Computer Aided Design for Sustainable Industrial Processes: Specific Tools and Applications

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Chemical Process Sustainability can be estimated using different sustainability indicators. The quantitative estimation of those indicators is necessary (i) for evaluating the environmental impact of a chemical process and (ii) for choosing the best design among different available alternatives. To accomplish these goals, the computerized calculation of sustainability indicators requires the use of at least three computer tools: (i) process simulation, (ii) molecular modeling and a (iii) sustainability indicators software code. In this work, a complete software platform, Process Sustainability Prediction Framework, integrated with process simulation programs, which support the CAPE-OPEN interfaces, is presented and discussed. The article contains also description and application of molecular modeling techniques to estimate different toxicological data, which are used in the calculation of sustainability indicators. A representative example of one chemical process and thermo-physical properties used in the calculation of toxicological data calculation, are reported to demonstrate the applicability of the software to real cases. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 1065–1078, 2009

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Introduction

Sustainable development has been defined as the creation of goods and services using processes and systems that are non-polluting; conserving energy and natural resources; economically viable; safe and healthy for employees, communities and consumers; socially and creatively rewarding for all working people.[1]

In the sustainable development context, an important role is played by chemical engineering, basically for two main reasons: (i) the production of chemical process plants contributes greatly to national income and is absolutely essential to modern society; thus, the society development depends on the development of the chemical process industry and vice versa; (ii) many critical environmental problems can be associated directly with chemical processes or to the use of chemical products and by-products that result in waste streams to soil, water, and air.[2] Chemical industry produces materials for multiple consumer markets, which need to be produced, used and recycled by manufacturing processes that

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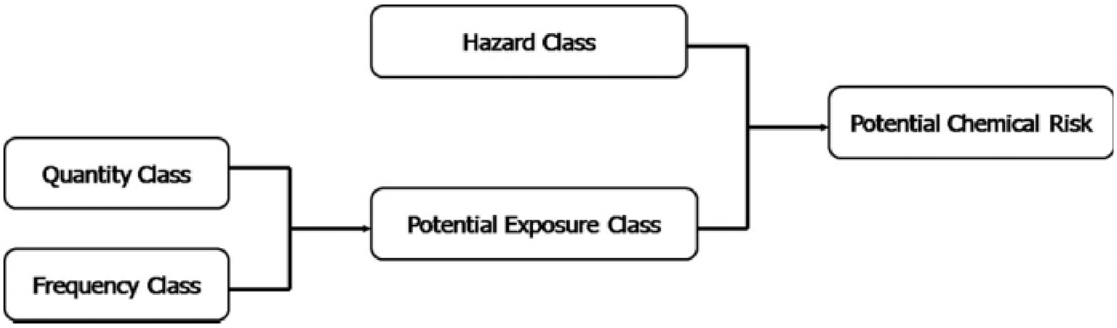

Figure 1. Potential Chemical Risk Evaluation.

are clean, safe and economical.[3] To eliminate or reduce the environmental impact, the environmental performance of chemical processes should be identified and quantified at an early stage of process design. Taking into account the environmental aspects at design time, an answer to ''which design is more environmentally friendly, and implicitly more sustainable, for a specific chemical process?'' can be provided.

The present work deals with the development, implementation and application of sustainable industrial development concept in the design stage of a chemical plant. In particular, the development and implementation of a specific software tool, Process Sustainability Prediction (PSP) Framework, is presented. The framework is intended to be used in the design stage of a chemical process, for selecting the best solution in terms of environmental impact, among different design alternatives. The PSP software framework developed in this work contains also a toxicological data estimation methodology, using molecular modeling techniques, and the implementation of a toxicological database. Applications of the PSP Framework are discussed and an example is presented. The aforementioned listed issues are discussed in detail in the next sections.

There are several advantages deriving from the application of the PSP Framework. The most important advantage is the possibility of including the potential environmental impact criteria in the optimization of a chemical process and not only the technical and economical criteria. Modern tools such as molecular modeling and process simulation, both used in the present work, are of crucial importance because they can evaluate possible technical solutions faster and with much lower costs then experimental activity. Benefits from the coupling of molecular modeling with process simulation and design include but are not limited to: (i) shortened product-process development cycles, (ii) optimization of existing processes to improve energy efficiency and minimize production of waste, (iii) efficient design of new products and processes; and (iv) improvements in health, safety, and environment.[4]

Sustainability Evaluation

Economy, society and environment are three basic elements of sustainability. Each of these elements is connected to and dependent upon the others.[5] It is generally acknowledged that sustainability results from a balance among the three aspects. The selection of an adequate set of indicators for sustainability evaluation is very important, for comparative analysis between different versions of a process.[6] With the objective of providing an easy-to-implement method for applying indicators for the purpose of analyzing industrial systems for sustainability, Sikdar[6] proposed a typology of indicators, considering the three dimensions of sustainability in three distinct hierarchical groups: (i) one dimensional (1D) indicators, which provide information about only one dimension of sustainability: economical, ecological, or social; (ii) two dimensional (2D) indicators, which provide information simultaneously about two dimensions of sustainability: socio-ecological, socio-economical, or economic-ecological; (iii) three dimensional (3D) indicators, which provide information about all three dimensions of sustainability.[7]

Four 3D and four 1D indicators have been studied, implemented and analyzed in the present work. A brief description of those is presented later to understand the significance of each factor and their relation to process data on one side and to toxicological data on the other side.

Three dimensional indicators

The *Material Intensity (MI) Indicator* measures the amount of non-renewable resources required to obtain a unit mass of products. It includes raw materials, solvents, and other ingredients.[7] Details regarding the calculation of this indicator are given by Schwarz et al.[8] The *Energy Intensity (EI) Indicator* measures the energy demands of the process. It is calculated per unit mass of products and focuses primarily on the use of non-renewable energy.[7] Details about the calculation of this indicator are given by Tanzil et al.[9] The *Potential Chemical Risk Evaluation (PCRE) Indicator* regards the risk associated with the manipulation, storage and use of hazardous chemical substances in the process. It is schematically represented in Figure 1.

The chemicals used in the process under study are classified depending on their relative quantity, frequency of use, danger characteristics and potential exposure. Thus, for each chemical, the designated ''frequency class,'' ''quantity class,'' ''hazard class,'' and ''potential exposure class'' are determined according to Vincent et al.[10]

The Potential Environmental Impact (PEI) Indicator is due to the emissions and discharge of hazardous chemicals to the environment. It is similar to the one for the potential

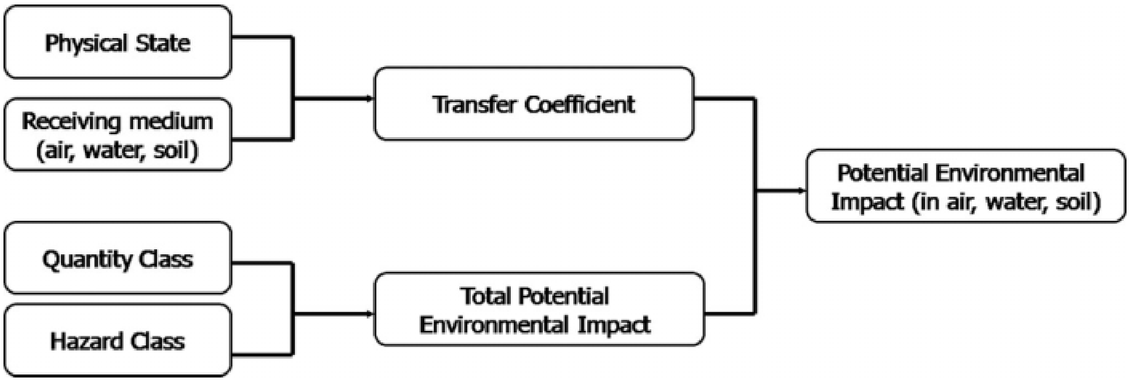

Figure 2. Potential Environmental Impact Evaluation.

