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A Hierarchical Approach for the Estimation of Environmental Impact of a Chemical Process: from Molecular Modeling to Process Simulation

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Abstract

The concept of sustainable development is a common one in the 21st century. The three important elements of the sustainability are: economy, society and environment. The chemical processes, which are directly connected with the economy, affect in different ways the environment and the society.
The Waste Reduction Algorithm (WAR Algorithm), the methodology developed by Cabezas with the goal of determining the potential environmental impact (PEI) of a chemical process, is used in this work as a decision support tool to choose the best environmental solution from different alternative design for a chemical process. The equations of the WAR Algorithm have been implemented in a standard computer code, CAPE OPEN, and the code was tested in different process simulators.
One possible limitation for the applicability of WAR Algorithm to a given process is the availability of toxicological data. At present the Environmental Protection Agency (EPA) has a databank of toxicological properties that covers 1707 compounds that may not be enough for some particular process. In this paper we present a methodology for predicating the toxicological data in the form compatible with the EPA data bank, from molecular modelling. Several different approaches are used for the estimation of the thermo-physical properties including quantum chemistry, molecular dynamics, Monte Carlo and QSAR.

Keywords: WAR Algorithm, Sustainability, Process simulation, CAPE OPEN, Molecular Modelling

1. Introduction

The concept of sustainable development is a common one in the 21st century. The field of chemical engineering plays an important role in the debate on sustainable development because the products of the chemical industry are absolutely essential to a modern society, but, in the meantime, it is well known that many environmental problems can be linked directly to the chemical processes or to the use of chemical products [1].
To reach the objective of sustainable development incorporation of environmental principles and constraints at the planning and design stage of new plants and processes is necessary. The design step of a chemical process together with the environmental procedures can give an answer to the following question: "Which design is more environmentally friendly, and implicitly more sustainable, for a specific chemical process?" Even if the previous question has an answer in the developed countries, this does not solve the problem of the global sustainability. A valid tool in developing and emerging countries is absolutely necessary for a complete support to the global sustainability.

2. Problem Statement, background

The WAR Algorithm is a methodology for determining the potential environmental impact (PEI) of a chemical process. A key element in the evaluation of environmental impact is represented by the calculation of environmental impact indexes. After the calculation, the indexes are used in a comparative manner, in the process design stage, to choose from different alternative design the best one [2, 3, 4]. In order to obtain the environmental information during the process design a process simulator should be used. The goal is to evaluate the friendliness or unfriendliness of a chemical process independently of the process simulator used. In this context the equations of the WAR Algorithm were implemented in a standard computer code, CAPE OPEN, and the code was tested in different process simulators. To evaluate the environmental impact toxicological data are required. When toxicological data are not available molecular modeling techniques can be used for their estimation.

3. Paper Approach

3.1 Methodology

A general schema regarding the implementation of WAR is presented in Table1. The WAR Algorithm was implemented in a CO Module using: CAPE-OPEN Unit Wizard 0.9.3 and Visual Basic (version 6.0). One subroutine of the program contains the code with the environmental impact equations balance. The unit operation has one input port, one output port and three real parameters. The ports make the connections with the streams of the process flow-sheet.

Table 1 Implementation of WAR Algorithm in CO

	STEPS	**Tools**	**Results**
1. Development of CO Unit Operation	1.1 Build the CO Unit Operation	CAPE-OPEN Unit Wizard	CO Unit Operation
	1.2 Modify the IcapeUnit_Calculate	VB, EPA Data Base	CO Unit Operation with WAR Algorithm
	1.3 Build the dll	VB	dll of CO
	1.4 Install the dll	VB	CO installed
	1.5 Test the CO Unit Operation	CAPE Tester	CO tested
2. Development of the process flow sheet	2.1 Design the flow sheet	Process Simulator	The flow sheet of the chemical process
	2.2 Define the components	Process Simulator	The flow sheet of the chemical process
	2.3 Define the thermodynamic method	Process Simulator	The flow sheet of the chemical process
	2.4 Define the streams	Process Simulator	The flow sheet of the chemical process
	2.5 Define the units operation	Process Simulator	The flow sheet of the chemical process
	2.6 Design specifications	Process Simulator	The flow sheet of the chemical process
3. Calculation of the chemical process impact	3.1 Recognize the CO Unit Operation in process simulator	Process Simulator	CO Unit Operation recognized in the process simulator
	3.2 Insert the CO Unit Operation in the chemical process flow sheet	Process Simulator	Process flow sheet for the chemical process with CO Modules
	3.3 Run the simulation	Process Simulator	The convergence of chemical process flow sheet
Calculation of the energy generation process impact	3.4 Insert the CO Unit Operation in the energy generation process flow sheet	Process Simulator	The flow sheet of the energy process
	3.5 Run the simulation	Process Simulator	The convergence of the energy process

Using the results of the process simulation (for the chemical process and for the energy generation process) and environmental data for eight impact categories the PEI is calculated. The eight impact categories taken into consideration are:

Global Worming Potential, Ozone Depletion Potential, Acidification Potential, Photochemical Oxidation Potential, Human Toxicity Potential by Ingestion, Human Toxicity Potential by Exposure, Terrestrial Toxicity Potential. The lack of toxicological data can be considered a limitation of WAR. In this case, molecular modelling methods are very useful and powerful tools for the estimation of environmental impact categories. A general schema regarding the molecular modelling methods used for the calculation of thermo-physical properties, and implicitly, for the calculation of environmental impact categories is presented in Fig. 1.

