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EXERGY DISSIPATIONAND POTENTIAL PROFITS COMPARISON FOR SUSTAINABILITY ASSESSMENT OF VINYL CHLORIDE SYNTHETIC ROUTES GENERATED FROM 'CREATE-REACTIONSET' SOFTWARE THAT RUNS ON MATLB

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ABSTRACT
In this work, fourteen synthetic routes of vinyl chloride are generated from 'create-reactionset' software that runs on MATLAB using the molar constraints of all the molecules of the reactants, products and the by-products involved in the manufacture of one unit of vinyl chloride. In order to quantitatively evaluate the energy performance and the potential profits of the process routes, comparison of the fourteen synthetic routes showed that eight synthetic routes is heat absorbing reactions requiring energy input, while six are heat generating reactions resulting to negative energy quality. Route (R_9), with synthetic reaction Cl_2+HCl+O_2 + C_2H_4-->2H_2O + 3C_2H_3Cl, and with exergy dissipation of -1370.1563Kcal/g-mol and a potential profit of 51c/lb is considered as being sustainable. The comparison rendered it possible to rapidly screen out synthetic routes that are highly unlikely to be sustainable at the earliest possible stage thereby preventing the enormous expenditure required for developing such processes. Definitions and calculation formulas of exergy and potential profits of a substance, a mixture, a stream, and a unit (process) are illustrated.

KEYWORDS: Vinyl chloride, sustainability, process routes, software

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INTRODUCTION

Limiting energy utilization and achieving economically viable processes is one of the main challenges of chemical engineering at present for sustainable chemical process route development. To develop and design a less energy consuming processes and cost effective alternative to replace or retrofit a current inefficient process, it is essential to establish a method for quantitatively evaluating and comparing the energy performance and the potential profits of chemical processes.

The choice of chemical process routes is one of the major important decisions in the early stages of process design, especially processes involving energy intensive and less economic viable chemical reactions which are considered unprofitable and not sustainable (Cave and Edwards (1997). Chemical process route is defined as the raw material(s), and the sequence of reaction steps that convert them to the desired product(s) (Fan et al, 2007). To develop chemical process routes and design a greener alternative to replace or retrofit a current inefficient and inefficient process, it is essential to establish a method for accurate identification of all the possible alternative synthetic routes of manufacture and quantitatively evaluating the process energy efficiency and cost effectiveness (Palaniappan et al, 2002).

Vinyl chloride industry is an important to a nation's economic development; but its process routes require high consumption of energy making its operation and production cost intensive (Edwards and Lawrence, 1993). However, the material stream in a vinyl chloride process routes are multi-component mixtures and its integrative energy efficiency should be estimated with respect to the exergy of each substance in the stream and the overall stream composition in order to estimate the profit potentials of any of the synthetic routes (Lakshmanan and

Beigler1997). Exergy of each substance in vinyl chloride synthetic route is regarded as an integrated value considering different categories of energy (physical and chemical energy) in vinyl chloride process route (Graveland and Gisolf, 1998).

The sustainability-potential of any chemical process synthetic route is a notion of profit-potential which makes it possible to screen out economically non-viable processes from the alternative synthetic routes at the earliest development stage (Fan et al, 2007). In this work, "comparison of exergy dissipation and potential profits" method is proposed in order to quantitatively identify all possible routes of vinyl chloride in order to find out their energy utilization and profit potentials.

EXERGY ANALYSIS

Exergy analysis provides a powerful tool for assessing the quality of energy and quantifying the portion of energy that can be practically recovered in chemical processes although not all forms of energy are equally valuable for energy recovery (Moran and Sciubba, 1994). For example, in an energy balance, 1,000 Btu of low pressure steam would compare equally to 1,000 Btu of electricity. In reality, the low-pressure steam has less than a third as much usable energy as the electricity. The steam could be used for heating until its temperature is brought down to the plant environment temperature. At this point the gas still contains energy, but the energy is not useful or available for recovery hence, it has no exergy.

Exergy dissipation of the alternative synthetic routes are obtained from the combination of first and second laws of thermodynamics which accounts for every material species involved in the process (Moran and Sciubba, 1994). Exergy analysis is useful in identifying the causes, magnitudes and locations of process inefficiencies through the application of the principle which shows that energy cannot be created or destroyed, but can be degraded in quality (Moran and Sciubba, 1994). Hence, exergy analysis is useful in improving the efficiency of energy-resource use, quantifies, locations, types and magnitudes of wastes and losses (Moran and Sciubba, 1994).