chemical risk, as represented in Figure 2. The chemicals are classified according to their relative quantity and hazard characteristics. These lead to the calculation of the total potential environmental impact. Furthermore, the potential environmental impact of interest is dependent on the transfer to a receiver medium, such as air, water or soil, which is governed by physicochemical characteristics and transfer coefficients as shown in Figure 2.[7]

One dimensional indicator: waste reduction algorithm

The Waste Reduction (WAR) Algorithm, based on the concept of environmental impact balance, analogous to mass or energy balances, uses data from the process (stream flowrates and mass fractions) and toxicological data to calculate the environmental impact of a chemical plant.[11–13]

According to the algorithm, toxicological data are grouped in different environmental impact categories. Eight environmental impact categories: Global Warming Potential (GWP), Acidification Potential (AP), Ozone Depletion Potential (ODP), Photochemical Oxidation or Smog Formation Potential (PCOP), Human Toxicity Potential by Ingestion (HTPI), Human Toxicity Potential by Inhalation or Dermal Exposure (HTPE), Aquatic Toxicity Potential (ATP), Terrestrial Toxicity Potential (TTP) are used in evaluation of potential environmental impact using the WAR Algorithm.[12] A brief description of each category is presented later.

GWP is determined by comparing the extent to which a unit mass of a chemical absorbs infrared radiation over its atmospheric lifetime to the extent the CO_2 absorbs infrared radiation over its respective lifetimes. AP is determined by comparing the rate of release of H^+ in the atmosphere as promoted by a chemical to the rate of release of H^+ in the atmosphere as promoted by SO_2. ODP is determined by comparing the rate at which a unit mass of chemical reacts with ozone to form molecular oxygen to the rate at which a unit mass of CFC-11 (trichlorofluoromethane) reacts with ozone to form molecular oxygen. PCOP is determined by comparing the rate at which a unit mass of chemical reacts with a hydroxyl radical OH to the rate at which a unit mass of ethylene reacts with OH. HTPI is calculated for a chemical if it existed as a liquid or solid at a temperature of 0°C and atmospheric pressure. As a first approximation, the lethal-dose that produced death in 50% of rats by oral ingestion (LD_{50}) has been used as an estimate for the HTPI. HTPE was determined for that chemical if it existed as a gas a temperature of 0°C and atmospheric pressure. ATP was estimated by using toxicological data for a single, representative species of fish, Pimephales Promelas (Fathead Minnows). The data for this assay comes in the form of a LC_{50}, a lethal concentration which causes death in 50% of the test specimens.[11–13] Different molecular modeling methods will be presented for the evaluation of the thermo-physical properties which lead to environmental impact categories.

The four 1D environmental impact indexes used in WAR Algorithm and in the PSP Framework are: the total rate of impact output—$\dot{I}^{(t)}_{\text{out}}$, the total impact output per mass of products—$\hat{I}^{(t)}_{\text{out}}$, the total rate of impact generation—$\dot{I}^{(t)}_{\text{gen}}$ and the total impact generated per mass of product—$\hat{I}^{(t)}_{\text{gen}}$. Those indexes have been defined by Cabezas and Young[11–13] and are referred in the PSP Framework as Iout, Iout_mp, Igen and Igen_mp. The comparison of the aforementioned presented indexes permits to choose the most environmentally friendly design between different process alternatives.

PSP framework: design and development

The PSP Framework implementation has been made according to Martins and Vincent for 3D Indicators[7,10] and to Young and Cabezas for 1D Indicators.[11–13] A general schema illustrating the main steps of the development is given in Figure 3.

The two starting points for calculating the sustainability indicators are the process simulator and the database containing toxicity and risk phrases data. One of the main goals of the present work is to incorporate the toxicology data calculation issue into process simulation. For this aim, toxicological effects of the substances, present in the process flowsheet, and their quantities are processed in special unit operations, implemented using the CAPE OPEN (CO) methodology. The choice of the CO technology has been made according to a precise goal: to develop a module able to interact with all the process simulator software programs which support the CO interfaces. Once the module is created it is ready to be used anywhere, being independent of the

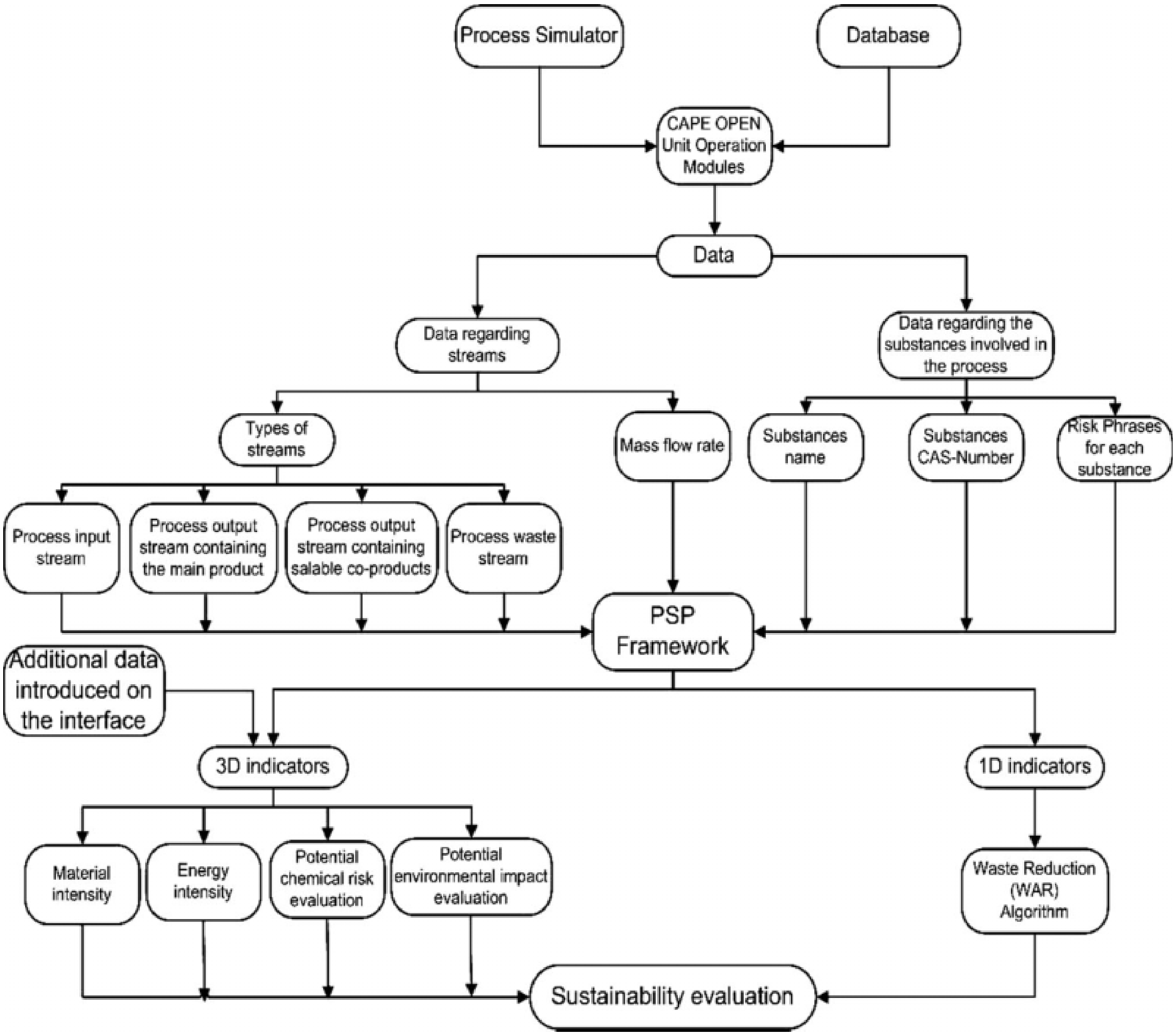

Figure 3. General schema of the PSP Framework.