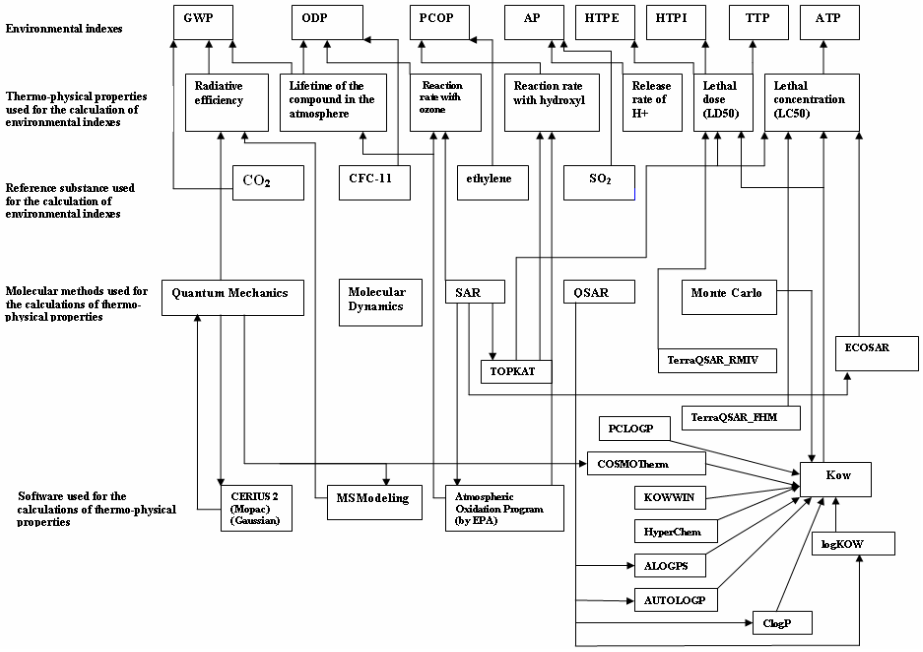

Fig. 1 Molecular modelling software used for the calculation of impact categories

In the example presented in this paper some impact categories are calculated using molecular techniques. The values calculated are compared with the values present in EPA's database and a sensitivity analysis to see the effect of the environmental impact categories on the final PEI is performed.

3.2 Case study

In the present work, the production of dimethyl ether(DME) from methanol was simulated using PROII process simulator. The plant is capable to produce 50.000 tons of DME per year via the catalytic dehydration of methanol. The essential operations in the process are the preheating of the raw material,

reacting methanol to form DME, product separation, contaminant separation and methanol separation and recycle. Fresh methanol is combined with recycled reactant and vaporized prior to being sent to a fixed bed reactor operating between 250°C and 368°C.The following reaction occurs in the reactor: 2 CH3OH→ (CH3)2O + H2O.The conversion of methanol in the reactor is 80%. The reactor effluent is cooled and sent to the first distillation column. DME product is obtained in the top of the first column. The second column separates the water from the unused methanol. The methanol is recycled back to the front end of the process, while the water is sent to waste water treatment to remove trace amounts of organic compounds [5].

3.3 Results & discussions

The WAR Algorithm was applied in two design alternative of the process. The first case corresponds to the description given above and the second case represents the process with heat integrated. The PEI obtained in both processes are presented in Table2 (Case1 and Case2). It has to be specified that the impact indexes presented above were calculated using values for impact categories present in EPA's database.

Table 2 PEI for DME production obtained using the CO method

Name of PEI	**Meaning of PEI**	**Name of the cases**		
		Case 1	Case 2	Case 3
Iout (PEI/hr)	The total rate of PEI leaving the system	160.75	153.18	153.14
Iout_mp0 (PEI/kg)	The total rate of PEI leaving the system per mass of product	2.75e-2	2.57e-2	2.57e-2
Igen (PEI/hr)	The total rate of PEI generated within a system	-2472.35	-2479.93	-2479.96
Igen_mp0 (PEI/kg)	The total rate of PEI generated within a system per mass of product	-0.4145	-0.4158	-0.4158

From the environmental point of view the best choice, between Case1 and Case2, is the second alternative design. Making the heat integration, the energy supplied from external source is minor so the impact of the energy generation (gaseous emissions) process will be minor. The choice of the second alternative design is stressed, one more time, by economical factor too. Less energy is supplied from external source so a less amount of money is spent for this alternative design.

The best solution between the two cases was simulated again using impact categories data estimated with molecular modelling techniques (Case3). Some impact categories data were estimated for methanol because it is present in the waste stream of the process. The value modified in the database was the

octanol-water partition coefficient. The value of the database *logKow = -0.*77 was calculated using QSAR methods. The new value *logKow = -1.53* was calculated using quantum chemical methods- COSMO*therm* software (version 2.1) [6]. The comparison between the environmental indexes obtained using the new value of octanol-water partition coefficient are presented also in Table2 (Case2 and Case3). It can be noticed that a modification of one property (octanol-water partition coefficient) has a minor impact on the final environmental impact indexes.

4. Conclusions and future work

A specific tool to choose the best environmental process design for a chemical plant was studied and developed. The attention was focused on the implementation of the algorithm in a general methodology. The methodology was applied to several processes and here is reported the process of production of DME. Another conclusion is that molecular modeling can be used for the estimation of impact categories and the results obtained are good. The procedure developed in this paper will be implemented in a framework: Process Sustainable Prediction (PSP) that will consider also the environmental risk of the substances. The paper will be presented at ICheaP-8, 24-27 June 2007, Ischia, Italy.

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