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SUSTAINABILITY ASSESSMENT OF VINYL CHLORIDE PROCESS ROUTES GENERATED FROM SOFTWARE 'CREATE-REACTIONSET'THAT RUNS ON MATLAB

Nwali C. J.
Industrial Chemistry Department, Ebonyi State University PMB 053, Abakaliki, Ebonyi State

ABSTRACT
The sustainability assessment of vinyl chloride process routes was studied by exhaustive identification of all alternative synthetic routes generated from MATLAB software 'create_reaction set', and hierarchically assessments of all the identified synthetic routes in terms of available energy (or exergy) dissipation, potential profit and toxicity index. The results showed nine feasible routes for the manufacture of vinyl chloride, although through manual decision fourteen synthetic routes are identified. Assessment using criteria of available energy (or exergy) dissipation showed that eleven synthetic routes are further assessed in terms of other criteria eliminating three routes. Also assessment using criteria of potential profit, synthetic route 8, (Cl_2 + 2HCl + C_2H_4 + $3C_2H_2$--> $4C_2H_3Cl$) with a potential profit of 51¢/lb was considered for further assessment in terms of the toxicity eliminating other synthetic routes. Synthetic route 8 is assessed in terms of the toxicity as the only synthetic route that survived all the scrutiny , hence considered sustainable. Assessment of all the identified alternative synthetic routes render it possible to rapidly screen out process routes that are highly unlikely to be sustainable, at the earliest possible stage, thereby preventing the enormous expenditure required for developing such processes.

KEYWORDS: Sustainability, chemical process, synthetic routes, software

INTRODUCTION

Choice of chemical process synthetic routes is one of the major key decisions in the early stages of process design, especially processes involving toxic and hazardous chemical reactions which are considered unsafe and not sustainable (FanL, 2007). The chemical process route is defined as the raw material(s), and the sequence of reaction steps that convert them to the desired product(s) (FanL., 2007). To develop chemical process routes and design a greener alternative to replace or retrofit a current inefficient and hazardous process, it is essential to establish a method for accurate identification of all the possible alternative synthetic routes of manufacture and quantitatively evaluating the energy efficiency, cost and health, safety and environmental impact of the process (Xiangping, 2008).

The sustainability-potential of a 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 (FanL. H, 2007). This can be achieved through individual alternative synthetic route assessment in downward order of quantifiability, in terms of exergy dissipation (physical, thermal, and chemical exergy), the potential profit, and the toxicity index(Palaniappan, 2002).

The available energy balance from 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 (Graveland, 1998).However, according toGraveland, exergy analysis is useful in identifying the causes, magnitudes and locations of process inefficiencies. Available energy (or exergy) analysis applies the principle which shows that energy cannot be created or destroyed, but can be degraded in quality. It is useful in improving the efficiency of energy-resource use, quantifies, locations, types and magnitudes of wastes and losses (Graveland, 1998).

Chemical process sustainability-potential comprises many factors such as material and energy requirements; profit and cost; health and safety effects; environmental and ecological impacts; regulatory constraints and societal concerns (FanL. H, 2007). The safety and health effects of the synthetic routes are determined in terms of the toxicity indices of the materials involved in the process (Tyler, 1996). The Performance of process route with respect to thermodynamics is evaluated in terms of the available energy (or exergy) dissipation due to the reaction(s), subject to criteria on the basis of the extent of dissipation (Graveland, 1998).

Chemical process route selection is defined as the raw material(s) and the sequence of reaction steps that converts them to the desired product(s) (Edwards, 1993). Therefore, chemical process route with least potential hazard to the environment are usually selected in the early stage of plant design and development for inherently environmentally friendly (Edwards, 2004). During this stage the objectives is to identify the hazards and processing problems that are associated with reactions, and chemicals involved in the process route and rank the available process routes (Tyler,1996). However, in this stage, raw materials, byproducts, intermediates, catalysts, and the reaction conditions are selected with respect to into intended and unintended reactions (Edwards, 1996).

The benefits of sustainability potentials assessment encompasses economic benefits through cost savings by reduce raw materials usage and energy efficiency, health and safety benefits by reducing the risk associated with handling hazardous materials, and legal benefits by reducing the risk of breaching environmental regulations (Achour, 2005).

'CREAT_REACTIONSET SOFTWARE: This 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 comprises two parts: (i) identification of all the possible synthetic route of vinyl chloride manufacture using MATLAB software set-up 'create-reactionset', and (ii) assessment of all the generated synthetic routes using criteria of available energy (or exergy) dissipation, potential profit and toxicity index.