process simulator software used. This is one of the greatest advantages offered by the CO technology. Four CO Modules have been developed (two CO Modules for 3D Indicators and two CO Modules for 1D Indicators). These modules are inserted in the process flow-sheet, as any other unit operation (e.g. a heat exchanger, a reactor, a pump, etc.), with the aim of extracting all the necessary data requested for further calculations (flow-rate quantities, flow-rate composition, energy demand of the process, toxicological data, risk phrases data). It is important to mention that the two CO Modules used in the 1D calculation are directly linked with the toxicological database (TDB), containing the environmental impact categories, and one of the CO Module used in the 3D calculation is linked with the same toxicological database which contains the risk-phrases (R-Phrases) for several chemical compounds. The modules have been tested successfully using different process simulators such as: PROII, Aspen Plus, COCO/COFE. The connection between the CO Modules and the database is done using ActiveX Data Objects (ADO) technology. The environmental impact categories and the R-Phrases are obtained from the TDB as a function of the Chemical Abstract Service (CAS) Number. The TDB contains about 4900 compounds.

The process data and toxicological data obtained through the CO Modules are processed in the PSP software. Other information such as H_2O, O_2, N_2 quantities formed in the reaction; energy demand of the process; frequency of use and physical state of each substance involved in the process should be supplied by the user on the PSP graphical user interface. The software has been implemented in Microsoft Visual Basic (version 6.0) and generates the 3D and 1D sustainability indicators. After the calculation, the indicators will be used in a comparative manner to choose the best environmental design between different design alternatives.

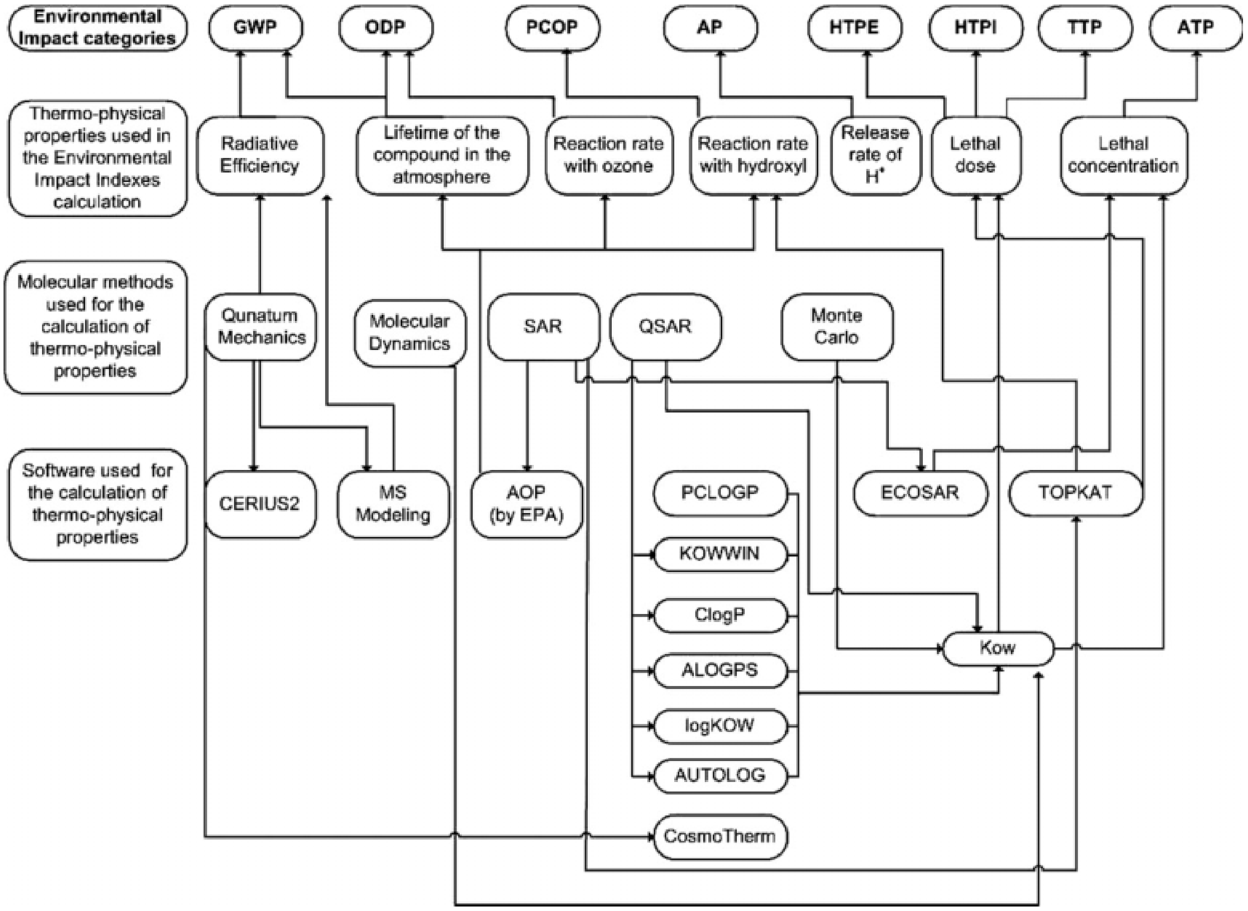

Figure 4. Thermo-physical properties and software programs used in the calculation of the Environmental Impact Categories.

Details regarding the implementation of the CO Modules, the development of the toxicological relationship database, the PSP software and its applications are given by Toma.[14]

Estimation of Toxicological Properties by Molecular Modeling

The rapid increase in the world's human population and the development of human society have been accompanied by an equally rapid increase in the utilization of chemical compounds and the subsequent deterioration of the environment by the release of these compounds.[15] Toxicological data are usually necessary to assess the impact of such compounds on the environment and on human health. However, because of the time and financial resources required, it is impractical to perform toxicity tests for all the chemical compounds in use.[16] In this context, molecular simulation methods become an important tool for toxicological data prediction. As it has been mentioned in the previous sections, GWP, ODP, PCOP, AP, HTPE, HTPI, TTP, and ATP are the necessary data on which the WAR Algorithm is based. In view of developing a strategy for the estimation of these eight environmental impact categories from the molecular structure of the compound under investigation, it is interesting to map such indexes on some reference intermediate physical properties that could be in turn estimated by some molecular simulation method. Figure 4 summarizes such intermediate physical properties and the relevant methods for their calculation starting from the molecular structure. Each physical property is then mapped to the related environmental impact category (top of the figure) and to the molecular simulation method allowing its calculation (bottom of the figure).

The Atmospheric Oxidation Program (AOP), based on Structure Activity Relationship (SAR) calculation, was developed by U.S.EPA. The program has been used in the present work for the estimation of the lifetime of a compound in the atmosphere, for the reaction rate with ozone and reaction rate with hydroxyl.

