

# Process simulation coupled with LCA for the evaluation of liquid - liquid extraction processes of phenol from aqueous streams

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## ARTICLE INFO

### Keywords:

Phenol removal  
Liquid-liquid extraction  
Process modelling  
Life cycle assessment

## ABSTRACT

The steel industry is currently a major water pollution source, releasing high quantities of chemicals. One of the pollutants is phenol, known for its toxicity even when it is present in low concentrations. Liquid-liquid extraction employing various aromatics and cycloalkanes (i.e., benzene, toluene, cyclohexane, ethylbenzene) and ketones (i.e., methyl isobutyl ketone, cyclohexanone and mesityl oxide) as solvents, is studied in the present paper. A comparison among the seven solvents is performed based on process modelling simulation tools and Life Cycle Assessment (LCA). The simulations of the seven cases under study are conducted at the same wastewater flowrate of 100 tons/h, with a phenol content of 0.2 wt.% and compared using various parameters (i.e., quantity of solvent, steam and power used, quantity of solvent present in the output phenol streams). The simulation results show that the lowest quantity of solvent is registered in the phenol removal which uses cyclohexanone as solvent (e.g., 34,212.40 kg/h), followed by the case which uses mesityl oxide for the liquid-liquid extraction (e.g., 34,759.80 kg/h) and by the case involving cyclohexanone (e.g., 37,490.60 kg/h). The lowest steam consumption is registered also in the case of cyclohexanone usage (e.g., 47.56 GJ/h) while the lowest power consumption corresponds to mesityl oxide usage (e.g., 11.20 MJ/h). The simulation results are then used to perform an environmental analysis, quantified in terms of environmental key performance indicators, embedding several solvents production methods as well as various fuels. Our life cycle assessment leads to the conclusions that the most environmentally friendly design is phenol removal using cyclohexanone as a solvent, whose provision comes from cyclohexane, which in turn is produced from benzene in conjunction with steam production from natural gas. For instance, the lowest global warming potential indicator score is about 342 kg CO<sub>2</sub> equivalents per kg of phenol, while the same indicator for the worst solvent, i.e., toluene produced using reforming technology and steam being produced using hard coal as fuel, is almost double (e.g., 341.94 kg CO<sub>2</sub> equivalents per kg of phenol vs. 575.30 CO<sub>2</sub> equivalents per kg of phenol). Lower values for other impact indicators are also obtained in the phenol removal using cyclohexanone as a solvent with steam being generated from natural gas (e.g., acidification potential indicator is 0.42 kg SO<sub>2</sub> equivalents per kg of phenol, eutrophication potential is  $4.21 \times 10^{-2}$  kg PO<sub>4</sub><sup>3-</sup> equivalents per kg phenol, ozone depletion potential is  $1.13 \times 10^{-9}$  kg R11 equivalents per kg phenol).

## 1. Introduction

The efficient removal of toxic substances from industrial wastewater is considered to be a topic of paramount importance and interest [1]. Wastewaters, from different industries, can contain different quantities of phenols. For instance, the concentration of phenol from refineries are in the range 6–500 mg/L; from cooking operations from 28 to 3900 mg/L, while the one derived from coal processing is about 9–6800 mg/L

[2]. One of the industries which generates considerable quantities of phenolic wastewater is the iron and steel industry. Iron and steel industry plays a significant role in the development of a country, steel being a valuable construction material. Steel production process, being a raw material and labour-intensive process, exhibits high energy consumption, which is considered one of its major drawbacks. It is also known that the environmental emissions from the iron and steel industry are quite significant, therefore, ecological regulations impose strict limits on iron and steel production phases [3]. One crucial step in the

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## Nomenclature

|             |  |
|-------------|--|
| AP          | Acidification Potential  |
| ADP         | Aquatic Depletion Potential  |
| COSMO - SAC | Conductor-like Screening Model - Segment Activity Coefficient          |
| CML         | Centre of Environmental Science, University of Leiden, The Netherlands |
| DCB         | Dichlorobenzene  |
| EC-JRC      | European Commission Joint Research Centre                              |
| EP          | Eutrophication Potential   |
| EURAR       | European Union Risk Assessment Report                                  |
| GWP         | Global Warming Potential   |
| FAETP       | Freshwater Aquatic Toxicity Potential                                  |
| HTP         | Human Toxicity Potential   |
| LCA         | Life Cycle Assessment  |

|       |  |
|-------|--|
| LCI   | Life Cycle Inventories                 |
| LCIA  | Life Cycle Impact Assessment           |
| LLE   | Liquid - Liquid Equilibria             |
| LL    | Liquid - Liquid                        |
| IEA   | International Energy Agency            |
| ISO   | International Standard Organization    |
| MAETP | Marine Aquatic Ecotoxicity Potential   |
| MIBK  | methyl isobutyl ketone                 |
| MJ    | Mega Joule                             |
| NRTL  | Non-Random Two Liquid                  |
| ODP   | Ozone Depletion Potential              |
| PCOP  | Photochemical Oxidation Potential PCOP |
| R11   | Refrigerant (Trichlorofluoromethane)   |
| TEP   | Terrestrial Toxicity Potential         |
| wt.   | weight                                 |

steel production process is represented by coke production.

Coke is the main product of the coke production process. A cradle-to-gate Life Cycle Assessment (LCA) study of coke production process focused on blowing cooler system, sulphur, ammonia and benzene recovery systems was performed by Li and co-authors [4]. Despite the broad perspective of the study, it does not take into consideration the phenol removal from wastewater. Besides coke, a harmful by-product of coke production is represented by coke oven wastewater, which contains highly hazardous contaminants such as phenol (and other related compounds), ammonia, thiocyanide, cyanide, sulphides, heterocyclic nitrogenous compounds as well as poly-nuclear aromatic compounds [5,6].

Since phenol is known as a dangerous pollutant, due to its strong toxicity for aquatic life and humans alike, it is essential to remove it from effluent water. The average phenol concentration in wastewater from steel cooking facilities is 2000 mg/L equivalent to 0.2 wt.%, which is

also used in the simulations presented in this paper. Furthermore, its usage in various industries makes it valuable enough to recover and reuse. Phenol and its compounds have carcinogenic effects even when they are present in low concentrations [7]. Consequently, in several countries, phenol and its compounds have been included into high priority pollutants lists and their removal is considered a necessary task to protect health and ecosystems [8].

Besides the environmental factor, phenol is a valuable chemical for many plastics: bisphenol-A (precursor to polycarbonates and epoxide resins), phenolic resins (Bakelite), cyclohexanone (precursor to nylon); but also, herbicides and pharmaceutical drugs (aspirin) [9]. For this reason, it's important to recover the phenol from wastewater and reuse it as a raw material.

Many techniques and processes have been employed for treatment of phenolic wastewater, as reported in the scientific literature [10,11]. These works assign each method to a conventional or advanced

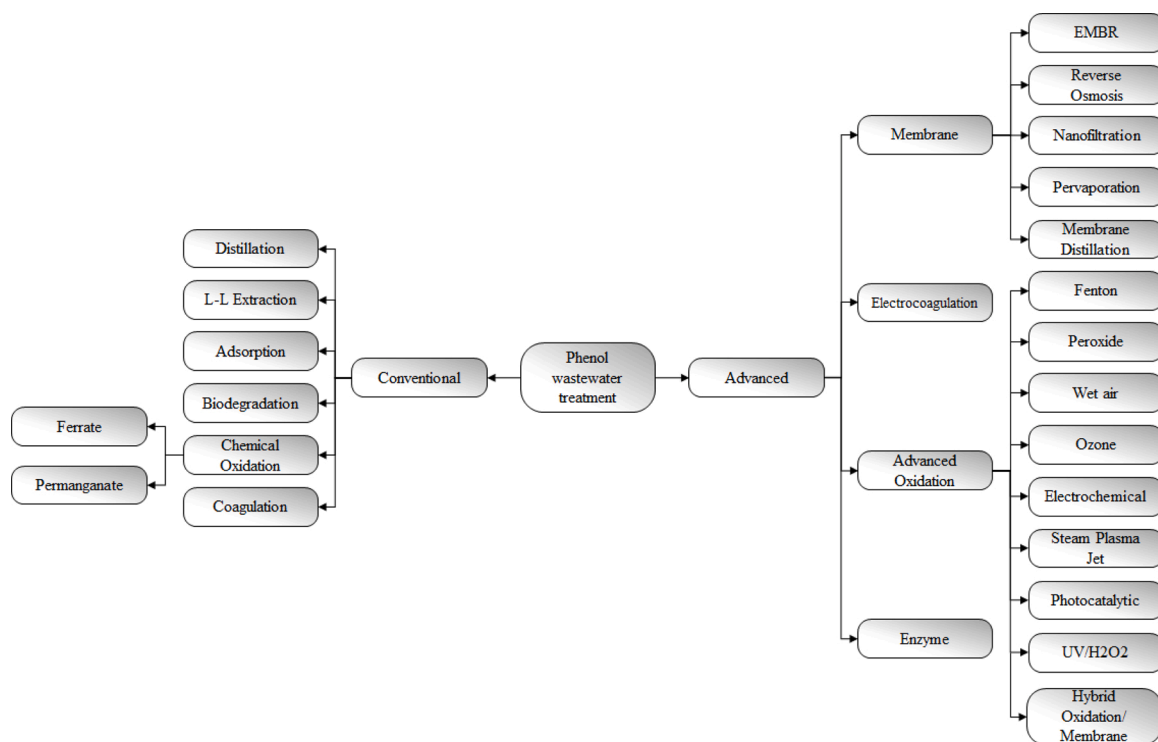


Fig. 1. Phenol removal methods.

category, describing principles, applications, advantages and drawbacks of each technique. Among the conventional methods, a multitude of technologies can be retrieved, as shown in Fig. 1.

Traditional (i) steam or azeotropic distillation based on relative volatility of phenol is often used, as well as (ii) extraction of phenol using various solvents. For instance, Cui and co-authors studied phenol removal utilizing a mixture of methyl isobutyl ketone (MIBK) and toluene [12]; Cesari and co-authors studied the phenol removal using choline bis(trifluoromethylsulfonyl)imide as solvent [13]; mesityl oxide as a novel extractant was investigated by Feng's research group [14]; the usage of biomass-based solvents for the extraction process was the subject of an interesting research carried out by Li and co-authors [15]; finally liquid-liquid (LL) extraction of phenol using ionic liquid was investigated by Sas and co-authors [16]. Conventional methods also include (iii) adsorption on various substrate, e.g., olive mill solid waste [7], supported nanoparticles [17], or activated carbons [18], (iv) biological degradation [19,20], (v) coagulation/flocculation [21], and (vi) chemical oxidation using various substances, such as ferrate-based [22] or permanganate-based chemicals [23].

