recovery with ternary cut scheme is significantly better than the incineration. The difference can be explained mostly by the relative high prices of the pure solvent components and low prices of fuel oil providing cheap energy for the recovery which do not express the real environmental impacts of their industrial production.

This example shows that since strategic decisions of companies and governments are usual made on the basis of economic calculations that can be misleading and, according to the concept of the sustainable development, it is highly desired that total cost and environmental impacts referring to the same process correspond to each other.

6 Conclusions

The comparison of two basically different waste solvent treatment options (incineration and recovery) is elaborated from environmental and economic viewpoints. Since the investigated waste solvent mixture is a highly non-ideal quaternary one, separation techniques with considerable heat requirement are needed to carry out the separation of the solvent components. Two possible recovery alternatives have been evaluated for demonstrating the difference between similar treatment options.

The results highlighted a contradiction between economic and environmental evaluation of the treatment options. Based on the economic evaluation, the recovery of the solvents is preferred to incineration, however, the recovery with ternary cut scheme has even higher environmental impacts than the incineration. In this case, this difference is emerging because of the relative high prices of pure solvents in comparison to the price of light fuel oil that might raise economic and environmental management problems. As a conclusion, it can be stated that economic evaluation in the field of waste solvent treatment is not sufficient. Decision making should be also preceded by environmental evaluation. Economic and environmental evaluations agree in that the more efficient solvent recovery process (EHAD) is the most attractive treatment option. This motivates engineers to design more effective recovery processes and proves the importance of the 'green engineering' and the concept of the sustainability.

The environmental and economic investigations show that the economic evaluation does not support environmental decision making, since they do not always give the same result. Therefore, when making decisions both the economical and environmental features of design alternatives should be considered.

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References

- [1] World Commission on Environment and Development ("Brundtland Committee"): Our Common future, Oxford Univ. Press., 1987.
- [2] R.B. Bakshi and J. Fiksel: "The Quest for Sustainability: Challenges for Process Systems Engineering", *AIChE J.*, Vol. 47, (2003), pp. 1350–1358.
- [3] T.D. Allen and R.D. Shonnard: "Green Engineering: Environmentally Conscious Design of Chemical Processes and Products", AIChE J., Vol. 47, (2001), pp. 1906– 1910.
- [4] C.J. Periera: "Environmentally friendly processes", Chem. Eng. Sci., Vol. 54, (1999), pp. 1959–1973.
- [5] U.S. Environmental Protection Agency: The Presidential Green Chemistry Challenge Awards Program, EPA 744-K-96-001, 1996.
- [6] U.S. Environmental Protection Agency: The Presidential Green Chemistry Challenge Awards Program, EPA 744-S-97-001, 1997.
- [7] P. Mizsey: "Waste reduction strategy in the chemical industry", J. Hazardous Mat., Vol. 37, (1994), pp. 1–13.
- [8] Y. Sardessai and S. Bhosle: "Tolerance of bacteria to organic solvents", Res. Microbiol., Vol. 153, (2002), pp. 263–268.
- [9] E.N. Pistikupoulus and S.K. Stefanis: "Optimal solvent design for environmental impact minimization", Computers & Chem. Eng., Vol. 22, (1998), pp. 717–733.
- [10] S.K. Stefanis, A. Buxton, A.G. Livingston, E.N. Pistikopoulus: "A methodology for environmental impact minimization: solvent design and reaction path synthesis issues", *Comp. & Chem. Eng.*, Vol. 20 Suppl., (1996), pp. S1419–S1424.
- [11] M. Sinha, L.E.K. Achenie and G. Ostrovksy: "Environmentally benign solvent design by global optimization", *Comp. & Chem. Eng.*, Vol. 23, (1999), pp. 1381–1394.
- [12] T.B. Hofstetter, C. Capello, K. Hungerbühler: "Environmentally preferable treatment options for industrial waste solvent management A Case Study of a Toluene Containing Waste Solvent", *Trans I. Chem. E*, Vol. 81, Part B, (2003), pp. 189–202.
- [13] H. Chen and R.D. Shonnard: "Systematic Framework for Environmentally Conscious Chemical Process Design: Early and Detailed Design Stages", *Ind. Eng. Chem. Res.*, Vol. 43, (2004) pp. 535–552.
- [14] M. Goedkoop and R. Spriensma: *The Eco-indicator 99, a Damage Oriented Method for Life Cycle Assessment*, Methodolgy Report, Pre Consultants, the Netherlands, 2000, www.pre.nl.
- [15] ISO 14040: Life cycle assessment principles and framework, 1997.
- [16] H. Wenzel, M. Hauschild and L. Alting: Environmental Assessment of Products -

- Methodology, Tools and Case Studies in Product Development, Chapman & Hall, London, 1997.
- [17] T. Hofstetter: Abfallösunsmittelbewirtschaftung in der chemischen Industrie, Forschungsprogramm UAW, Bundesamtes für Energie, 2002.
- [18] Sima Pro 5.1, more details at http://www.pre.nl/simapro/default.htm.
- [19] P. Mizsey, A. Raab, J. Manczinger, A. Szanyi and Z. Fonyo: *Intensification of a Solvent Recovery Technology Through the Use of Hybrid Equipment*, Oral lecture on ESCAPE 12, Danemark, Haag, 2002.
- [20] A. Szanyi, P. Mizsey and Z. Fonyó: "Novel Hybrid Separation Process For Solvent Recovery Based on Positioning the Extractive Heterogeneous-azeotropic Distillation", Chem. Eng. Proc., Vol. 43, (2004), pp. 327–338.
- [21] A. Raab: Separation of a Highly Nonideal Mixture for Solvent Recovery, Thesis (Diploma), Budapest University of Technology and Economics, Department of Chemical Engineering, Hungary, Budapest 2001.
- [22] P.T. Anastas and J.C. Warner: *Green Chemistry*, Theory and Praxis, Oxford University Press, Oxford, 1998.
- [23] Ch. Seyler: Ein inputabhängiges Ökoinventar-Modell für die thermische Verwertung von Abfall-Lösungsmittel in der chemisch-pharmazeutischen Industrie, Thesis (PhD), Eidgenössiche Technische Hochschule Zürich, Zürich, 2003.
- [24] J.M. Douglas: Conceptual Design of Chemical Processes, McGraw-Hill, New York, 1989
- [25] "Economic indicators", Chemical Engineering, Vol. 111, (2004), pp. 79–80.