For the calculation of the octanol-water partition coefficient (Kow), different molecular modeling methods can be used. For example KOWWIN, the Log Octanol-Water Partition Coefficient Program, is software developed by U.S.EPA which is based on SAR. ClogP is a program, based on group-contribution methods, which can be also used for the octanol-water partition coefficient. ALOGPS is software based on neural networks developed by the Virtual Computational Chemistry Laboratory. Conductor like Screening Model Thermodynamics (COSMOTherm) is a software tool based on quantum mechanical methods, which calculates different thermo-physical properties such as: vapor pressures, boiling points, activity coefficients, excess enthalpy and entropy, Henry's Law constants, solubility, octanol-water partition coefficient, vapor-liquid equilibrium, liquid-liquid equilibrium, solid-liquid equilibrium, density and viscosity for pure compounds.[17]

ECOSAR, developed by the Risk Assessment Division of the U.S.EPA, is a computer program based on SAR, used to predict the aquatic toxicity of chemicals based on their similarity of structure to chemicals for which the aquatic toxicity has been previously measured. TOPKAT, a computer program developed by Accelrys, employs robust and cross-validated Quantitative Structure Toxicity Relationship (QSTR) models for estimating 16 toxicity endpoints (e.g. Mutagenicity, Rat Oral LD50, Carcinogencity, Developmental Toxicity, etc.).[18]

It is evident, form Figure 4, that some properties are of fundamental importance for the calculation of the eight environmental impact categories. As it can be noticed, HTPE, HTPI, ATP and TTP impact categories are related to a phase equilibrium property, namely the Kow. The other four impact categories: GWP, ODP, PCOP and AP are related to transport properties such as the release rate of H^+ or to reactivity properties such as reaction rate with hydroxyl, reaction rate with ozone (lifetime) and therefore can be calculated using quantum mechanics (QM) or (Q)SAR methods. Based on these considerations, the octanol-water partition coefficient, the lifetime of a chemical compound in the atmosphere, the reaction rate with ozone and the reaction rate with hydroxyl are discussed in the next section.

Thermo-physical properties estimation

Octanol-Water Partition Coefficient. Numerous properties, including bioavailability, skin permeability, toxicity and environmental fate, have all been successfully related to the differential solubility of solutes in aqueous and organic solvents.[19] Octanol-water partition coefficient is one of the most effective parameters used in the toxicity evaluation of four Environmental Impact Categories: HTPI, HTPE, ATP, TTP (see Figure 4). The Kow is defined as the ratio of the concentration the component of interest has in octanol phase to its concentration in the aqueous phase in a two-phase octanol-water system.[20] In recent years, the Kow has become a key parameter in studies of the environmental fate of organic chemicals. It has been found to be related to water solubility, soil/sediment adsorption coefficients, and bio concentration factors for aquatic life. Because of its increasing use in the estimation of these properties, Kow is considered a required property in studies of new or problematic chemicals.[16,20] The successfulness of Kow in predicting bioaccumulation and toxicity has been attributed to the fact that the octanol-water partitioning is a good representative of a compound going from more aqueous like-phases (extra cellular phase) to organic-like phases (cellular phase) inside the body, which is the rate controlling step during the interaction of a compound and a biological system.[21] Because Kow is a free energy function, it is directly related to the energy of transfer between two phases. There are different methods, available in literature, to calculate Kow using molecular simulations. Some of these methods are: Free Energy Perturbation, Monte Carlo and Molecular Dynamics Method[19,21]; Free Energy Calculation—Expanded Ensemble Method[21,22]; the configurational-bias Monte Carlo (CBMC)[22]; Continuum Solvation Model (CSM); Quantitative Structure Activity Relationship (QSAR) Method.[23–27] The last two approaches have been applied in the present work.

Lifetime. To evaluate the environmental impact of a given gas molecule, one needs to know, first, how long it remains in the atmosphere.[28] The environmental damage caused by atmospheric pollutants is proportional to the duration of their effects. The global impacts of greenhouse gases, as measured by global warming potential, and ozone depleting substances, as measured by ozone depletion potential, have traditionally been calculated using the atmospheric lifetime of the source gas as a quantitative measure of the impact's duration, assuming that the gas quickly reaches a steady state pattern which decays exponentially according to the lifetime.[29] Consequently, lifetime is another important parameter used in the calculation of two environmental impact categories: GWP and ODP (see Figure 4). Lifetime of chemical compounds in the atmosphere can be estimated using Structure Activity Relationship (SAR) methods.

Reaction Rate with Ozone. Ozone plays a central role in tropospheric chemistry. Not only is it a highly reactive and toxic species, but it absorbs both infrared and ultraviolet light, contributing to the "greenhouse effect" and providing protection from exposure to damaging UV.[30] The reaction with ozone represents one of the most common reactions which take place in the atmosphere and the reaction rate with ozone is used to calculate the ODP environmental impact category. It should be also specified that ozone concentrations are very difficult to model because of the different interactions between pollutants and meteorological variables.[31] Reaction rate of chemical compounds with ozone in the atmosphere can be estimated using the QSAR method.[32]

Reaction Rate with Hydroxyl. Organic chemicals emitted into the troposphere are degraded by several important transformation processes that include reaction with hydroxyl OH radicals or other photo chemically-produced radicals, reaction with ozone or direct photolysis. The dominant transformation process for most compounds that occur in the troposphere is the daylight reaction with OH radicals. The reaction rate with hydroxyl is used to calculate the PCOP environmental impact category. The rates at which organic compounds react with OH radicals are a direct measure of their atmospheric persistence.[33] As experimental measurements can be difficult, time-consuming, and expensive, the ability to estimate rate constants has become very important. The estimation methods have become an important tool to reduce the number of compounds for which measurements are necessary.[34] Several methods are used to calculate the reaction rate with hydroxyl, such as: Empirical Models; QSAR models (QSAR models with measured physicochemical descriptors and QSAR models with structural descriptors); ab initio molecular orbital calculations. A complete overview of the methods, found in the scientific literature, that calculate the reaction rate with hydroxyl was published by Sablijic and Peijnenburg in the IUPAC Technical Report for 2001[35] and by Güsten.[36] In the present work, the reaction rate with hydroxyl radical has been evaluated using group contribution (GC) and QSAR methods.

Results and Discussions on the Estimation of Thermo-Physical Properties

Octanol-water partition coefficient

Our attention was focused on two methods: QSAR and CSM. The choice of these methods as well as the advantages and disadvantages correspondent to each of them is briefly summarized later.

The advantages of QSAR methods are: these methods are very fast, allowing them to be applied to large databases of structures, in many cases they require only 2-D molecular connectivity, and can be very accurate for molecules with well-defined group equivalents. The disadvantages of QSAR methods are that they require large numbers of empirically derived parameters; they cannot be used to examine conformational effects in the solute and, many times, no parameters exist for calculating the logKow for the new chemical classes.[19] Another problem with such models is their extremely limited scope. In other words, they perform well, but only for very narrow classes of compounds.[24] Direct calculation of octanol-water partition coefficients, using the CSM methods, offers the promise of calculating accurate partition coefficients for a wide variety of molecules with a degree of generality not available from the fragment-based methods.[19] The CSM used in this work are based on the original theory of COSMO, based on computational quantum mechanics that allows us to predict different thermo-physical properties without any experimental data. The COSMO method has been implemented in the literature in two models: conductor like screening model-realistic solvation (COSMO-RS) and conductor like screening models-segment activity coefficient (COSMO-SAC). The two methods are very similar and they predict intermolecular interactions based only on molecular structure and a few adjustable parameters. COSMO-RS is the first extension of dielectric continuum solvation model to liquid-phase thermodynamics, and COSMO-SAC is a variation of COSMO-RS.[37]