Due to the great interest around the phenol removal from wastewater, more advanced techniques dedicated to this purpose have been studied by numerous research groups. Concerning oxidations phenomena, advanced processes comprehend Fenton and electro-Fenton [24, 25], peroxide usage [26,27], wet air oxidation [28], ozone oxidation [29], electrochemical oxidation [30], steam plasma jet degradation [31], photocatalytic oxidation [32], and UV/H<sub>2</sub>O<sub>2</sub> treatment [33].

Another advanced application contemplates the phenol removal using membrane-based separations [34,35]. A selection of notable examples includes extractive membrane bioreactors [36], trickle bed reactor - reverse osmosis process [37], nanofiltration [38], pervaporation [39], photocatalytic membrane reactors [40], and membrane distillation [41].

Our attention was focused on the LL extraction method. Its fundamentals reside on the basic separation of the wastewater stream into two or more effluent streams (depending whether the wastewater contains high quantities of other pollutants and if the processes take place all at once), one of which must contain the target compound, which is represented by phenol in our study [42]. The LL process generally exhibits three main stages: the actual pollutant extraction, solute removal and solvent recovery.

The critical step in the design of a LL separation process is the identification of the most suitable solvent. The best way to undertake solvent screening is to rely on molecular modeling methods for the *in-silico* estimation of the relevant thermodynamic properties. Chen and co-authors used Conductor-like Screening Model - Segment Activity Coefficient (COSMO-SAC) model for screening solvents to extract phenol from aqueous solutions [43]. They compared commonly used solvents taken from different families, namely alkanes, arenes, alcohols, ethers, esters and ketones. COSMO-SAC is a quantum-mechanics method for thermodynamic properties estimation, which adopts the chemical structure of the molecules and does not employ any adjustable parameter for the estimation of mixture properties [44,45].

Solvent screening can be easily accomplished by comparing selectivity and solvent power: both quantities can be calculated for infinite dilution activity coefficients of solvents in water and in phenol. The solvent screening performed by Chen and co-authors [43] highlights a preference for ketones, ethers and esters for phenol extraction, due to their relatively high distribution coefficients and selectivity. However, since extraction operations are industrially conducted above 333 K, esters and ethers become unsuitable due to the formation of azeotropes with water at working temperatures. For these reasons, we decided to focus on three industrially employed ketones (i.e., MIBK, mesityl oxide and cyclohexanone), comparing their performance with traditional solvents such as benzene, toluene, cyclohexane and ethylbenzene.

This paper aims at comparing, technically but also from an environmental standpoint, LL extraction method using different solvents.

The comparison between different solvents for LL extraction applications, taking into account their molecular structure, their efficiencies [43], their price and their environmental impact [46] have already been performed by other research groups. The production technologies of the solvents, the production of steam used for solvent recovery, as well as the electricity generation to run the machineries was not included yet in the environmental analysis. This is fundamental in order to reach a broad perspective of the whole supply chain of the system.

## 2. Methods and tools

### 2.1. Processes description and modelling assumptions

Seven cases of phenol removal from wastewater using LL extraction are discussed in the present paper. A flowrate of 100 tons / h of raw wastewater is considered in each case, in order to be able to compare them. The chosen flowrate represents an average value for a coke wastewater plant [47]. The initial phenol concentration in the wastewater is assumed to be 2000 mg/L. The goal is to reduce the phenol concentration under 0.2 mg/L, this value representing the European limit for phenol in wastewater [48]. All the simulations presented were performed using ChemCAD [49] process simulator software (version 6.5.6).

Two categories of solvents have been chosen to perform the LL extraction of phenol, as shown in Table 1. The first category is represented by aromatics and cycloalkanes such as benzene, toluene, ethylbenzene, cyclohexane (Cases 1 - 4), which are quite common solvents. The second category is represented by ketones such as MIBK, cyclohexanone and mesityl oxide (Cases 5 - 7). High distribution coefficients, high selectivities and high solvent power to extract phenol from water are reported in the scientific literature for this category of solvents [43], stressing their importance as promising substances for phenol extraction.

Next section contains several details about the cases under investigation. Phenol extraction with various solvents is schematically represented in Fig. 2.

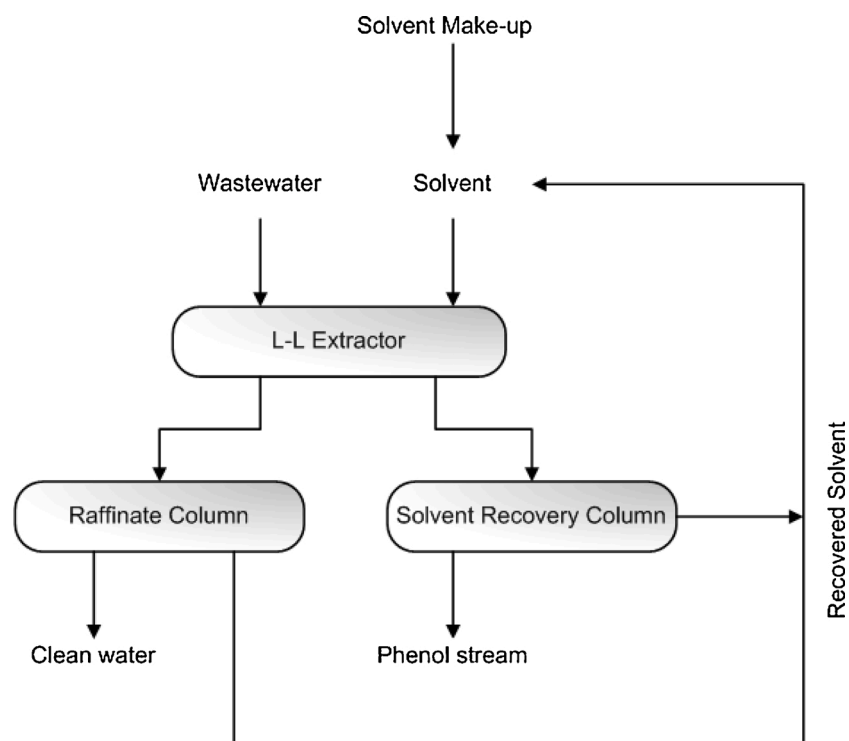
This plant model uses a LL extractor, where the solvent removes phenol from wastewater. The phenolic water is fed to the plant at 30 °C from the top of the extractor, while the solvent enters from the bottom, both at atmospheric pressure. The phenol is extracted at the top of the LL extractor. The obtained stream, containing a mixture of phenol and solvent, enters the solvent recovery column. Concentrated phenol is obtained as a residue while the solvent is recovered as distillate and recycled. Water stream mixed with some solvent from the bottom of the LL extractor is then sent to the raffinate column. Almost pure water is obtained at the bottom of this column. The recycled solvent stream from the solvent recovery column is pumped and mixed with the raffinate column distillate stream and integrated with solvent make-up. The mixed solvent stream is cooled down to 30 °C in a heat exchanger and sent to the LL extractor. Low pressure steam is used in the raffinate and solvent recovery distillation columns.

The assumptions used in process modelling and simulation are summarised in Table 2. The thermodynamic model chosen for describing the cases under study is Non-Random Two-Liquid (NRTL), which has been selected based on the components and plant operation conditions (i.e., temperature and pressure). NRTL binary interaction parameters have been taken from the ChemCAD internal data base and checked versus phase equilibria data (vapour-liquid equilibria VLE and liquid-liquid equilibria LLE). The NRTL model is able to represent VLE quite well and gives the correct size and shape of the miscibility gap for all the ternary diagrams considered in this work. For the binary LLE the model shows an average relative % deviation of solubility mole fraction in the aqueous phase of 0.54 % (average among the seven water - solvents systems) with a maximum value of 3.2 % (Table 3).

**Table 1**

Categories of solvents used for the case studies.

| Category | Alkanes and Cycloalkanes |         |              |             | Ketones |               |               |
|----------|--------------------------|---------|--------------|-------------|---------|---------------|---------------|
| Case     | 1                        | 2       | 3            | 4           | 5       | 6             | 7             |
| Solvent  | Benzene                  | Toluene | Ethylbenzene | Cyclohexane | MIBK    | Cyclohexanone | Mesityl Oxide |

**Fig. 2.** Phenol extraction with various solvents (simplified schema).**Table 2**

Main assumptions used in phenol wastewater removal (Cases 1 - 7).

| Unit Operation                                     | Parameter                              | Unit of measure | Case 1 | Case 2 | Case 3 | Case 4 | Case 5 | Case 6 | Case 7 |
|--|--|-----------------|--------|--------|--------|--------|--------|--------|--------|
| Liquid-Liquid Extractor (EXTR unit in ChemCAD)     | Number of stages                       | –               | 10     | 10     | 10     | 10     | 10     | 10     | 10     |
|  | Feed tray for wastewater stream        |                 | 1      | 1      | 1      | 1      | 1      | 1      | 1      |
|  | Feed tray for solvent stream           |                 | 10     | 10     | 10     | 10     | 10     | 10     | 10     |
|  | Distillate component fraction recovery | %               | 99.99  | 99.99  | 99.99  | 99.99  | 99.99  | 99.99  | 99.99  |
| Solvent Recovery Column (SCDS column in ChemCAD)   | R/Rmin                                 | –               | 1.5    | 1.5    | 1.5    | 1.5    | 1.5    | 1.5    | 1.5    |
|  | Column pressure                        | atm             | 1      | 1      | 1      | 1      | 1      | 1      | 1      |
|  | Outlet pressure                        | atm             | 4.5    | 4.5    | 4.5    | 4.5    | 4.5    | 4.5    | 4.5    |
| Pump (PUMP unit in ChemCAD)                        | Efficiency                             | %               | 65     | 65     | 65     | 65     | 65     | 65     | 65     |
|  | Outlet temperature                     | °C              | 30     | 30     | 30     | 30     | 30     | 30     | 30     |
| Solvent Recycling Heat Exchanger (HTXR in ChemCAD) | Distillate component fraction recovery | %               | 99.99  | 99.99  | 99.99  | 99.99  | 99.99  | 99.99  | 99.99  |
|  | Number of trays                        | –               | 20     | 20     | 20     | 20     | 40     | 40     | 40     |
|  | Feed tray                              | –               | 10     | 10     | 10     | 10     | 15     | 15     | 15     |
|  | Column pressure                        | atm             | 1      | 1      | 1      | 1      | 1      | 1      | 1      |