(i) Identification of all the possible synthetic route of vinyl chloride manufacture using MATLAB software set-up 'create-reactionset': 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 MATLAB software set-up 'create-reactionset' to generate all potential synthetic routes of vinyl chloride manufacture. Using the component processes reactions of vinyl chloride manufacture represented thus (Lakshmanan,1997):

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

Oxychlorination of ethylene: $C_2H_4 + 2HCl + \frac{1}{2}O_2 \rightarrow 2C_2H_4Cl_2 + H_2O$

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

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

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

Species	A Cl_2	B HCl	C H_2O	D C_2H_3Cl	E O_2	F C_2H_4	G C_2H_2	H $C_2H_4Cl_2$
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) Assessment of all the generated synthetic routes using criteria of available energy (or exergy) dissipation, potential profit and toxicity index:

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, Unit price and toxicity index of the reacting species

Reacting Species	Chemical energies (Kcal/g-mol)	Unit price (₵/lb)	Toxicity Index
C_2H_4 (gas)	324	36	4
C_2H_2 (gas)	301.24	64	4
Cl_2 (gas)	123.8	17	5
O_2 (gas)	0.9263	0	4
HCl (gas)	1980.79	4	1
C_2H_3Cl	353.12	36	5
H_2O	0	0	4

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

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

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

Hence, the mean value of available energy (or exergy) dissipation of any of the synthetic route $(\Delta\epsilon_o)$ is given as:

$$\overline{\Delta\epsilon_o}=\frac{\sum_{i=1}^{N}\Delta\epsilon_{o,i}}{N} \quad (2)$$

Where N is the number of synthetic routes

The standard deviation of available energy (or exergy) dissipation of any of the synthetic route of the $(\Delta\epsilon_{o,i})$ values from the mean is then calculated as:

$$\delta_{\Delta\epsilon_o}=\sqrt{\frac{1}{N}\sum_{i=1}^{N}(\Delta\epsilon_o,i-\overline{\Delta\epsilon_o})^2} \quad (3)$$

Applying second law of thermodynamics, the available energy (or 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. This implies, that it is unlikely that synthetic route whose available energy (or exergy) dissipation, $\Delta\epsilon_o$ is excessively more negative than average available energy (or exergy) dissipation, $\overline{\Delta\epsilon_o}$ will be sustainable. However, any alternative synthetic route that will be considered for further assessment in terms of other criteria are those ones whose negative difference between it's available energy (or exergy) dissipation, $\Delta\epsilon_o$ and average available energy (or exergy) dissipation, $\overline{\Delta\epsilon_o}$ value is negative standard deviation of the $\Delta\epsilon_{o,i}$ values from the mean $(-\delta_{\Delta\epsilon_o})$ or greater. Thus, variance of the mean values of available energy (or exergy) dissipation $(\Delta\epsilon_o), L\Delta\epsilon_o$ is then computed as:

$$L\Delta\epsilon_o = \overline{\Delta\epsilon_o} - \delta_{\Delta\epsilon_o} \quad (4)$$

The value of variance of the mean values of available energy (or exergy) dissipation $(\Delta\epsilon_o), L\Delta\epsilon_o$ serves as the lower bound for eliminating any synthetic route on the basis of exergy dissipation.The variance of the mean values of available energy (or exergy) dissipation $(\Delta\epsilon_o), L\Delta\epsilon_o$ serves as the lower bound for eliminating any synthetic route as it measures the volatility or the risk that might be taken into account choosing a specific route.
Potential profit:Alternative synthetic route that are considered for further assessment in regards of potential profit are these routes that survive the scrutiny of the available energy (or exergy) dissipation. Potential profit of any synthetic route i $(\Delta\varsigma_i)$ is 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 reactants $(\sum reactants(v\varsigma)reactants)$.

$$(\Delta\varsigma_i) = \sum_{Product}(v\varsigma)products - \sum_{Reactants}(v\varsigma)reactants \quad (5)$$

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 and therefore is worthy of further assessment in terms of toxicity indices, otherwise unsustainable, hence eliminated. $\Delta\varsigma_i > 0$ (6)

Toxicity index:Databaseadopted for this work is a quantitative carcinogenicity database available in public domain in: http://:monographs.iarc.fr/ENG/Classications/index.php. Using this database, five groups of chemicals or reagents is assigned five indices according to the level of toxicity to humans comprising (Table 3).

Table 3: Assigned five indicesofchemicals according to the level of toxicity to humans

Chemical group	Assigned indices	Toxicity index
Group 1	Chemicals that are carcinogenic to humans	1
Group 2A	Chemicals that are probably carcinogenic to humans	2
Group 2B	Chemicals that are possibly carcinogenic to humans	3
Group 3	Chemicals that are not classified in regards to their carcinogenicity to humans.	4
Group 4	Chemicals that are probably not carcinogenic to humans	5

The toxicity index of a reacting species not in the database will be estimated from those of similar chemicals found in the database and hence, the overall toxicity index of a synthetic route i represented by TID_i will be calculated as the sum of the toxicity indexes of all reacting species $(Tidj)$ involved in the overall reaction.