Kow is calculated by the COSMO-RS by considering the activity coefficients for the systems of interest. The theory is based on considering the ideally screened molecules as starting points for the description of molecules in solution. The deviations from ideal screening, which occur in any real solvent, are described as pair wise misfit interactions of the ideal screening charges on parts of the molecules in contact in the fluid. Because COSMO-RS does not depend on experimental data or any parameterization for the solvent, it efficiently enables the calculation of the chemical potential of almost any solute in almost any solvent. Basically, COSMO-RS method assumes that the molecule is made up of small surface elements. The charge density of each of these elements is evaluated by means of quantum mechanics calculations. An ensemble of interacting molecules is replaced by the corresponding ensemble of interacting surface pieces characterized by a screening charge density, namely, the contribution of all of the differences in polarity obtained when the molecules are not isolated. The characteristic distribution of charges obtained by considering all of these surface elements is the sigma profile (σ-profile) of the molecule. The sigma profile describes the amount of surface in the ensemble having a screening charge density between σ and $\sigma + \Delta\sigma$.[38] Sigma profiles depict the surface charge density distribution over the entire molecule. It has to be specified that each molecule's profile is unique and the profiles are sensitive to conformation. The sigma profiles provide a rich and detailed quantitative information about the polarity of molecules.[17,39] The difference in the σ-potentials between the two phases can be considered as the local contribution to the partition coefficient, and the partition coefficient can be visualized as a surface property.[40] Many are the advantages of the method. First, because each molecule is characterized by a sigma profile, the method can treat proximity effects, can distinguish among isomers, and can also take into account the result of a conformational analysis.[38]

The above-presented methods for Kow calculation have been implemented in different software programs: COSMO-RS method has been implemented in COSMOTherm software and QSAR has been implemented in Estimation Programs Interface (EPI) Suite software developed by EPA. The results of the calculations performed are presented in Table 1. Analyzing the results shown in Table 1, it can be noticed that the logKow relative absolute deviation (RAD) between the experimental and the calculated value, has lower values for nine substances when the COSMO-RS method is used. The nine substances considered are: methanol, phenol, chloroform, toluene, methyl ethyl chloride, benzene, methane, ethane and propane. Also the mean relative absolute deviation (MRAD) has lower value (0.00765 vs. 0.10715) when the COSMO-RS method is used. These results confirm what stated earlier about the reliability of the methods and the good accuracy of the QM-COSMO method.

Lifetime

As it has been mentioned earlier, SAR method has been used for the lifetime estimation. The Atmospheric Oxidation Program (AOPWIN) is a computer program, based on SAR, developed by US EPA, used to calculate atmospheric half-lives for organic compounds. The program belongs to the EPI suite software. The only data required for AOPWIN to estimate the half-life of a chemical substance is the chemical structure of the compound. The chemical structure is entered into the program as a SMILES notation.[41] The procedure has been applied to calculate the lifetime for several substances.

Table 2 contains the experimental lifetime values for some representative chemical compounds as well as the results obtained using SAR. The experimental values have been taken from the World Meteorological Organization Global Atmosphere Watch Report.[42]

By analyzing the results shown in Table 2, it can be noticed that the lifetime relative absolute deviation (RAD) has a variation range of −0.0235–0.4514. The mean relative absolute deviation (MRAD) is 0.04843. Taking into account the complexity of the problem and the limited number of methods, software programs and experimental data available in the literature, the results obtained using the SAR method are considered satisfactory.

Reaction rate with ozone

As it has been mentioned earlier, SAR method has been used for the reaction rate with ozone estimation. The AOPWIN has been used to calculate the reaction rate with ozone. It should be specified that the program is able to estimate the reaction rate with ozone only for two classes of

Table 1. Kow Results Using Different Methods

				LogKow Calculated		LogKow RAD	
Substance Name	Substance Formula	Substance CAS	LogKow (exp.)	Using QSAR method(1) KOWWIN-software	Using CSM Method(2) COSMOTherm software	RAD for (1)	RAD for (2)
Methanol	CH_4O	67-56-1	−0.77	−0.63	−0.7292	0.1818	0.0529
Naphthalene	$C_{10}H_8$	91-20-3	3.30	3.17	3.0939	0.0393	0.0625
Phenol	C_6H_6O	108-95-2	1.46	1.51	1.4319	−0.0342	0.0192
Chloroform	$CHCl_3$	67-66-3	1.97	1.52	2.1001	0.2284	−0.0660
Toluene	C_7H_8	108-88-3	2.73	2.54	2.6549	0.0696	0.0275
Anisole	C_7H_8O	100-66-3	2.11	2.07	2.2271	0.0189	−0.0555
Methyl ethyl chloride	CH_2Cl_2	75-09-2	1.25	1.34	1.2591	−0.0720	−0.0073
Benzene	C_6H_6	71-43-2	2.13	1.99	2.1043	0.0657	0.0121
Methane	CH_4	74-82-8	1.09	0.78	1.0162	0.2844	0.0677
Ethane	C_2H_6	74-84-0	1.81	1.32	1.6319	0.2707	0.0984
Propane	C_3H_8	74-98-6	2.36	1.81	2.1782	0.2330	0.0770
Benzoic acid	$C_7H_6O_2$	65-85-0	1.87	1.87	2.2379	0	−0.1967
							MRAD
						0.10715	0.00765

substances: acetylene and olefins. The procedure has been applied to calculate the reaction rate with ozone for several substances. Table 3 contains the experimental reaction rate with ozone values for some representative chemical compounds as well as the results obtained using SAR. The results shown in Table 3, shows also the relative absolute deviation (RAD) of the reaction rate with ozone. As it can be noticed the method is able to calculate the reaction rate for isomers too (for example 2-butene cis and trans, 1-3 dichlorpropene cis and trans). The mean relative absolute deviation (MRAD) is 0.271. The results obtained using the SAR method are reasonable taking into account the complexity of the problem and the limited number of methods, software programs and experimental data available in the literature.

Reaction rate with hydroxyl

As it has been mentioned earlier, the reaction rate with hydroxyl radical has been evaluated using GCM and QSAR methods. The QSAR method has been implemented in the Atmospheric Oxidation Program (AOP). The MOOH-GCM method has been implemented in AM1-MOOH code developed by Klamt. The code runs under MOPAC software. The results obtained are presented in Table 4. Analyzing the results shown in Table 4, it can be noticed that the relative absolute deviation (RAD) between the experimental and the estimated values (see formula) is lower for eight substances using the QSAR method. Investigating the results, we can conclude that the QSAR method is more accurate for the estimation of reaction rate with hydroxyl than the GCM.

Process Sustainability Prediction Framework Application

Ten chemical processes have been simulated, using PROII and/or Aspen Plus process simulators, and analyzed using the PSP Framework. The processes can be divided, in the following four categories: (i) processes where one or more parameters have been modified: Acrylic Acid Production Process, Sweetening Natural Gas by DGA Absorption, Formaldehyde Production Process, Ethanol Production Process from Sugar Cane Molasses; (ii) processes where the same product is obtained starting from two different raw materials: Phthalic Anhydride Production Process, Maleic Anhydride Production Process, (iii) processes with heat integration: Dimethylether Production Process, R-134a Production Process, Multiple Effect of Sugar Cane Juice Process, (iv) processes with different streams recovery: Electroplating Wastewater Discharge Process. Details of all the ten processes[14]

Table 2. Lifetime of Different Chemical Substances

			Lifetime			
Substance Name	Substance Formula	Substance CAS	Experimental Value (days)	Methods Used to Measure Experimental Values	SAR AOP Value (days)	Lifetime RAD
Methanol	CH_4O	67-56-1	12	GC/FID PTR-MS	17.364	−0.4470
Toluene	C_7H_8	108-88-3	2	GC/FID GC/MS	2.047	−0.0235
Benzene	C_6H_6	71-43-2	10	GC/FID GC/MS	5.486	0.4514
Ethane	C_2H_6	74-84-0	45	GC/FID	39.323	0.1262
Propane	C_3H_8	74-98-6	11	GC/FID	8.432	0.2335
n-Butane	C_4H_{10}	106-97-8	5	GC/FID GC/MS	4.064	0.1872
Formaldehyde	H_2CO	50-00-0	1	DOAS	1.316	−0.3160
Acetone	C_3H_6CO	67-64-1	51	GC/FID PTR-MS	52.431	−0.0280
Ethanol	C_2H_5OH	64-17-5	4	GC/FID PTR-MS	2.991	0.2523
						MRAD
						0.04843

GC-FID, gas chromatography-flame ionization detection; GC-MS, gas chromatography-mass spectrometry; DOAS, differential optical absorption spectroscopy; PTR-MS, proton transfer reaction mass spectrometry.