## 2.2. Environmental evaluation using life cycle assessment (LCA)

LCA methodology is focused on the evaluation of the environmental impacts generated by manufacturing, usage and disposal of products, materials and chemicals. Its principles and procedures are reported in the International Standard Organization (ISO) series 14,040 guidelines [50,51], allowing the estimation of the emissions regarding each environmental compartment (i.e., soil, water and atmosphere). It is based on the material and energy balances related to the overall life cycle of the

product system under investigation, which comprehends extraction of raw materials, manufacturing, distribution, use phase, recycling, final disposal and the transportations between life cycle stages [52]. The results of life cycle studies are presented using various environmental indicators, which encompass a multitude of environmental issues, avoiding burden shifting among the environmental compartments. The LCA methodology, as extensively discussed on a series of publications [53,54], prescribes the fulfilment of four stages as follows:

**Table 3**Most relevant input streams for **Cases 1 - 7**.

| INPUTS  | UNITS | Case 1  | Case 2  | Case 3  | Case 4  | Case 5  | Case 6  | Case 7  |
|---|-------|---------|---------|---------|---------|---------|---------|---------|
| Raw Wastewater stream                             |       |         |         |         |         |         |         |         |
| Temperature                                       | °C    | 30      | 30      | 30      | 30      | 30      | 30      | 30      |
| Pressure  | atm   | 1       | 1       | 1       | 1       | 1       | 1       | 1       |
| Total mass flow-rate                              | kg/h  | 100,000 | 100,000 | 100,000 | 100,000 | 100,000 | 100,000 | 100,000 |
| Component weight                                  |       |         |         |         |         |         |         |         |
| Phenol  | wt. % | 0.20    | 0.20    | 0.20    | 0.20    | 0.20    | 0.20    | 0.20    |
| Water   | wt. % | 99.80   | 99.80   | 99.80   | 99.80   | 99.80   | 99.80   | 99.80   |
| Solvent stream to extractor (including recycling) |       |         |         |         |         |         |         |         |
| Temperature                                       | °C    | 30      | 30      | 30      | 30      | 30      | 30      | 30      |
| Pressure  | atm   | 1       | 1       | 1       | 1       | 1       | 1       | 1       |
| Total mass flow-rate                              | kg/h  | 100,412 | 119,956 | 37,491  | 54,241  | 41,862  | 34,213  | 34,760  |
| Component weight                                  |       |         |         |         |         |         |         |         |
| Water   | wt. % | 0.08    | 0.01    | 0.03    | 0.01    | 5.93    | 20.85   | 18.89   |
| Phenol  | wt. % | –       | –       | –       | –       | –       | –       | –       |
| Benzene   | wt. % | 99.92   | –       | –       | –       | –       | –       | –       |
| Toluene   | %     | –       | 99.99   | –       | –       | –       | –       | –       |
| Cyclohexane                                       | %     | –       | –       | 99.97   | –       | –       | –       | –       |
| Ethylbenzene                                      | %     | –       | –       | –       | 99.99   | –       | –       | –       |
| MIBK  | %     | –       | –       | –       | –       | 94.07   | –       | –       |
| Cyclohexanone                                     | %     | –       | –       | –       | –       | –       | 79.14   | –       |
| Mesityl Oxide                                     | %     | –       | –       | –       | –       | –       | –       | 81.10   |

- 1 Goal and scope definition: this stage requires the practitioner to specify the aim of the study, the system boundaries, the quality of data source, the assumptions and limitations introduced and the functional unit (i.e., the amount of final product on which the life cycle input/output streams are normalized).
- 2 Life cycle inventory analysis (LCI): during this step, the practitioner needs to collect the mass and energy balances of the product system under investigation. The employment of primary data is preferred, since actual process data provide highest accuracy in comparison to secondary data, which are retrieved on acknowledged databases, i.e., ecoinvent [55] or GaBi [56].
- 3 Life cycle impact assessment (LCIA): this phase assigns specific environmental impacts to inventory data through recognized characterization factors, which typify the contribution of each substance to a determined impact category, providing harmonization on a shared unit of measure.
- 4 Life cycle interpretation: this stage provides an evaluation of the results obtained by previous steps. Although the interpretation comes last, it embeds the overall LCA procedure including comments and recommendations adapted to the goal and scope previously defined. Usually, sensitivity analysis and uncertainty are assessed during this phase [57].

GaBi software was used to perform the present LCA study. GaBi is one of the most popular decision support LCA software for product sustainability used in numerous applications such as design products for low environmental impact, improve efficiency, or develop profiles of carbon, water, and product environmental footprints [56].

The functional unit, to which all the quantities are reported, is one kilogram of phenol extracted. The plant is considered to be located in Central Europe. Material and energy balances derived from the simulation phase [58] as well as data from the GaBi database are used in the present LCA study. The present LCA study envisages a cradle-to-gate perspective, considering all the life cycle phases from resource extraction (cradle) to the production plant gate before entering the market. The assessment performed in the current research study considers the production of the solvents (i.e., benzene, toluene, cyclohexane, ethylbenzene, MIBK, cyclohexanone and mesityl oxide), the production of steam used to recover the solvents after the extraction phase, as well as the production of electricity to run the machineries. The production technologies of the solvents, as well as the production of steam used for solvent recovery, but also the electricity production to run the machineries were not considered in the environmental analysis performed

by other research groups. The authors consider that the inclusion of these aspects in the environmental evaluation is fundamental in order to reach a broad perspective of the whole supply chain of the system.

The cases which are taken into consideration, as well as the boundary conditions, are presented in Figs. 3 and 4.

Some details regarding Figs. 3 and 4 and the cases under study considered in the LCA should be provided: i) the first number in each case study denotes the solvent used for phenol extraction, as reported in Table 4; ii) the production technologies for the solvents are denoted with capital letters, i.e., “A”, “B”, “C” and “D”, where “A” represents benzene or toluene production from pyrolysis fuel, cyclohexane from benzene, ethylbenzene production mix, MIBK from acetone, acetone from cumene, etc.; iii) the fuel used for the steam generation necessary for solvent recovery is denoted with small letters (i.e., “a” for natural gas, “b” for hard coal and “c” for biomass).

According to Table 4, for instance, Case 1Aa represents phenol extraction using benzene as a solvent, benzene being produced from pyrolysis fuel and steam is produced from natural gas; Case 2Bc represents phenol removal using toluene as a solvent, toluene being produced using reforming technology and steam is produced using biomass as a fuel. Case 5Ab represents phenol extraction using MIBK as a solvent, MIBK being produced from acetone, acetone, in turn, is produced from cumene and steam is produced from hard coal; Case 7Bc represents phenol removal using mesityl oxide as a solvent, mesityl oxide being produced from acetone, acetone is produced from isopropanol and steam is produced using biomass as fuel.

A total number of 42 subcases have been defined for the LCA comparison. The subcases are distributed as presented in Table 5.

Details regarding the technologies used for solvent production are provided in Table 6. Table 7 contains details regarding the LCA assumptions for steam production using three different sources (i.e., natural gas, hard coal and biomass).

LCI is the LCA phase focused on the quantification of inputs and outputs data [59]. Due to the vast amount of data used in the present analysis for all the subcases, a relevant example of an LCI used in the present study can be found in Table 8.

After the inputs and outputs quantification, the next step of an LCA study, is represented by the LCIA phase. The CML 2001 method assessment available in GaBi software [56] was used for environmental evaluation and comparison. Our choice is based on two fundamental reasons: 1) we wanted to avoid the subjectivity and uncertainty of endpoint approach and 2) CML 2001 has been recognized as one of the most well-established and world-widely used methodology [60]. The

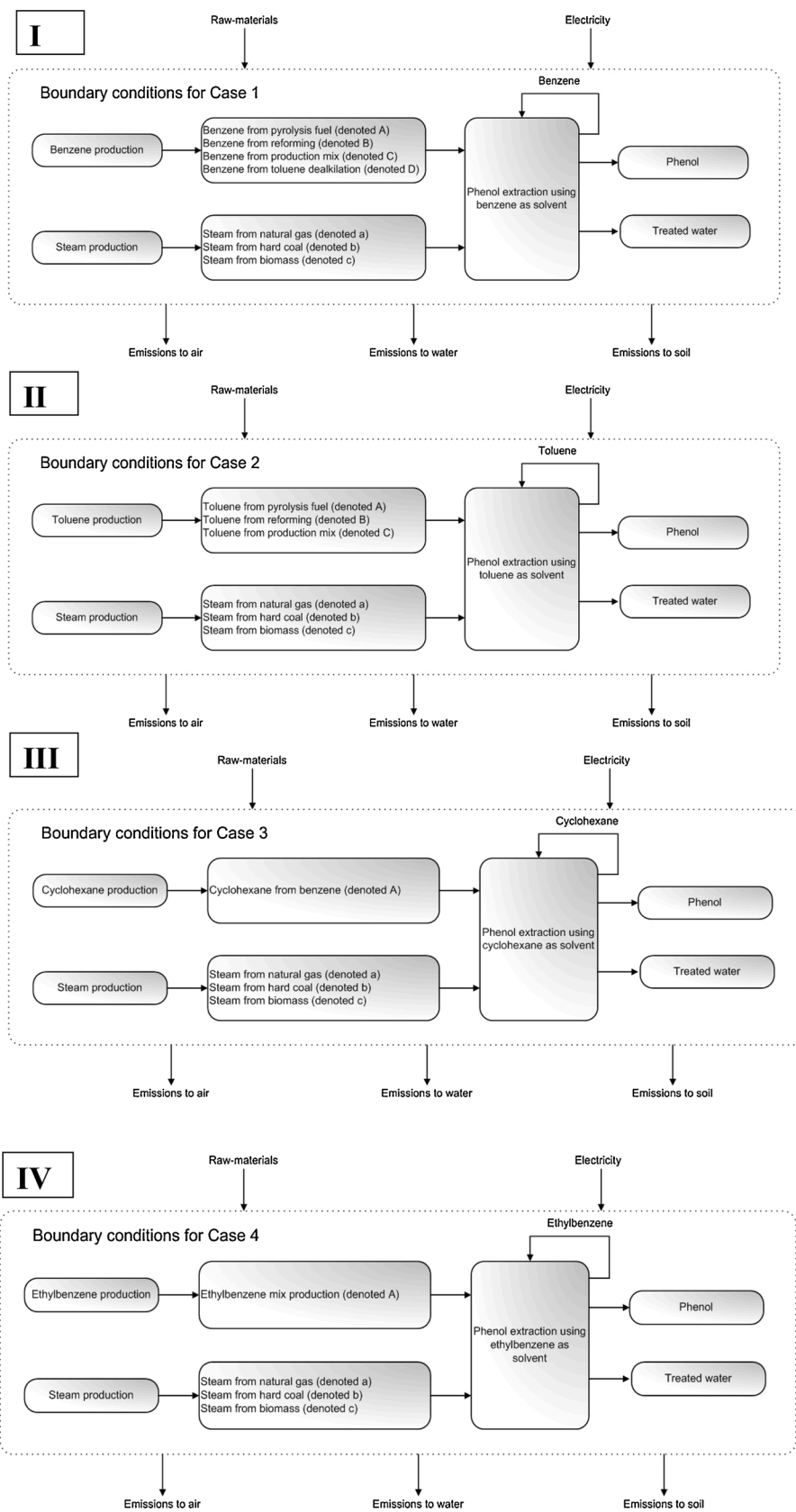


Fig. 3. LCA boundaries for phenol extraction using alkanes (Cases 1 - 4) I benzene, II toluene, III cyclohexane, IV ethylbenzene.