'CREAT_REACTIONSET' SOFTWARE: This software runs on matrix Laboratory (MATLAB) which is a commercial software product available from the Mathworks (http://www.mathworks.com/) and creates reaction matrices reactset based on a set of plausible reactions generated by mass balances. It is assumed that the relative molecular mass (RMM) for each species is known exactly. It creates reactionset for system of R_order by generating a reaction matrix set reactset based on the system specified by system. R_order is the maximum reaction order for each side of a stoichiometric equation. It uses a default reaction order of 2 to allow for general case of atomic matrix in the field of system relative molecular mass (RMM) and also create additional equations N fields in which equations that is stoichiometrically equivalent equations are removed (such as equations with terms on both sides) and stoichiometric multiples are removed. In this article, a software, 'create_reactionset' that on MATLAB is used to generate all possible process routes of vinyl chloride before their sustainability potential assessment.

METHODOLOGY

The methodology proposed for this work encompasses two parts: (i) identification of all the possible synthetic route of vinyl chloride manufacture using 'create-reactionset' software that runs on MATLAB, (ii) comparison of all the generated synthetic routes using criteria of available energy (or exergy) dissipation and potential profit. This methodology will help to pinpoint vinyl chloride process route inefficiencies, the quality of energy losses and analyses the profit potentials that can be derived from each synthetic route.

(i) Identifying all the likely synthetic route of vinyl chloride using software that runs on MATLAB 'create-reactionset':

First, knowing that the component processes reactions of vinyl chloride manufacture are represented thus (Lakshmanan and Beigler, 1997):

Direct chlorination of ethylene: $C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$

Oxychlorination of ethylene: $C_2H_4 + 2HCl + ½O_2 \longrightarrow 2C_2H_4Cl_2 + H_2O$

Pyrolysis of ethylene dichloride: $C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$

Hydrochlorination of acetylene: $C_2H_2 + HCl \longrightarrow C_2H_3Cl$

Using software 'create-reactionset'that runs on MATLAB, the molar balance of the reactants (C_2H_2, Cl_2, O_2, HCl), intermediates (C_2H_4Cl), target product (C_2H_3Cl) and the by-product (H_2O) are fed in a matrix structure to generate all potential synthetic routes of vinyl chloride manufacture.

Table 1: Matrix of molar constraints of all species for vinyl chloride manufacture

Tag	A	B	C	D	E	F	G	H
Species	Cl_2	HCl	H_2O	C_2H_3Cl	O_2	C_2H_4	C_2H_2	$C_2H_4Cl_2$
Cl	2	1	0	1	0	0	0	2
H	0	1	2	3	0	4	2	4
O	0	0	1	0	2	0	0	0
C	0	0	0	2	0	2	2	2

The species tagged A= Cl_2, B= HCl, C= H_2O, D= C_2H_3Cl, E= O_2, F= C_2H_4, G= C_2H_2 and H= $C_2H_4Cl_2$ respectively.

(ii) Comparison of all the generated synthetic routes using criteria of available energy (or exergy) dissipation and potential profit:

Assumptions:

(i) The reactants (precursors) are the exact stoichiometric ratio reactant isothermally, and are completely converted to the products in an idealized reaction space or reactor.

(ii) The individual reactants enter the reactor separately and individual reaction products leave the reactor also separately.

Table 2: Chemical exergies and Unit price of the reacting species

Reacting Species	Chemical energies (Kcal/g-mol)	Unit price (c/lb)
C_2H_4 (gas)	324	36
C_2H_2 (gas)	301.24	64
Cl_2 (gas)	123.8	17
O_2 (gas)	0.9263	0
HCl (gas)	1980.79	4
C_2H_3Cl	353.12	36
H_2O	0	0

Source: www.chemical market Reporter January 17, 2005. Vol. 265, No. 3, p31 for unit price

Exergy dissipation of any synthetic route, i, $(\Delta\epsilon_{o,i})$: This is evaluated as the difference between the sum of the chemical exergies of the final reaction products and the starting reactants.

$$\Delta\epsilon_o, i = \left(\sum_{products}(v\epsilon_o)products\right) - \left(\sum_{reactants}(v\epsilon_o)reactants\right) \quad (1)$$

Applying second law of thermodynamics, exergy dissipation of an isolated system where the system or reactor resides is magnified when physiochemical processes like heat transmission into or out of the system or reactor maintain isothermal condition and mixing of the reactant species. Hence, it is unlikely that any synthetic route whose exergy dissipation, $\Delta\epsilon_o$ is excessively more negative will be sustainable.