Table 3. Reaction Rate with Ozone for Different Chemical Substances

Substance Name	Substance Formula	Substance CAS	Reaction Rate with Ozone: Experimental Values (cm^3/molecule-sec)	Reaction Rate with Ozone: AOP Values (cm^3/molecule-sec)	Reaction Rate with Ozone RAD
Acetylene	C_2H_2	74-86-2	4.8e −20	3e −20	0.375
Hexene	C_6H_{12}	592-41-6	1.17e −17	1.2e −17	−0.0256
1-pentene	C_5H_{10}	109-67-1	1e −17	1.2e −17	−0.2
1,3 dichlorpropene	$C_3H_4Cl_2$	10061-01-5	1.5e −19	1.126e −19 (cis)	0.249 (cis)
				2.25e −19 (trans)	−0.5 (trans)
2-butene	C_4H_8	107-01-7	2e −16	1.3e −16 (cis)	0.35 (cis)
				2e −16 (trans)	0 (trans)
1-propene	C_3H_6	115-07-1	1.13e −17	1.2e −17	−0.062
Ethene	C_2H_4	74-85-1	1.75e −18	1.75e −18	0
2-methyl 1-pentene	C_6H_{12}	763-29-1	1.31e −17	1.2e −17	0.084
					MRAD
					0.271

are available from the authors upon request. In this article, one representative example taken from the list above is reported in details.

In the example, we show: (i) that the PSP Framework is applicable to the process of interest and that could be used in direct connection with a process simulator for evaluating the sustainability of a process, (ii) the sensitivity of the process to the predicted values of toxicological data from molecular modeling and (iii) the use of the predictive methods to enhance the evaluation when the toxicological data are missing.

Maleic anhydride production process

Maleic anhydride is a versatile chemical intermediate used to make unsaturated polyester resins, lube oil additives, alkyd resins, and a variety of other products. There are different ways to obtain maleic anhydride. The most common ways are: (i) production of maleic anhydride from butane and (ii) production of maleic anhydride from benzene. Both process have been considered and simulated in the following section. The goal of this study is to analyze the processes, to evaluate the toxicological data of the substances involved in the processes and identify the best alternative in terms of environmental impact using the PSP methodology described in this work.

Production of maleic anhydride from butane (CASE 1). The described chemical plant is capable to produce 40 million pounds of maleic anhydride per year from n-butane. The following reactions occur when butane is mixed with oxygen:

$$\underset{\text{butane}}{C_4H_{10}} + 3.5O_2 \rightarrow \underset{\text{maleic anhydride}}{C_4H_2O_3} + 4H_2O$$

$$\underset{\text{butane}}{C_4H_{10}} + 5.5O_2 \rightarrow 2CO + 2CO_2 + 5H_2O$$

$$\underset{\text{butane}}{C_4H_{10}} + 3.5O_2 \rightarrow \underset{\text{acrylic acid}}{C_3H_4O_2} + CO_2 + 3H_2O$$

$$\underset{\text{butane}}{C_4H_{10}} + 6O_2 \rightarrow \underset{\text{formic acid}}{CH_2O_2} + 3CO_2 + 4H_2O$$

Process schema is presented in Figure 5. Pure butane, S2, and air, S1, are mixed and fed to the first rector R-1. The reaction is exothermic, therefore, one could consider either a fluidized bed or a packed bed reactor with heat removal. The reactor effluent, S5, is cooled and sent to the absorber F-1, where it is in contact with water, S7, to remove the light gases, S8. All maleic anhydride reacts with water, in R-2, to form maleic acid. The output reactor stream, S16, is flashed. The bottom flash stream, S12, is sent to R-3 where maleic acid is broken down to maleic anhydride and water. The reactor

Table 4. Reaction Rate with Hydroxyl for Different Chemical Substances

Substance Name	Substance Formula	Substance CAS	Reaction Rate with Hydroxyl: Experimental Value (cm^3/molecule-sec)	Reaction Rate with Hydroxyl: GCM AOP Value (cm^3/molecule-sec)	Reaction Rate with Hydroxyl: QSAR AM1-MOOH Value	Reaction Rate with Hydroxyl RAD: GCM-AOP RAD	Reaction Rate with Hydroxyl RAD: QSAR AM1-MOOH RAD
Methanol	CH_4O	67-56-1	9.44e −13	6.16e −13	9.3e −13	0.3470	0.0148
Toluene	C_7H_8	108-88-3	5.96e −12	5.226e −12	4.79e −12	0.1231	0.1963
Benzene	C_6H_6	71-43-2	1.23e −12	1.9498e −12	1.51e −12	−0.5852	−0.2280
Ethane	C_2H_6	74-84-0	2.68e −13	2.7e −13	3.51e −13	−0.0075	−0.3097
Propane	C_3H_8	74-98-6	1.15e −12	1.2686e −12	1.276e −12	−0.1031	0.1095
n-Butane	C_4H_{10}	106-97-8	2.54e −12	2.6322e −12	2.519e −12	−0.0363	0.0083
Formaldehyde	H_2CO	50-00-0	9.37e −12	8.13e −12	9.77e −12	0.1323	−0.0427
Acetaldehyde	CH_3CHO	75-07-0	15.8e −12	16.98e −12	15.5e −12	−0.0747	0.0189
Acetone	C_3H_6CO	67-64-1	2.19e −13	2.04e −13	2.3e −13	0.0685	−0.0502
Ethanol	C_2H_5OH	64-17-5	3.27e −12	3.5763e −12	3.27e −12	−0.0937	0
Dimethyl ether	CH_3OCH_3	115-10-6	2.98e −12	1.6592e −12	4.177e −12	0.4430	−0.4017

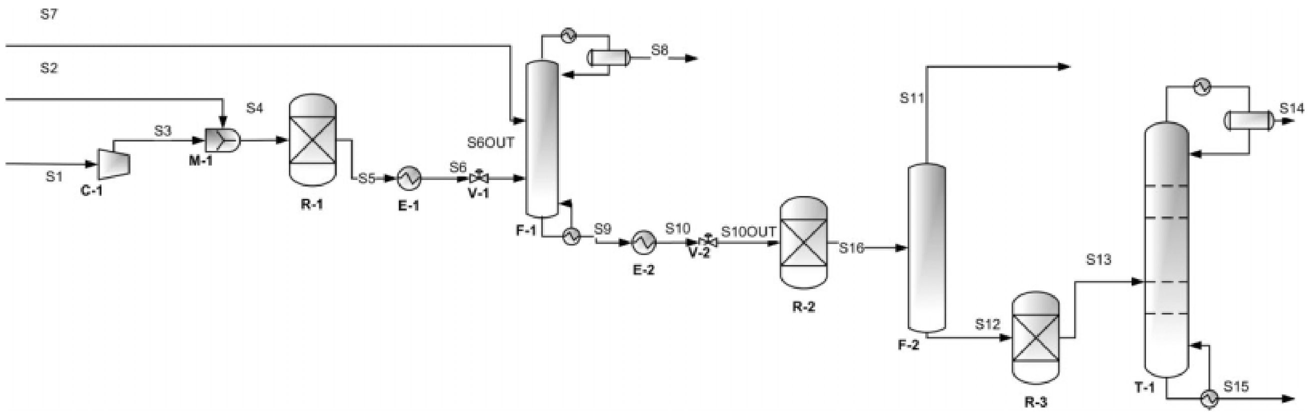

Figure 5. Maleic anhydride production process from butane.

effluent, S13, is sent to the distillation column T-1 where maleic anhydride and water are separated. The distillate, S14, is sent to waste treatment. The bottom stream, S15, consists of 99-wt% maleic anhydride.