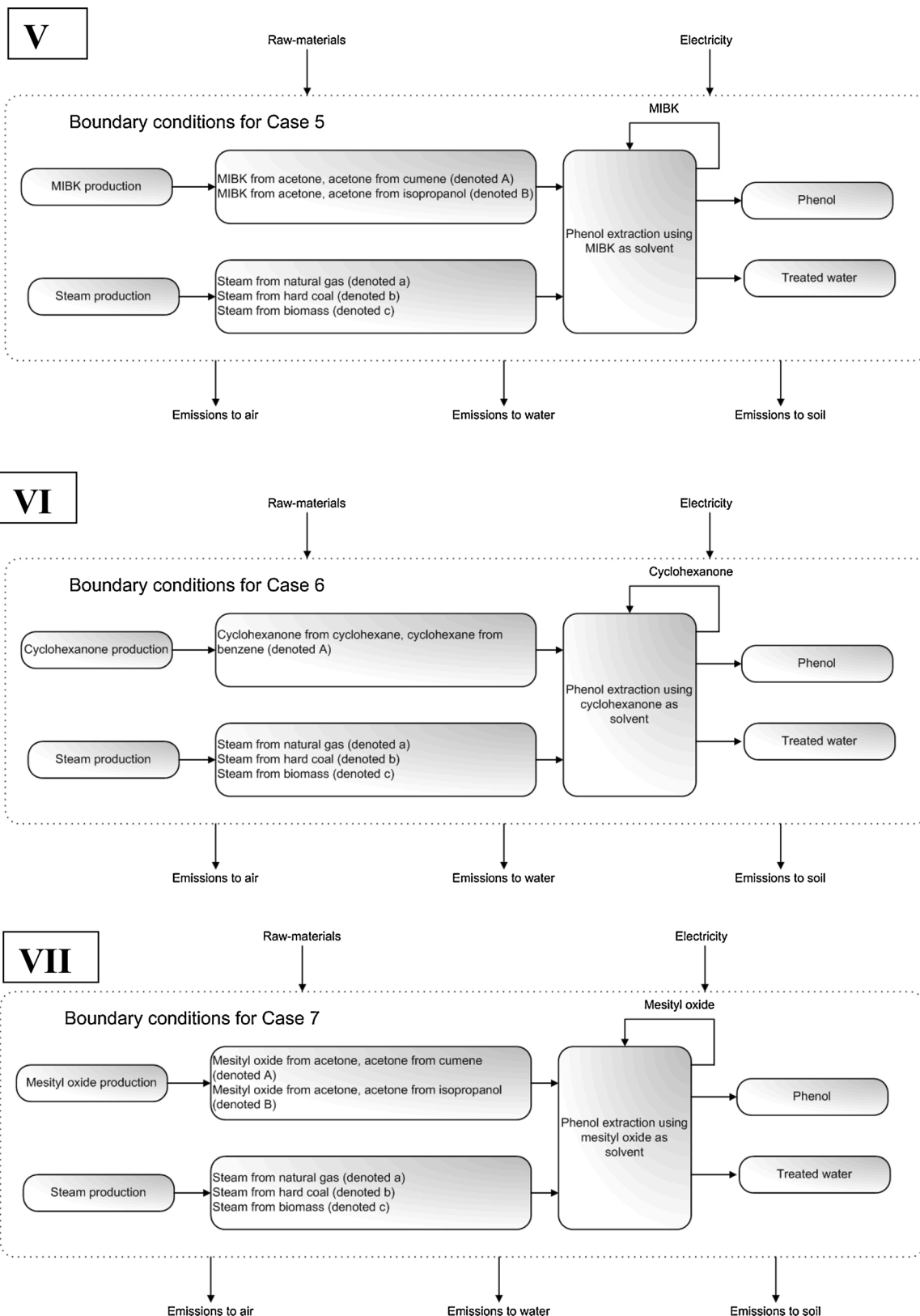


Fig. 4. LCA boundaries for phenol extraction using ketones (Cases 5 - 7) V MIBK, VI Cyclohexanone, VII Mesityl oxide.

method was developed by the University of Leiden, Netherlands, and it considers the following impact categories: Global Warming Potential (GWP), Acidification Potential (AP), Eutrophication Potential (EP), Ozone Depletion Potential (ODP), Aquatic Depletion Potential (ADP), Freshwater Aquatic Toxicity Potential (FAETP), Human Toxicity

Potential (HTP), Photochemical Oxidation Potential (PCOP), Terrestrial Toxicity Potential (TEP), and Marine Aquatic Ecotoxicity Potential (MAETP) [61].

Life Cycle Interpretation is the technique used for identifying, quantifying, checking, and evaluating the LCA results. Useful

**Table 4**  
Subcases investigated in the LCA.

| Solvent           | Production process                 | Steam production |          |             |
|-------------------|------------------------------------|------------------|----------|-------------|
|                   |                                    | (a) Natural Gas  | (b) Coal | (c) Biomass |
|                   |                                    | Subcases name    |          |             |
| (1) benzene       | (A) Pyrolysis fuel                 | 1Aa              | 1Ab      | 1Ac         |
|                   | (B) Reforming                      | 1Ba              | 1Bb      | 1Bc         |
|                   | (C) Production mix                 | 1Ca              | 1Cb      | 1Cc         |
|                   | (D) Toluene dealkylation           | 1Da              | 1Db      | 1Dc         |
| (2) toluene       | (A) Pyrolysis fuel                 | 2Aa              | 2Ab      | 2Ac         |
|                   | (B) Reforming                      | 2Ba              | 2Bb      | 2Bc         |
|                   | (C) Production mix                 | 2Ca              | 2Cb      | 2Cc         |
| (3) cyclohexane   | (A) from benzene                   | 3Aa              | 3Ab      | 3Ac         |
| (4) ethylbenzene  | (A) Production mix                 | 4Aa              | 4Ab      | 4Ac         |
| (5) MIBK          | (A) from acetone, from cumene      | 5Aa              | 5Ab      | 5Ac         |
|                   | (B) from acetone, from isopropanol | 5Ba              | 5Bb      | 5Bc         |
| (6) cyclohexanone | (A) from cyclohexane, from benzene | 6Aa              | 6Ab      | 6Ac         |
|                   | (A) from acetone, from cumene      | 7Aa              | 7Ab      | 7Ac         |
| (7) Mesityl Oxide | (B) from acetone, from isopropanol | 7Ba              | 7Bb      | 7Bc         |

**Table 5**  
Number of subcases correspondent to each case.

| Cases                                    | Case 1 | Case 2 | Case 3 | Case 4 | Case 5 | Case 6 | Case 7 |
|--|--------|--------|--------|--------|--------|--------|--------|
| Number of subcases considered in the LCA | 12     | 9      | 3      | 3      | 6      | 3      | 6      |

conclusions and recommendations for the study are the main outputs of the interpretation phase. The interpretation of the environmental indicators is presented in Section 3.

The present study is subjected to the following limitations: we do not envisage the production of the machinery for solvents production as well as the machinery used in the extraction process, the construction of infrastructure or the construction of trains and trucks for transportation. However, the impacts related to machinery production looks negligible in relation with the functional unit endorsed in our study, therefore the results are not considerably influenced by this assumption.

### 3. Results and discussions

#### 3.1. Results and discussions on process modelling and simulation

The raw wastewater stream is set to 100 tons/h for all cases, with a phenol content representing 0.2 % wt.%. The goal, in all cases, is to lower the phenol concentration in the clean water under 20 mg/L. Parameters such as solvent power and selectivity play a crucial role in removal efficiency.

Table 9 reports the input/output streams of each process simulation. It is possible to notice how the raw wastewater input stream is the same in all seven cases (e.g., 200 kg/h of phenol and 99,800 kg/h of water) and that different quantities of solvents are needed for each extraction. The lowest quantity of solvent is used in Case 6 (e.g., 34,212.40 kg/h) which uses cyclohexanone as solvent followed by Case 7 (e.g., 34,759.80 kg/h) which employs mesityl oxide and by Case 3 (e.g., 37,490.60 kg/h) using cyclohexane. The highest quantity of solvent is used in Case 2, toluene being the solvent for LL extraction.

It can be also noticed that higher quantities of solvents are present in the phenol stream when aromatics are used in comparison with ketones. The higher quantities of solvents present in the output phenol streams in the aromatics / cycloalkanes cases lead to lower quality of the output phenol stream. The exception is represented by cyclohexane (Case 3) when 1.12 kg/h of cyclohexane is found on the final phenol stream. Considering the ketones cases, the lowest quantity of solvent retrieved in the phenol stream appears in Case 7 (e.g., 0.47 kg/h) when mesityl

oxide is used.

Table 10 shows the steam and electricity consumptions for all cases under study. It can be noticed that the lowest steam consumption is obtained in Case 3 (e.g., 47.56 GJ/h) while the highest steam consumption is obtained in Case 5. Case 7, when mesityl oxide is used, has the lowest value for power consumption (e.g., 11.20 MJ/h). In a power consumption ranking Case 7 is followed by Case 6 (e.g., 18.79 MJ/h) and by Case 3 (e.g., 28.13 MJ/h).

Cases 3, 6 and 7 seem to be the best options considering the lowest quantity of solvent employed and the lowest power consumption. Taking into account also the steam consumption for Case 7 and Case 6 these quantities are higher compared to Case 3. The final decision on the best solvent will be based on the technical evaluation as well as on the environmental one.

Sensitivity analysis performed on extraction processes of interest indicates that, as expected, all processes are sensitive to reflux ratio and number of stages in the distillation column. The reflux ratio was modified with  $\pm 5\%$  with respect to the original value; the same range being also valid for the number of stages. The effects of these modifications are similar for all the systems investigated in this work and can be summarized in the graphs in Figs. 5 and 6. The main effects of the sensitivity studies are that energy consumption depends on both the reflux ratio and the number of stages, while phenol purity is not affected and the solvent lost in water phase is negligible. This is valid for all the systems investigated.