Potential profit of any synthetic route i ($\Delta\varsigma_i$): This calculated as the revenue derived from the sales of the final reactions products which are the sum of the unit prices of the pure final reaction products ($\sum products(v\varsigma)products$) minus that of the pure starting reactant(s) ($\sum reactants(v\varsigma)reactants$).

$$(\Delta\varsigma_i) = \sum_{Product}(v\varsigma)products - \sum_{Reactants}(v\varsigma)reactants \quad (2)$$

Pure chemicals prices are obtained from the Chemical Marketing Reporter *(www.chemical marketerporter.com)* for the computations of the potential profit of the synthetic routes. From the computations of the potential profit of each individual synthetic route, any synthetic route with a positive potential profit ($\Delta\varsigma_i > 0$) is regarded as being sustainable.

RESULTS AND DISCUSSION

Table 3:Routes, Software equation, Synthetic reaction, Exergy Dissipation and Potential Profits

Route	*Software equation*	*Synthetic Reaction*	Energy dissipation, Kcal/g-mol	POTENTIAL PROFIT ,c/lb
1	A + F + G --> 2D	Cl_2+C_2H_4+C_2H_2--> 2C_2H_3Cl	-42.80	-45.00
2	A + F --> B + D	Cl_2 + C_2H_4 --> HCl + C_2H_3Cl	1886.11	-13.00
3	B + G --> D	HCl+C_2H_2 -->C_2H_3Cl	-1928.91	-32.00
4	3A + 3F + G--> 2B + 4D	3Cl_2+3C_2H_4 + C_2H_2 -->2HCl +4C_2H_3Cl	3729.42	-71.00
5	3A + 3F --> 3B + 3D	3Cl_2 + 3C_2H_4 --> 3HCl + 3C_2H_3Cl	5658.33	-39.00
6	2A + 2F + 2G --> 4D	2Cl_2 + 2C_2H_4 +2C_2H_2 --> 4C_2H_3Cl	-85.84	-90.00
7	2A + 2F + G --> B + 3D	2Cl_2 + 2C_2H_4 + C_2H_2 --> HCl + 3C_2H_3Cl	1843.31	-58.00
8	A + 2B + F + 3G --> 4D	Cl_2 + 2HCl + C_2H_4 + 3C_2H_2--> 4C_2H_3Cl	-3900.62	-109.00
9	A + B + E + 3F --> 2C + 3D	Cl_2 + HCl + O_2 + C_2H_4 -->2H_2O + 3C_2H_3Cl	-1370.16	51.00
10	2B + E + 2F --> 2C + 2D	2HCl + O_2 + 2C_2H_4 -->2H_2O + 2C_2H_3Cl	-3904.27	-8.00
11	2A +B + E +4F +G--->2C+ 5D	2Cl_2+HCl +O_2 +4C_2H_4 + C_2H_2 --> 2H_2O +5C_2H_3Cl	-2060.96	-66.00
12	A + 3B + E + 3F + 2G-->2C+5D	Cl_2+3HCl +O_2 +3C_2H_4+2C_2H_2 -->2H_2O+ 5C_2H_3Cl	-5875.98	-85.00
13	5A + 5F + 2G--> 2B + 7D	5Cl_2 + 5C_2H_4 + 2C_2H_2--> 3HCl + 7C_2H_3Cl	5572.73	-129.00
14	4A + 4F + 4G --> 8D	4Cl_2 + 4C_2H_4 + 4C_2H_2-->8C_2H_3Cl	-171.20	-180.00