Production of maleic anhydride from benzene (CASE 2). The following reactions occur during the reaction of benzene with oxygen:

$$\underset{\text{benzene}}{C_6H_6} + 4.5O_2 \rightarrow \underset{\text{maleic anhydride}}{C_4H_2O_3} + 2CO_2 + 4H_2O$$

$$\underset{\text{benzene}}{C_6H_{16}} + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$

$$\underset{\text{maleic anhydride}}{C_4H_2O_3} + 3O_2 \rightarrow 4CO_2 + H_2O$$

$$\underset{\text{benzene}}{C_6H_6} + 1.5O_2 \rightarrow \underset{\text{quinone}}{C_4H_4O_2} + 4H_2O$$

Process schema is shown in Figure 6. Benzene, S1, is vaporized in E-1 and mixed with compressed air, S4. The mixed stream, S6, is heated in E-2, prior to being sent to a packed catalytic reactor, R-1. The reactions described earlier take place in R-1. The reactor has been simulated as a plug flow reactor with 10% of input stream by-passing the reactor. The reactor effluent, S12, containing small amounts of un-reacted benzene, maleic anhydride, quinone and combustion products are cooled in E-3. Water can react with some maleic anhydride to form maleic acid. This phenomenon takes place in R-2. The R-2 output stream, S17, is sent to an absorber where it is contacted with heavy organic solvent (dibutyl phtalate), S16. This solvent absorbs the maleic anhydride, quinone, and small amounts of water. The F-1 top output stream, S18, contains off gasses, which are released into the atmosphere. The bottom stream, S19, is sent to T-1 where dibutyl phtahlate is recovered as the bottom product and recycled back to the absorber, S21. The product process,-maleic anhydride, S20, is obtained in the top of T-1 column.[43]

PSP framework application

Both processes have been simulated using PROII process simulator and their environmental impact has been estimated. The goal is to choose, from these two cases (production

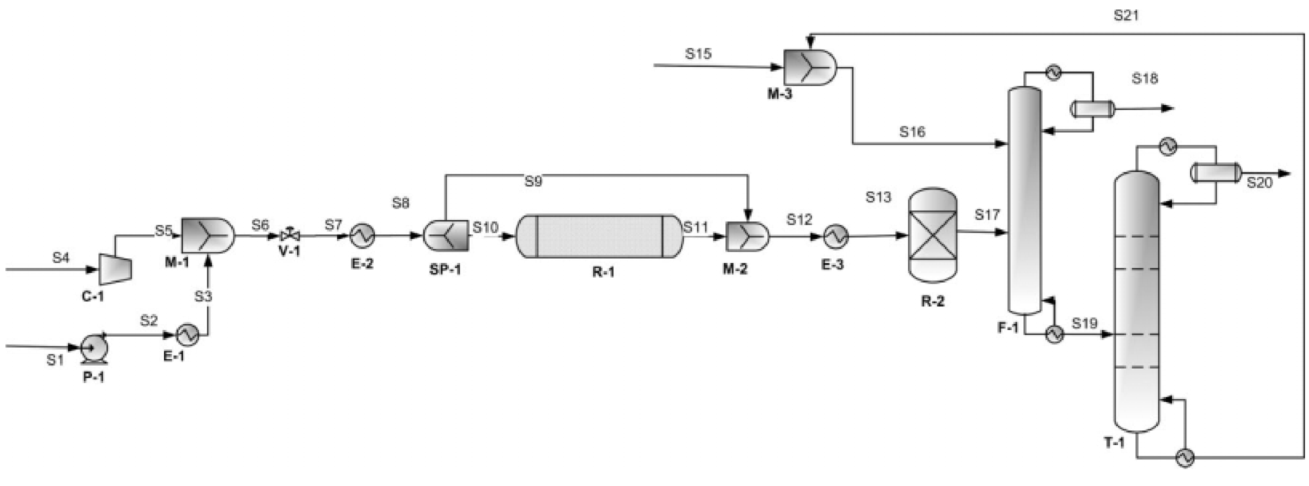

Figure 6. Maleic anhydride production process from benzene.

Table 5. 3D Indicators Obtained in the Maleic Anhydride Production Process

	3D Indicators			
Case Study	MI	EI	PCR	PEI
CASE 1	29,734.45	677.55	20,070	8776.601
CASE 2	7416.67	62.9629	10,110	16,289.101

from butane and production from benzene) the best process in terms of environmental impact. For this purpose, 3D and 1D indicators have been calculated using the mass flow-rates, the input and output streams composition (mass fraction) and toxicological and risk information data. The 3D indicators calculated using data from the process simulators and from the database are presented in Table 5. From Table 5, it can be noticed, MI, EI and PCR are lower in the second case while PEI is lower in the first alternative design. To decide which design is more environmentally friendly, 1D indicators must be considered.

Table 6 reports the environmental impact categories, as extracted from the EPA toxicological data base, that are directly used for the calculation of the 1D indicators according to the WAR Algorithm. Table 7 contains the Environmental Impact Indexes of the WAR Algorithm which are calculated in the PSP Framework by coupling the toxicological data reported in Table 6 with the mass flow-rates and composition of the input and output streams of the processes of interest. Taking into account the 1D indicators it can be noticed that the best alternative design in terms of environmental impact is the second one, CASE 2.

As it can be noticed from Table 6 not all the environmental impact categories for all substances are present in EPA's database: this is where molecular modeling comes into play. In fact, the molecular modeling techniques, described in the previous sections, have been used here to predict some thermo-physical properties which lead to the environmental impact categories calculation. The molecular modeling results are presented in Table 8. These thermo-physical properties lead to the environmental impact categories presented in Table 9.

To validate the proposed methodology, the values of one environmental impact category—HTPE for two substances (butane and benzene) have been replaced in the EPA' DB with the values calculated using MM techniques to evaluate the sensitivity of the final calculation to the estimation method of the thermo-physical properties. The results, in terms of Environmental Impact Indexes, are presented in Table 10. As it can be noticed from Table 10 the results in terms of Environmental Impact Indexes are very similar, showing that the experimental values can be safely substituted by the predicted ones.

These results allow as moving further more in this direction and completing some missing data of the original database with values calculated using MM techniques (from Table 9). The results obtained in this case are presented in Table 11. It can be noticed that the missing environmental impact categories inserted in the DB contribute to increase the values of the environmental impact indexes. The index reported in Table 11 should be considered more reliable of the ones reported in Table 10 because all the data for all the substances are now taken into account.

Comparing the results obtained using MM calculation the best environmental solution still remain the second alternative design: production of maleic anhydride from benzene.