#### 3.2. Results and discussions on environmental assessment

Environmental evaluation results were generated using GaBi software (version 8) for each of the 42 subcases. The results for the seven cases and 42 subcases are reported in the supplementary information material. As a first task, all the subcases correspondent to each case were compared, and the best two configurations for each solvent were selected for further comparison (see Table 11).

For instance, for Case 1, the lowest values for all impact categories are obtained in subcases 1Ba and 1Bb (see Table S1). These cases correspond to phenol extraction using benzene as a solvent, benzene being produced via reforming and steam being produced from natural gas (i.e., subcase 1Ba) or from hard coal (i.e., subcase 1Bb). From Table S1, it can also be noticed a competition between subcases 1Bb and 1Bc, where steam is produced from biomass. Even if lower values for GWP impact and ADP<sub>fossil</sub> indicators can be noticed in subcase 1Bc, all the other impact categories are lower in subcase 1Bb. Consequently, subcases 1Ba and 1Bb were chosen as best subcases for Case 1. The same conclusions are valid for Case 2.

The environmental results for Case 2 are reported in Table S2. The best values are observed in subcases 2Ba and 2Bb. These subcases

**Table 6**  
Technologies used for solvents production [56].

| Solvent     | Technology                     | Description of the solvent production technology and assumptions for LCA   |
|-------------|--------------------------------|--|
| Benzene     | Production Mix                 | <ul style="list-style-type: none"> <li>Four different production routes, weighted according to their share of the total EU production: pyrolysis gasoline route 58.8 %, reformate-based production: 27.6 %, on-purpose and coal-based production: 13.6 %, split as 10 % for toluene dealkylation and 3.6 % for coal-based production.</li> <li>The "Mix" process consists of the distribution of technologies used for the production of benzene, representing the respective country.</li> </ul>  |
|             | Dealkylation                   | <ul style="list-style-type: none"> <li>Benzene is produced from toluene by means of hydrodealkylation.</li> <li>This process uses hydrogen to react with toluene to form benzene and methane as a by-product.</li> <li>Methane and residual hydrogen are removed from the recycle gas and the methane is cracked with water to hydrogen to meet the process requirements for the hydrodealkylation.</li> <li>The process of hydrodealkylation is conducted either thermally or on a catalyst. Unreacted toluene is separated from the benzene product by distillation and recycled.</li> </ul>   |
|             | Pyrolysis Fuel & Reforming     | <ul style="list-style-type: none"> <li>The aromatics benzene, toluene and xylenes are extracted from pyrolysis gasoline and separated either by azeotropic distillation or by extractive distillation.</li> <li>A typical composition of pyrolysis gasoline in wt.% is: benzene 40 %, toluene 20 %, xylene 4–5 %, ethyl benzene 2–3 %, higher aromatics 3% and non-aromatics 28–31 %.</li> <li>In azeotropic distillation, polar auxiliary agents are used to remove alkanes and cycloalkanes, while non-aromatics are removed from the benzene fraction by adding acetone and from the toluene and xylene fraction by adding methanol.</li> <li>In extractive distillation, various solvents for the aromatic fraction are used to decrease the aromatics volatility. The non-aromatic fraction is being distilled from the pyrolysis gasoline and the aromatic fraction with the solvents is separated in a stripping column, where steam may be added.</li> </ul> |
| Toluene     | Production mix                 | <ul style="list-style-type: none"> <li>Toluene is commercially produced based on two different feed stocks: pyrolysis gasoline and reformate.</li> <li>In Europe toluene is mainly produced via pyrolysis gasoline (30 %) and reforming technology (70 %).</li> </ul>  |
| Cyclohexane | Pyrolysis Fuel & Reforming     | <ul style="list-style-type: none"> <li>Same assumptions as in the benzene case.</li> </ul>   |
|             | Catalytic hydration of benzene | <ul style="list-style-type: none"> <li>The most common process for cyclohexane production is catalytic hydration of benzene. The process contains two steps.</li> <li>A mixture benzene and hydrogen pass over a nickel catalyst at 220 °C and 32 atm. The effluent is mixed with more hydrogen and feed into a second reactor where the same reaction occurs, hydrating the benzene. The stream from the second reactor is cooled and hydrogen is recycled.</li> </ul>  |

**Table 6 (continued)**

| Solvent              | Technology                             | Description of the solvent production technology and assumptions for LCA   |
|----------------------|--|--|
| Ethylbenzene<br>MIBK | Benzene alkylation<br>Mix technologies | <ul style="list-style-type: none"> <li>The liquid phase from the product stream is fractionated in order to purify cyclohexane.</li> <li>Reaction of benzene with ethylene.</li> <li>MIBK is considered to be obtained from mesityl oxide and hydrogen.</li> <li>Mesityl oxide is produced from acetone; hydrogen is produced from steam reforming processes and water electrolysis.</li> <li>Two routes are considered for acetone production: acetone from cumene and acetone from isopropanol.</li> </ul> |
| Cyclohexanone        | Cyclohexane oxidation                  | <ul style="list-style-type: none"> <li>Cyclohexanone is produced from cyclohexane oxidation.</li> <li>Cyclohexane production processes are described above.</li> </ul>   |
| Mesityl oxide        | Mix technologies                       | <ul style="list-style-type: none"> <li>Mesityl oxide is produced from acetone.</li> <li>Two routes considered for acetone production: acetone from cumene and acetone from isopropanol.</li> </ul>   |

correspond to phenol extraction using toluene as solvent, toluene being produced using reforming technology and steam being produced from natural gas or from hard coal.

When **Case 3** is considered (see Table S3), the lowest values for nine out of ten impact indicators (i.e., AP, EP, ODP, ADP<sub>fossil</sub>, FAETP, HTP, PCOP, TEP, MAETP) are obtained by subcases **3Aa** and **3Ab**. These correspond to phenol extraction using cyclohexane as a solvent, cyclohexane being produced from benzene and the steam used to regenerate the cyclohexane comes from natural gas (i.e., subcase **3Aa**) or from hard coal (i.e., subcase **3Ab**). The same conclusion is valid for **Case 4** when ethylbenzene is used as a solvent for phenol removal. The best two subcases belonging to **Case 4** are subcase **4Aa** and **4Ab** (see Table S4).

For **Case 5**, the environmental indicators are reported in Table S5. The best two subcases, from the six subcases considered, appear in subcases **5Aa** and **5Ab**. MIBK is used as a solvent in subcases **5Aa** and **5Ab**, the solvent is produced from acetone, acetone being produced from cumene. The steam requested in the proposed processes is considered to be generated using natural gas (i.e., subcase **5Aa**) or hard coal (i.e., subcase **5Ab**) as fuels.

Analysing **Case 6** (see Table S6), when cyclohexanone is used as a solvent for phenol extraction, the best subcases are represented by **6Aa** and **6Ab**. Cyclohexane is produced from benzene and steam, as in the previous cases, is produced from natural gas or from hard coal.

Table S7 summarizes the environmental indicators for **Case 7**. From the six subcases taken into account, the best values are obtained by subcase **7Aa** and **7Ab**. Mesityl oxide is produced from cumene. Steam from natural gas and from hard coal is used in subcase **7Aa** and **7Ab**, respectively.

Discussions about the best values obtained in all seven cases are presented in the next section (see Table 11).

### 3.2.1. GWP Indicator

Discussing the values reported in Table 11, it can be noticed that the highest GWP is obtained in subcase **2Bb** (e.g., 575.30 kg CO<sub>2</sub> equivalents per kg phenol), followed by subcase **4Ab** (e.g., 572.46 kg CO<sub>2</sub> equivalents per kg phenol). The major contributors to the GWP values are the toluene production process using reforming technology for subcase **2Bb** and ethylbenzene production process using technology mix for subcase **4Ab**. Toluene production using reforming technology contributes with 88.74 % to the total 575.30 kg CO<sub>2</sub> equivalents per kg phenol, while ethylbenzene production represents 92.34 % of the total 572.46 kg CO<sub>2</sub> equivalents per kg phenol. A common characteristic of **2Bb** and **4Ab** subcases is the utilisation of hard coal for steam generation. Indeed,

**Table 7**  
LCA assumptions for steam generation [56].

| Steam Source | LCA Assumptions   |
|--------------|---|
| Natural Gas  | <ul style="list-style-type: none"> <li>The process steam is produced in natural gas specific heat plants.</li> <li>The fossil power plant models use emission data from literature but also calculated values for non-measured emissions e.g., organics or heavy metals. For the emissions CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, CO, CH<sub>4</sub>, N<sub>2</sub>O, NMVOC and particulate matter (PM) measured/calculated data are used, taken from national inventory reports, emission inventory data bases, utility companies and other sources.</li> <li>The natural gas supply considers the whole supply chain of the energy carrier from exploration, production, processing and transport of the fuels to the heat plants. The supply chain is modelled in a specific national/regional natural gas consumption mix (i.e., domestic production and imports), and considers national / regional average natural gas properties (e.g., elemental composition and energy content).</li> <li>The process steam efficiency is 85 %.</li> </ul>  |
| Hard Coal    | <ul style="list-style-type: none"> <li>The process steam is hard coal specific heat plants.</li> <li>The fossil power plant models combine emission data from literature with calculated values for non-measured emissions e.g., organics or heavy metals. For the emissions CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, CO, CH<sub>4</sub>, N<sub>2</sub>O, NMVOC and particulate matter (PM) measured/calculated data are used, taken from national inventory reports, emission inventory data bases, utility companies and other sources.</li> <li>The calculations of other emissions within the models are based on energy carrier properties, transfer coefficients and power plant thermodynamics representing the applied flue gas treatment technologies and standards.</li> <li>Combustion residues from solid fuels, such as gypsum, bottom ash or fly ash are assumed to be reused (i.e., in construction work).</li> <li>Radioactive emissions from ashes are not considered in the coal power plant model.</li> <li>The hard coal supply considers the whole supply chain of the energy carrier from exploration, production, processing and transport of the fuels to the heat plants.</li> <li>The process steam efficiency is 85 %.</li> </ul>       |
| Biomass      | <ul style="list-style-type: none"> <li>The process steam is produced in biomass (solid) specific heat plants.</li> <li>The fossil power plant models combine emission data from literature with calculated values for non-measured emissions i.e., organics or heavy metals. For the emissions CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, CO, CH<sub>4</sub>, N<sub>2</sub>O, NMVOC and particulate matter (PM) measured/calculated data are used, taken from national inventory reports, emission inventory data bases, utility companies and other sources.</li> <li>Combustion residues from solid fuels, such as gypsum, bottom ash or fly ash are assumed to be reused e.g., in construction work. Waste treatment for these substances is therefore not considered.</li> <li>The biomass (solid) supply considers the whole supply chain of the energy carrier from production, processing and transport of the fuels to the heat plants. The supply chain is modelled in a specific national/regional biomass (solid) consumption mix (i.e., domestic production and imports), and considers national/regional average biomass (solid) properties (e.g., elemental composition and energy content).</li> <li>The process steam efficiency is 85 %.</li> </ul> |