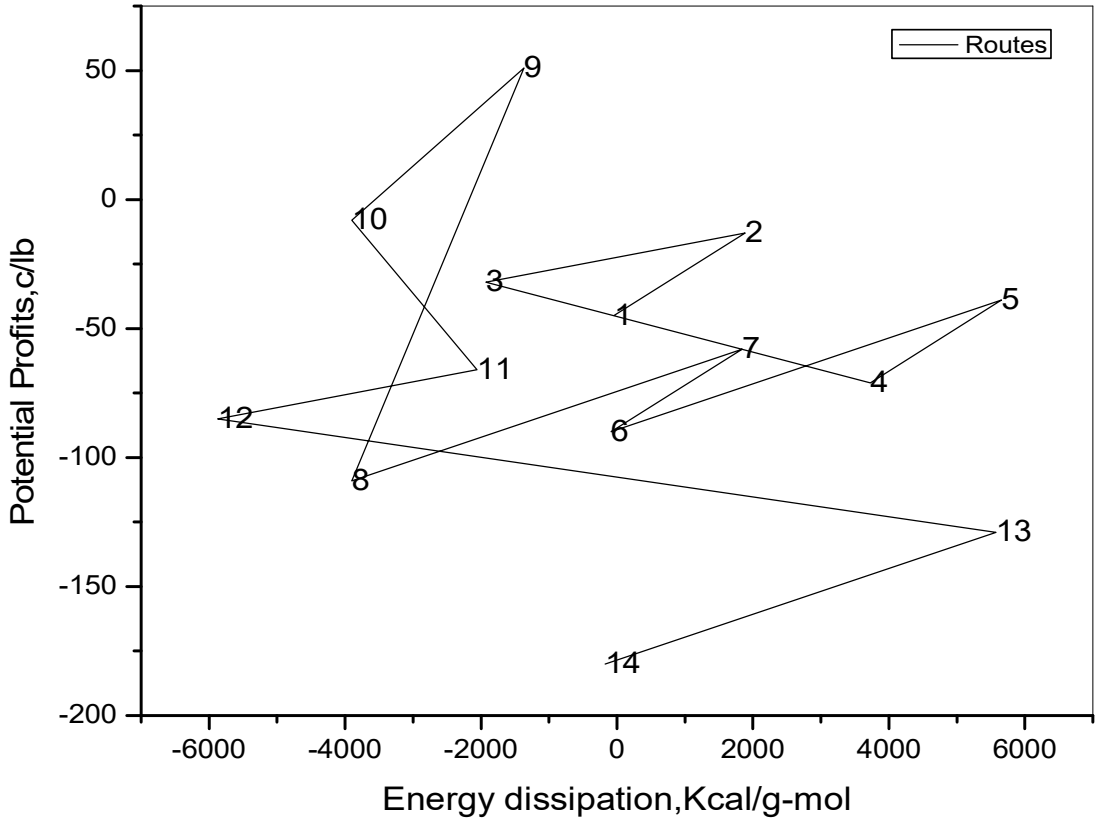

Table 4: Graph showing exergy dissipation and potential profits comparison of vinyl chloride synthetic routes

From Table 3, fourteen synthetic routes of vinyl chloride were generated from 'create-reactionset' software that runs on MATLAB. Eight synthetic routes are heat absorbing reactions (endothermic reactions) requiring energy input, while six are heat generating reactions (exothermic reactions) resulting to negative energy quality. Comparison of the result obtained, show that route (R_9), of synthetic reaction $Cl_2 + HCl + O_2 + C_2H_4 \rightarrow 2H_2O + 3C_2H_3Cl$ with exergy dissipation of -1370.1563 Kcal/g-mol and a potential profit 51c/lb, has a positive potential profit, which is greater than zero ($\Delta\varsigma_i > 0$) . Also from the graph of figure 1, it shows comparison of exergy dissipation and potential profits of vinyl chloride synthetic routes is considered as being sustainable sine the profit potential is positive.

CONCLUSION

The fundamental basis of this work was to compare exergy dissipation and potential profit of all the possible synthetic route of vinyl chloride, to determine their energy efficiencies and profit possibilities. The fourteen vinyl chloride synthetic routes are obtained from stimulation result of the software 'create-reactionset'that runs on MATLAB. Comparison of synthetic routes renders it possible to rapidly screen out all vinyl chloride process routes that are highly unlikely to be sustainable, at the earliest possible stage, thereby preventing the enormous expenditure required for developing such processes. This proposed method of comparison can be applicable to any chemical process manufacture to assess its sustainability potential.

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