Conclusions

This article presents and discusses a methodology to quantify the environmental impact of a chemical process. The methodology, used in the early stages of process design,

Table 6. Environmental Impact Categories of the Substances Involved in the Maleic Anhydride Production Process (data from EPA's DB)

	GWP	ODP	PCOP	HTPE	HTPI	TTP	AP	ATP
Production from butane								
Butane	–	–	0.8425	0.0001553	0.2867	0.2867	–	0.2867
CO_2	0.0003174	–	–	0.00003278	–	–	–	–
CO	–	–	–	0.0053647	–	–	–	–
Formic acid	–	–	–	0.03278	0.31982	0.31982	–	0.31982
Acrylic acid	–	–	–	0.05	10.5017	10.5017	–	10.5017
Maleic anhydride	–	–	–	0.295	0.8795	0.8795	–	0.8795
Maleic acid	–	–	–	–	0.4969	0.4969	–	0.4969
Production from benzene								
Maleic anhydride	–	–	–	0.295	0.8795	0.8795	–	0.8795
Dibutyl phtalate	–	–	–	0.05901	0.04397	0.04397	–	0.04397
Benzene	–	–	0.38837	0.092207	0.1064147	0.1064147	–	0.106415
Quinone	–	–	–	0.73765	2.706208	2.706208	–	2.706208
CO2	0.000317	–	–	0.00003278	–	–	–	–
Maleic acid	–	–	–	–	0.4969	0.4969	–	0.4969

Table 7. Environmental Impact Indexes Obtained in the Maleic Anhydride Production using WAR Algorithm

	Enivoronmental Indexes Name			
Case Study Name	Iout (PEI/hr)	Iout_mp (PEI/kg)	Igen (PEI/hr)	Igen_mp (PEI/kg)
Case 1	4056.57	1.54	1643.38	0.625
Case 2	1095.02	0.44	−988.00	−0.398

Table 8. Thermo-Physical Properties Obtained Using MM

	Log Kow (QSAR)	Log Kow (QM)	lifetimeOH (SAR) (hr)	lifetimeO3 (SAR) (hr)	rOH (SAR) (cm3/molecule-sec)	rO3 (SAR) (cm3/molecule-sec)
Production from butane						
Butane	2.31	3.078	48.762	–	2.63 E −12	–
CO_2	0.83	–	–	–	–	–
CO	1.78	1.71	18710.184	–	6.90 E −15	–
Formic acid	−0.46	−0.17	246.828	–	5.20 E −13	–
Acrylic acid	0.44	0.642	13.198	78.588	9.73 E −12	1.75 E −18
Maleic anhydride	1.62	1.29	56.894	78.588	2.26 E −12	1.75 E −18
Maleic acid	0.05	0.66	1.041	24.179	7.95 E −12	8.75 E −19
Production from benzene						
Maleic anhydride	1.62	1.29	56.894	78.588	2.26 E −12	1.75 E −18
Dibutyl phtalate	4.61	6.49	13.836	–	9.28 E −12	–
Benzene	2.1043	1.99	65.827	–	1.95 E −12	–
Quinone	0.25	0.5788	28.447	78.583	4.51 E −12	3.50 E −18
CO_2	0.83	–	–	–	–	–
Maleic acid	0.05	0.66	1.041	24.179	7.95 E −12	8.75 E −19

Table 9. Environmental Impact Categories of the Substances Involved in the Maleic Anhydride Production Process (Data Calculated Using MM Techniques)

	GWP	ODP	PCOP	HTPE	HTPI	TTP	AP	ATP
Production from butane								
Butane	–	–	0.6349	0.000145811	0.2691888	0.2691888	–	0.0454
CO_2	–	–	–	0.00003401	–	–	–	0.0024
CO	–	–	0.0017	0.005584308	–	–	–	0.0289
Formic acid	–	–	0.1254	0.038486484	0.3754409	0.3754409	–	0.0667
Acrylic acid	–	–	2.3455	0.040917836	8.5923	8.5923	–	0.0370
Maleic anhydride	–	–	0.5441	0.370544293	1.1044884	1.1044884	–	0.0060
Maleic acid	–	–	1.9172	0.001412429	0.3613818	0.3613818	–	0.2000
Production from benzene								
Maleic anhydride	–	–	0.5441	0.370544293	1.1044884	1.1044884	–	0.0060
Dibutyl phtalate	–	–	2.2375	0.06042072	0.0450192	0.0450192	–	0.5914
Benzene	–	–	0.4703	0.093333335	0.1077144	0.1077144	–	0.0167
Quinone	–	–	1.0882	0.708151296	2.1649664	2.1649664	–	0.0455
CO_2	–	–	–	0.00003401	–	–	–	0.0024
Maleic acid	–	–	1.9172	0.001412429	0.3613818	0.3613818	–	0.2000

Table 10. Environmental Impact Indexes Obtained in the Maleic Anhydride Production: Comparison Between Indexes Obtained Using Initial HTPE Value (EPA's DB) and HTPE Value Calculated Using MM

	Enivoronmental Indexes Name			
Case Study Name	Iout (PEI/hr)	Iout_mp (PEI/kg)	Igen (PEI/hr)	Igen_mp (PEI/kg)
Case 1 (initial)	4056.57	1.54	1643.38	0.625
Case 1 (MM calculation)	4056.56	1.54	1643.39	0.625
Case 2 (initial)	1095.02	0.44	−988.00	−0.398
Case 2 (MM calculation)	1095.37	0.44	−991.374	−0.399

Table 11. Environmental Impact Indexes Obtained in the Maleic Anhydride Production: Comparison Between Indexes Obtained Using Initial DB (EPA's DB) and Final DB (Containing Data Estimated with MM)

	Enivoronmental Indexes Name			
Case Study Name	Iout (PEI/hr)	Iout_mp (PEI/kg)	Igen (PEI/hr)	Igen_mp (PEI/kg)
Case 1 (initial)	4056.57	1.54	1643.38	0.625
Case 1 (MM calculation)	4123.51	1.57	1710.31	0.651
Case 2 (initial)	1095.02	0.44	−988.00	−0.398
Case 2 (MM calculation)	1329.60	0.53	−815.71	−0.32

allows choosing the most environmentally friendly design among different process alternatives. The present work has considered several issues for the definition of the PSP Framework developed: Sustainable development concept analysis; Identification of different indicators for sustainability evaluation; Development and implementation of a specific software, PSP Framework, for industrial sustainability evaluation; Development of a toxicological database;

Analysis and application of different molecular modeling techniques for evaluating the toxicity of chemical compounds; PSP Framework application in various case studies.

The software developed contains interesting elements such as: (i) CAPE OPEN Modules ready to be used in any process simulator which provides CO interfaces, (ii) a toxicological database, (iii) various support program codes developed in Visual Basic and (iv) a methodology for calculating missing toxicological data from molecular modeling.

The CO modules developed in this work can be directly used in any process simulator and they automatically transfer the necessary data from process simulator and from the toxicological data base for calculating the environmental indexes. The modules have been tested successfully using different process simulators such as: PROII, Aspen Plus, COCO/COFE.

A relational database containing about 4900 substances has been created and implemented. Different thermo-physical properties correspondent to some toxicological data, such as the environmental impact categories HTPI, HTPE, TTP, ATP, GWP, ODP, PCOP, AP for various chemical substances have been estimated using molecular modeling techniques. The molecular modeling techniques used are: QSAR, GCM, QM, and COSMO. For each estimated thermo-physical: octanol-water partition coefficient, lifetime, reaction rate with ozone, reaction rate with hydroxyl, representative results, discussions, and interpretations are reported.

Some support programs are also included in the PSP Framework. The programs are able: (i) to set the weighting factors for the environmental impact categories according to local and political needs; (ii) to calculate the 3D indicators: MI, EI, PCR, and PEI; (iii) to calculate the 1D indicators: Iout, Iout_mp, Igen and Igen_mp used in WAR Algorithm.

Ten processes, taken from the literature developed ad hoc starting from real processes located in developing countries, have been simulated and analyzed from the environmental point of view using the PSP Framework. The maleic anhydride production process is reported here as a case study where the application of the entire PSP Framework is shown (including the effect of the prediction of the environmental indexes from molecular modeling).

In conclusion, for the sustainable development of the chemical industry, it is essential to consider environmental issues at design time. The PSP Framework presented in this article provides a complete and reliable tool that can quantify the environmental impact of the process under study.

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