**Table 8**  
LCI for Case 3Aa.

| INPUTS                       | UNITS | Case 3Aa | OUTPUTS                   | UNITS | Case 3Aa              |
|------------------------------|-------|----------|---------------------------|-------|-----------------------|
| <i>Raw wastewater stream</i> |       |          | <i>Phenol stream</i>      |       |                       |
| Water                        | kg/h  | 99,800   | • Phenol                  | kg/h  | 199.98                |
| Phenol                       | kg/h  | 200      | • Cyclohexane             | kg/h  | 1.12                  |
| <i>Solvent stream</i>        |       |          | <i>Clean water stream</i> |       |                       |
| Cyclohexane                  | kg/h  | 37,490.6 | • Water                   | kg/h  | 99,800                |
|                              |       |          | • Phenol                  | kg/h  | 0.02                  |
|                              |       |          | • Cyclohexane             | kg/h  | $3.82 \times 10^{-4}$ |
| Steam                        | MJ/h  | 47,557.1 |                           |       |                       |
| Electricity                  | MJ/h  | 34.26    |                           |       |                       |

higher amounts of CO<sub>2</sub> are released when hard coal is used compared to the subcases when natural gas or biomass are involved in steam generation. From the total GWP values previously mentioned steam

generation contributes with 11.26 % in subcase **2Bb** while the same process contributes with 7.66 % in subcase **4Ab**.

Among the other cases, the lowest values are obtained in subcase **6Aa** (e.g., 341.94 kg CO<sub>2</sub> equivalents per kg phenol) followed by subcase **6Ab** (e.g., 364.71 kg CO<sub>2</sub> equivalents per kg phenol). Subcase **6Aa** correspond to phenol extraction using cyclohexanone, cyclohexanone being produced from cyclohexane, which, in turn, is produced from benzene. The percentage correspondent to solvent production to the total 341.94 kg CO<sub>2</sub> equivalents per kg phenol is 88.65 %, the rest being represented by the steam generation using natural gas.

An interesting discussion between the GWP indicators obtained in **Case 3** and **Case 6** is presented in the next section. The two cases refer to the usage of cyclohexane as solvent for LL extraction, respectively the usage of cyclohexanone, which is derived from cyclohexane. Differences in the GWP indicator between cyclohexane (**Case 3**) and cyclohexanone (**Case 6**) come from different quantities of solvent, steam and electricity used in the two cases. In the cyclohexane case (i.e., **Case 3Aa**) a gravity analysis on the GWP value (e.g., 406.04 and 341.94 kg CO<sub>2</sub> equivalents per kg phenol for cases **3Aa** and **6Aa**, respectively) provides the following evidences: 387.40 kg CO<sub>2</sub> equivalents per kg phenol correspond to cyclohexane production, 18.6 kg CO<sub>2</sub> equivalents per kg phenol is due to steam production and a small quantity corresponds to electricity generation. In the cyclohexanone case (i.e., **Case 6Aa**) the total GWP value (e.g., 341.94 kg CO<sub>2</sub> equivalents/ kg phenol) is the sum of 303 kg CO<sub>2</sub> equivalents per kg phenol (which corresponds to solvent production), 38.8 kg CO<sub>2</sub> equivalents per kg phenol (coming from steam production) and the rest is generated by electricity production. In the cyclohexane case (**Case 3**), from **Table 3**, it can be noticed that the quantity of solvent stream to the extractor (including recycling) is 37,491 kg/h while for cyclohexanone (**Case 6**) is 34,213 kg/h. These recycled streams contain 37,479.75 kg/h of pure cyclohexane (component weight is 99.97 %) respectively about 27,076.17 kg/h of pure cyclohexanone (component weight is 79.14 %). These quantities of pure solvent will be the major contributor to the GWP indicator. Considering steam consumption (see **Table 10**) the quantity of steam used in **Case 3** is lower compared to the quantity of steam used in **Case 6** (e.g., 17,844.10 kg/h vs. 37,172.40 kg/h). Consequently, a higher GWP due to steam production is obtained for **Case 6**. Considering electricity consumption (see **Table 10**) for **Case 3**, when cyclohexane is used as a solvent for phenol extraction, the total electricity consumption is 34.26 MJ/h. In **Case 6**, when cyclohexanone is used for phenol removal the electricity consumption will be lower compared to **Case 3** (e.g., 31.56 MJ/h vs. 34.26 MJ/h).

### 3.2.2. AP indicator

The highest values for AP indicator correspond to subcases **4Ab** and **4Aa** (e.g., 1.77 kg SO<sub>2</sub> equivalents per kg phenol, respectively 1.73 kg SO<sub>2</sub> equivalents per kg phenol). Ethylbenzene is used as a solvent in both subcases, ethylbenzene being produced using mix technology. In subcase **4Ab** hard coal is the steam source while in subcase **4Aa** natural gas is the fuel source for steam generation. Solvent production process contributes with 92.34 % in subcase **4Ab** with 95 % in subcase **4Aa** to the total AP indicator value. Relevant substances which influence the AP indicator are SO<sub>x</sub>, NO<sub>x</sub>, HCl, HF and NH<sub>3</sub>. For ethylbenzene case, according to thinkstep database, for one kg of solvent  $2.85 \times 10^{-3}$  kg of NO<sub>2</sub>,  $4.06 \times 10^{-2}$  kg of SO<sub>2</sub>,  $2.83 \times 10^{-5}$  kg of HCl and  $1.06 \times 10^{-6}$  kg HF,  $8.32 \times 10^{-9}$  kg ammonia are released into the air.

Lower values for this impact indicator are obtained in subcases **6Aa** (e.g., 0.42 kg SO<sub>2</sub> equivalents per kg phenol) and **6Ab** (e.g., 0.47 kg SO<sub>2</sub> equivalents per kg phenol). For instance, AP obtained in subcase **6Aa** is more than four times lower than the highest value (e.g., 0.42 kg SO<sub>2</sub> equivalents per kg phenol vs. 1.77 kg SO<sub>2</sub> equivalents per kg phenol), while AP obtained in subcase **6Ab** is decreased by a factor of 3.77 compared to the highest value (e.g., 0.47 kg SO<sub>2</sub> equivalents per kg phenol vs. 1.77 kg SO<sub>2</sub> equivalents per kg phenol). In both subcases (**6Aa** and **6Ab**) phenol is extracted using cyclohexanone, cyclohexanone

**Table 9**

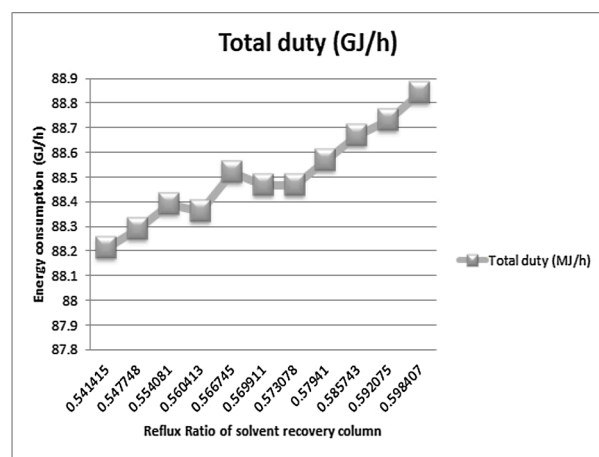
Comparison between process simulation results.

| Cases  | Input stream                                 |               |   | Output streams                             |  |   |  |
|--------|--|---------------|---|--|--|---|--|
|        | Input Wastewater Component flow-rates (kg/h) | Solvent used  | Input Solvent flow-rate to the extractor (kg/h) | Output Water Stream Total flow-rate (kg/h) | Output Water Stream Component flow-rates (kg/h)                              | Output Phenol stream Total flow-rate (kg/h) | Output Phenol stream Component flow-rate (kg/h)            |
| Case 1 | 99,800 H <sub>2</sub> O<br>200 phenol        | benzene       | 100,412.00                                      | 99,800.30                                  | 99,800 H <sub>2</sub> O<br>0.02 phenol<br>$9 \times 10^{-3}$ benzene         | 202.98                                      | 0 H <sub>2</sub> O<br>199.980 phenol<br>3.03 benzene       |
| Case 2 |  | toluene       | 119,956.00                                      | 99,800.81                                  | 99,800 H <sub>2</sub> O<br>0.02 phenol<br>$2 \times 10^{-3}$ toluene         | 203.57                                      | 0 H <sub>2</sub> O<br>199.98 phenol<br>3.59 toluene        |
| Case 3 |  | cyclohexane   | 37,490.60                                       | 99,800.02                                  | 99,800 H <sub>2</sub> O<br>0.02 phenol<br>$3.82 \times 10^{-4}$ cyclohexane  | 201.10                                      | 0 H <sub>2</sub> O<br>199.980 phenol<br>1.12 cyclohexane   |
| Case 4 |  | ethylbenzene  | 54,241.00                                       | 99,800.18                                  | 99,800 H <sub>2</sub> O<br>0.02 phenol<br>$6.99 \times 10^{-4}$ ethylbenzene | 201.61                                      | 0 H <sub>2</sub> O<br>199.98 phenol<br>1.63 ethylbenzene   |
| Case 5 |  | MIBK          | 41,861.80                                       | 99,800.87                                  | 99,800 H <sub>2</sub> O<br>0.02 phenol<br>0.07 MIBK                          | 201.12                                      | 0 H <sub>2</sub> O<br>199.980 phenol<br>1.22 MIBK          |
| Case 6 |  | cyclohexanone | 34,213.40                                       | 99,800.32                                  | 99,800 H <sub>2</sub> O<br>0.02 phenol<br>0.30 cyclohexanone                 | 201.32                                      | 0 H <sub>2</sub> O<br>199.980 phenol<br>1.34 cyclohexanone |
| Case 7 |  | mesityl oxide | 34,759.80                                       | 99,800.79                                  | 99,800 H <sub>2</sub> O<br>0.02 phenol<br>0.77 mesityl oxide                 | 200.45                                      | 0 H <sub>2</sub> O<br>199.980 phenol<br>0.47 mesityl oxide |

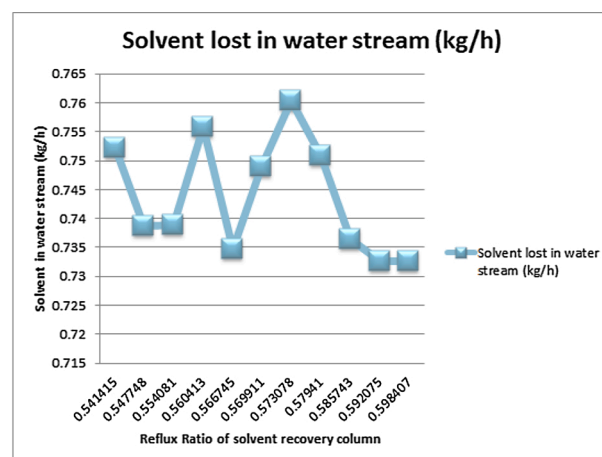
**Table 10**

Steam and electricity comparison (Cases 1 - 7).

| Solvent used                            | Units                | Case 1<br>Benzene | Case 2<br>Toluene | Case 3<br>Cyclohexane | Case 4<br>Ethylbenzene | Case 5<br>MIBK | Case 6<br>Cyclohexanone | Case 7<br>Mesityl oxide |
|---|----------------------|-------------------|-------------------|-----------------------|------------------------|----------------|-------------------------|-------------------------|
| Solvent flow-rate to the extractor      | kg/h                 | 100,412.00        | 119,956.0         | 37,490.60             | 54,241.00              | 418,618.80     | 34,213.40               | 34,759.80               |
| Reboiler duty (raffinate stripper)      | GJ/h                 | 88.61             | 74.63             | 18.13                 | 41.08                  | 32.17          | 30.61                   | 13.29                   |
| Reboiler duty (solvent recovery column) | GJ/h                 | 76.89             | 29.57             | 29.42                 | 29.46                  | 222.89         | 68.46                   | 70.87                   |
| Low pressure steam consumption          | GJ/h                 | 165.50            | 104.20            | 47.56                 | 70.50                  | 255.06         | 99.07                   | 84.16                   |
| Low pressure steam temperature          | °C                   | 136.20            | 136.20            | 136.20                | 136.20                 | 136.20         | 136.20                  | 136.20                  |
| Low pressure steam pressure             | atm                  | 3.19              | 3.19              | 3.19                  | 3.19                   | 3.19           | 3.19                    | 3.19                    |
| Low pressure steam flow-rate            | kg/h                 | 62,097.50         | 39,095.70         | 17,844.10             | 26,452.29              | 95,703.04      | 37,172.40               | 31,578.90               |
| Power consumption Pump extraction       | MJ/h                 | 66.85             | 83.01             | 28.13                 | 38.24                  | 31.49          | 18.79                   | 11.20                   |
| Power consumption Pump steam            | MJ/h                 | 21.34             | 13.43             | 6.13                  | 9.09                   | 32.89          | 12.77                   | 10.85                   |
| Power consumption total                 | MJ/h                 | 88.19             | 96.44             | 34.26                 | 47.33                  | 64.38          | 31.56                   | 22.05                   |
| <b>Phenol recovery</b>                  |                      | 99.99             | 99.99             | 99.99                 | 99.99                  | 99.99          | 99.99                   | 99.99                   |
| Solvent loss                            | kg/hx10 <sup>3</sup> | 8.89              | 2.42              | 0.38                  | 0.69                   | 67.94          | 300                     | 767.81                  |



a)



b)

**Fig. 5.** Effects of Reflux ratio modification on Energy consumption; b) Solvent in water stream (Case 6).

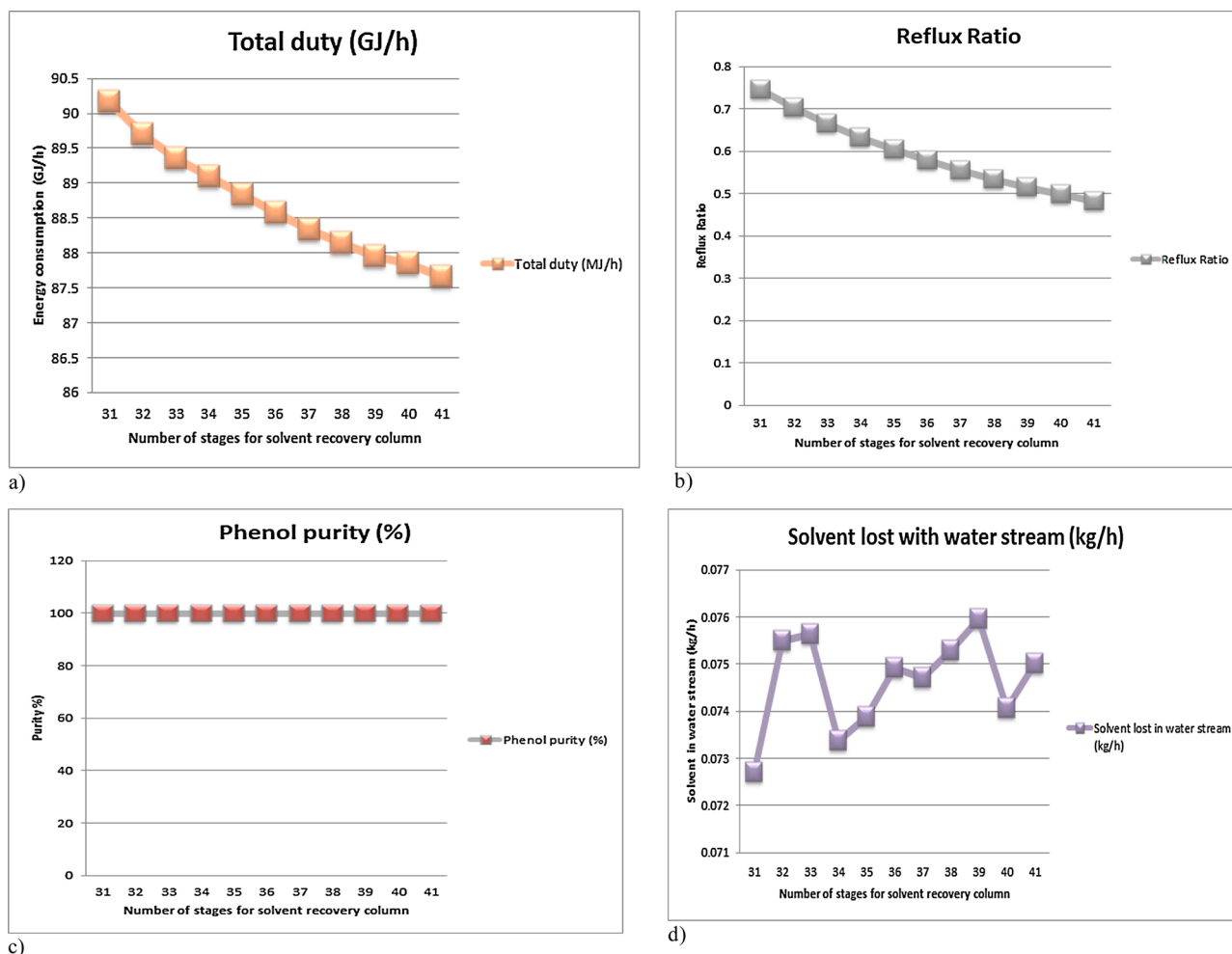


Fig. 6. Effects of number of stages modification on Energy consumption; b) Reflux ratio; c) Phenol purity and d) Solvent in water stream (Case 6).

being produced from cyclohexane, which, in turn, is produced from benzene. Different steam sources are used in these subcases, in particular natural gas is used in subcase **6Aa** and hard coal is used in subcase **6Ab**. Solvent production process contributes with 93.73 % in subcase **6Aa** and 82.76 % in subcase **6Ab**. In the cyclohexanone case, for the production of one kg of cyclohexanone  $1.38 \times 10^{-3}$  kg of  $\text{NO}_2$ ,  $1.28 \times 10^{-3}$  kg of  $\text{SO}_2$ ,  $6.00 \times 10^{-6}$  kg of HCl and  $1.43 \times 10^{-10}$  kg HF,  $9.11 \times 10^{-6}$  kg ammonia are released into the air.

### 3.2.3. EP indicator

According to Table 11, high values for Eutrophication Potential impact indicator are obtained in subcases **4Ab** and **4Aa** (e.g.,  $11.20 \times 10^{-2}$  kg  $\text{PO}_4^{3-}$  equivalents per kg phenol,  $10.80 \times 10^{-2}$  kg  $\text{PO}_4^{3-}$  equivalents per kg phenol, respectively). The lowest value for EP indicator (e.g.,  $4.21 \times 10^{-2}$  kg  $\text{PO}_4^{3-}$  equivalents per kg phenol) is gained by subcase **6Aa** corresponding to phenol extraction using cyclohexanone, cyclohexanone being produced from cyclohexane, which, in turn, is produced from benzene. From the total  $4.21 \times 10^{-2}$  kg  $\text{PO}_4^{3-}$  equivalents per kg phenol, the percentage correspondent to solvent production is 90.49 %, the rest being represented by the steam generation process from natural gas. Low values for EP impact indicator are also registered for subcase **6Ab** (e.g.,  $0.47 \times 10^{-2}$  kg  $\text{PO}_4^{3-}$  equivalents per kg phenol). From the above-mentioned value  $0.38 \times 10^{-2}$  kg  $\text{PO}_4^{3-}$  equivalents per kg phenol is due to the solvent production while  $9.71 \times 10^{-3}$  kg  $\text{PO}_4^{3-}$  equivalents per kg phenol is due to the steam production process. In subcase **6Ab** steam is generated from coal. Relevant substances which influence the EP impact indicator are ammonia and nitrogen oxides. For the

production of one kg of cyclohexanone, for instance, the quantities of ammonia and nitrogen oxides released into the atmosphere, are the same as those reported in the AP indicator.

### 3.2.4. ODP indicator

ODP indicator has the highest values in subcases **5Aa** and **5Ab**. In both subcases, MIBK is obtained from acetone, which in turn is obtained from cumene. Acetone production process using cumene as a raw material is the main responsible for the elevated values of subcases **5Aa** and **5Ab**. The solvent production contribution to the total ODP indicator is about 97.52 % in subcase **5Aa** while in subcase **5Ab** is about 96.65 %. Hydrogen production followed by steam generation and electricity generation are other processes which have a small contribution on this impact indicator. Hydrogen was assumed to be produced using mixed technologies (i.e., steam reforming, water electrolysis and steam cracking of ethane or naphtha).

Subcases **6Aa** and **6Ab** give the lowest values for the ODP indicator. For instance, in subcase **6Aa** from the total  $1.13 \times 10^{-9}$  kg R11 equivalents per kg phenol, 98.48 % is due to the solvent production process, the rest being generated by the steam process.

### 3.2.5. $\text{ADP}_{\text{fossil}}$ indicator

The highest values for  $\text{ADP}_{\text{fossil}}$  indicator are obtained by subcases **2Bb** and **2Ba** (e.g., 30,720 MJ per kg phenol and 30,712 MJ per kg phenol, respectively). These subcases are defined in Table 4. Solvent production is the process with major contribution to  $\text{ADP}_{\text{fossil}}$ . In subcase **2Bb** toluene production represents 97.87 % of the total  $\text{ADP}_{\text{fossil}}$

**Table 11**

LCA results according to CML 2001; best two subcases correspondent to each case.

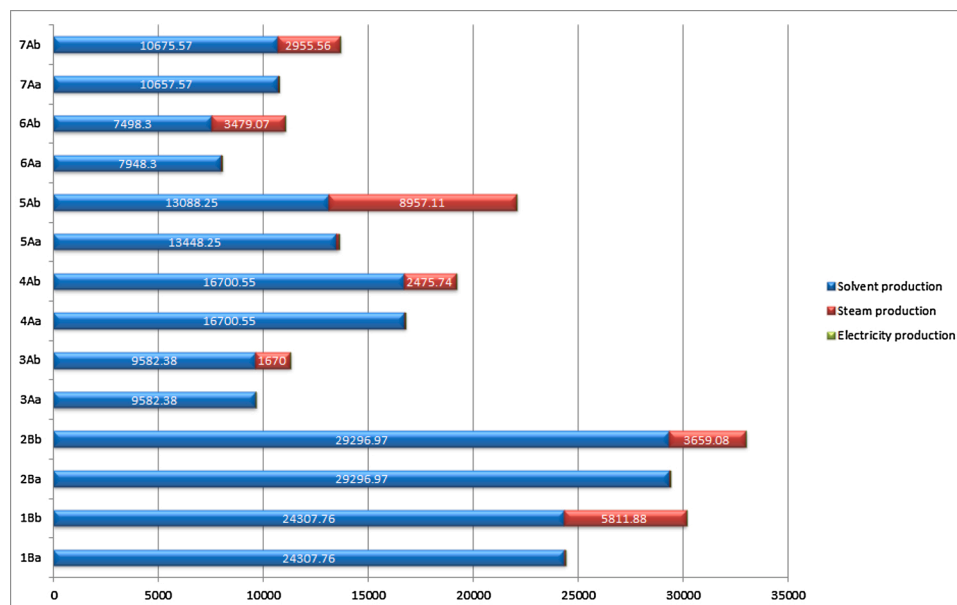
| KPI                   | Units  | 1Ba    | 1Bb    | 2Ba    | 2Bb    | 3Aa    | 3Ab    | 4Aa    | 4Ab    | 5Aa    | 5Ab    | 6Aa    | 6Ab    | 7Aa    | 7Ab    |
|-----------------------|--|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| GWP                   | kg CO <sub>2</sub> equivalents / kg phenol               | 488.41 | 526.44 | 551.36 | 575.30 | 406.04 | 416.97 | 556.26 | 572.46 | 505.09 | 563.70 | 341.94 | 364.71 | 364.76 | 384.10 |
| AP                    | kg SO <sub>2</sub> equivalents / kg phenol               | 1.13   | 1.23   | 1.34   | 1.39   | 0.51   | 0.54   | 1.73   | 1.77   | 0.72   | 0.86   | 0.42   | 0.47   | 0.55   | 0.60   |
| EP x 10 <sup>2</sup>  | kg PO <sub>4</sub> <sup>3-</sup> equivalents / kg phenol | 8.44   | 9.40   | 9.80   | 10.40  | 5.06   | 5.34   | 10.80  | 11.20  | 7.77   | 9.26   | 4.21   | 4.79   | 5.87   | 6.36   |
| ODP x 10 <sup>9</sup> | kg R11 equivalents / kg phenol                           | 1.40   | 1.43   | 1.67   | 1.69   | 1.42   | 1.43   | 1.25   | 2.44   | 4.44   | 4.48   | 1.13   | 1.14   | 3.69   | 3.70   |
| ADP <sub>fossil</sub> | MJ / kg phenol   | 25,990 | 25,978 | 30,720 | 30,712 | 12,242 | 12,238 | 17,873 | 17,867 | 15,365 | 15,345 | 9,973  | 9,965  | 11,620 | 11,613 |
| FAETP                 | kg 1,4 DCB equivalents / kg phenol                       | 8.98   | 9.02   | 10.82  | 10.85  | 3.20   | 3.22   | 1.72   | 1.74   | 3.73   | 3.79   | 0.026  | 0.025  | 2.99   | 3.01   |
| HTP                   | kg 1,4 DCB equivalents / kg phenol                       | 34.39  | 36.78  | 41.15  | 42.66  | 11.57  | 12.26  | 755.48 | 756.49 | 15.08  | 18.76  | 9.18   | 10.62  | 12.02  | 13.24  |
| PCOP                  | kg ethylene equivalents / kg phenol                      | 0.20   | 0.20   | 0.24   | 0.24   | 0.13   | 0.13   | 0.21   | 0.21   | 0.18   | 0.18   | 0.10   | 0.10   | 0.14   | 0.14   |
| TEP                   | kg 1,4 DCB equivalents / kg phenol                       | 0.22   | 0.28   | 0.27   | 0.30   | 0.10   | 0.12   | 2.19   | 2.22   | 0.19   | 0.28   | 0.08   | 0.11   | 0.16   | 0.19   |
| MAETP                 | kg 1,4 DCB equivalents / kg phenol                       | 24,386 | 30,128 | 29,351 | 32,966 | 9,606  | 11,256 | 16,735 | 19,181 | 13,203 | 22,052 | 7,544  | 10,980 | 10,714 | 13,634 |

indicator, while in subcase **2Ba** it represents 97.84 % of the total ADP<sub>fossil</sub> indicator. The lowest values for this indicator are registered in subcases **6Aa** and **6Ab** with values about three times lower compared to subcase **2Bb**.

**3.2.6. FAETP, HTP and TEP impact indicators**

Similar values for the subcases correspondent to each solvent are reported for FAETP, HTP and TEP impact categories. For instance, **Case 1** subcases **1Ba** and **1Bb** have the FAETP value around 9 kg 1,4 DCB equivalents per kg phenol. This happens because, within the same case study, the process that mainly contributes to this indicator is the solvent production process, which exhibits the same emissions in all subcases

correspondent to each case. Indeed, the steam generation process, phenol removal and electricity generation process have negligible influence on FAETP, HTP and TEP indicators. The lowest values for impact indicators are registered for subcases **6Aa** and **6Ab**. For instance, in subcase **6Aa**, the share of the solvent production process to the FAETP indicator is as follows: from the total 2.52 kg 1,4 DCB equivalents per kg phenol, 2.48 kg 1,4 DCB equivalents per kg phenol comes from the solvent production process, and the difference is represented by the effluent water stream which contains small traces of solvent. If the HTP indicator is considered for subcase **6Aa**, from the total value (e.g., 9.18 kg 1,4 DCB equivalents per kg phenol) 97.82 % is due to the solvent production process and 2.18 % is due to the steam generation using



**Fig. 7.** Main processes contributing to MAETP impact indicator for the best two subcases correspondent to each case.

natural gas as fuel source.

### 3.2.7. PCOP indicator

Low values for PCOP impact indicator are reported in all subcases summarised in Table 11. It can be noticed that the subcases corresponding to the same solvent case have the same PCOP value. This is because the solvent production process, which is the major contributor to this impact category, has the same impact for the subcases corresponding to each case. The lowest values are encountered in subcases 6Aa and 6Ab (e.g., 0.10 kg ethylene equivalents per kg phenol).

### 3.2.8. MAETP impact indicator

MAETP impact indicator gives also the best results in subcase 6Aa (e.g., 7,544 kg 1,4 DCB equivalents per kg phenol), followed by 3Aa (e.g., 9,606 kg 1,4 DCB equivalents per kg phenol). Fig. 7 presents the main sub-processes contributing to MAETP indicator.

As shown in Fig. 7 the main contributor to MAETP indicator is represented by the solvent production, followed by the steam production process. The highest impact for MAETP impact indicator is registered for subcase 2Bb.

Counting the best values for all the impact indicators presented in Table 11, it can be concluded that: i) the lowest values for all impact categories are gained by subcase 6Aa followed by subcase 6Ab; ii) the next lower values for various impact categories are encountered in subcases 3Aa and 7Aa; iii) there is a competition between subcases 3Aa and 7Aa. In fact, seven out of ten indicators (i.e., EP, AP, HTP, ODP, PCOP, MAETP and TEP) score lower values for subcase 3Aa, while the others three indicators (i.e., GWP, ADP<sub>fossil</sub> and FAETP) are lower for subcase 7Aa; v) the best solvent for phenol removal using liquid-liquid extraction is cyclohexanone; the regeneration of the solvent should be performed using steam produced from natural gas.

## 4. Conclusions

Seven different solvents (i.e., benzene, toluene, cyclohexane, ethylbenzene, MIBK, cyclohexanone and mesityl oxide) employed for treatment of phenol wastewater from an integrated steel plant using liquid-liquid extraction are compared in the present study. The comparison was performed based on process modelling and simulation data to obtain information for environmental assessment using LCA methodology.

The simulations performed using ChemCAD process simulator were conducted at the same raw wastewater flowrate of 100 tons / h, with a phenol content of 0.2 wt.%, representing average industrial data. The simulation results show that the best three solvents from the technical viewpoint (i.e., quantity of solvent, steam and electricity employed) are cyclohexane, cyclohexanone and mesityl oxide. A sensitivity analysis was also performed on extraction processes, exhibiting a relationship between process results and process parameters such as reflux ratio and number of stages in the distillation column.

Material and energy data generated by simulations were then used to perform an environmental evaluation based on LCA methodology. Different subcases were considered in the LCA, each one deriving from the combination of various solvent production routes as well as various fuels for steam production. Details about the LCA phases and discussions regarding the most significant environmental indicators (i.e., GWP, AP, ADP<sub>fossil</sub>, FAETP, HTP, TEP, PCOP, MAETP) are provided. The most environmentally friendly design, from the 42 subcases considered, was phenol removal using cyclohexanone, cyclohexanone being produced from cyclohexane, which, in turn, is produced from benzene. The steam used from solvent regeneration using natural gas as raw material is the option which leads to the lowest environmental impact.

### Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

The present research leading to the above-presented results has received funding from UEFISCDI under the project number PN-III-P3-36-H2020-2020-0058.

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jwpe.2021.102077>.

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