$$TID_i = \sum_{J=1}^{N_i'} (v.tid)j \quad (7)$$

Where N_i' is number of reacting species in the overall reaction of synthetic route i

The mean overall toxicity index of a synthetic route (TID_i) values from all the synthetic route is the calculated using the equation below,Where N' is number of these synthetic routes

$$\overline{TID}_i = \frac{\sum_{i=1}^{N'} (v.tid)j}{N'} \quad (8)$$

The standard deviation of the overall toxicity index of a synthetic route $(TIDi)$ a value from the mean is the calculated using the equation thus:

$$\delta_{TID} = \sqrt{\frac{1}{N'} \sum_{i=1}^{N'} (\mathrm{TID}_i - \overline{TID})^2} \quad (9)$$

However, the higher the toxicity index, then the lower the toxicity of a synthetic route, hence the greater the value of TID_i, the grater sustainability of the synthetic route.

Therefore, the variance of the mean values of the overall toxicity index of the synthetic route L_{TID} is computed as the negative difference between TID_i and $\overline{TID}$ values as:

$$L_{TID} = \overline{TID}\delta_{TID} - \delta_{TID} \quad (10)$$

At this point the variance of the mean values of the overall toxicity index of the synthetic routes, L_{TID}, serves as the lower bound for weeding out any synthetic route on the basis of toxicity index. Synthetic routes that have survived all the scrutiny of available energy dissipation, potential profits and toxicity index are tentatively deemed worthy of further development through pilot-scale experimentation and/ or preliminary design or process synthesis, hence proven to be sustainable through the assessment.

RESULTS AND DISCUSSION

Table 4: Identified alternative synthetic routes of vinyl chloride manufacture

Route	*Software equation*	*Synthetic Route equation*
$Route_1$	A + F + G --> 2D	$Cl_2 + C_2H_4 + C_2H_2$--> $2C_2H_3Cl$
$Route_2$	A + F --> B + D	$Cl_2 + C_2H_4$ --> $HCl + C_2H_3Cl$
$Route_3$	B + G --> D	$HCl + C_2H_2$ --> C_2H_3Cl
$Route_4$	3A + 3F + G--> 2B + 4D	$3Cl_2 + 3C_2H_4 + C_2H_2$ -->$2HCl + 4C_2H_3Cl$
$Route_5$	3A + 3F --> 3B + 3D	$3Cl_2 + 3C_2H_4$ --> $3HCl + 3C_2H_3Cl$
$Route_6$	2A + 2F + 2G --> 4D	$2Cl_2 + 2C_2H_4 + 2C_2H_2$--> $4C_2H_3Cl$
$Route_7$	2A + 2F + G --> B + 3D	$2Cl_2 + 2C_2H_4 + C_2H_2$--> $HCl + 3C_2H_3Cl$
$Route_8$	A + 2B + F + 3G --> 4D	$Cl_2 + 2HCl + C_2H_4 + 3C_2H_2$--> $4C_2H_3Cl$
$Route_9$	A + B + E + 3F --> 2C + 3D	$Cl_2 + HCl + O_2 + C_2H_4$-->$2H_2O + 3C_2H_3Cl$
$Route_{10}$	2B + E + 2F --> 2C + 2D	$2HCl + O_2 + 2C_2H_4$-->$2H_2O + 2C_2H_3Cl$
$Route_{11}$	2A +B + E +4F +G-->2C+ 5D	$2Cl_2$+HCl +O_2 +$4C_2H_4 + C_2H_2$->$2H_2O$ +$5C_2H_3Cl$
$Route_{12}$	A + 3B + E + 3F + 2G-->2C+5D	Cl_2+3HCl +O_2+$3C_2H_4$ +$2C_2H_2$->$2H_2O$+ $5C_2H_3Cl$
$Route_{13}$	5A + 5F + 2G--> 2B + 7D	$5Cl_2 + 5C_2H_4 + 2C_2H_2$-->$3HCl + 7C_2H_3Cl$
$Route_{14}$	4A + 4F + 4G --> 8D	$4Cl_2 + 4C_2H_4 + 4C_2H_2$--> $8C_2H_3Cl$

Table 5: Energy dissipation, Potential Profit and toxicity indexof vinyl chloride synthetic routes

Synthetic Route equation	Energy dissipation $(\Delta\epsilon_o)$, Kcal/g-mol	Potential Profit $(\Delta\varsigma_i)$, ₵/lb	Toxicity index
$Cl_2 + C_2H_4 + C_2H_2$--> $2C_2H_3Cl$	-42.8	-45	-
$Cl_2 + C_2H_4$ --> $HCl + C_2H_3Cl$	1886.11	-13	-
$HCl + C_2H_2$ --> C_2H_3Cl	-1928.91	-32	-
$3Cl_2 + 3C_2H_4 + C_2H_2$ -->$2HCl + 4C_2H_3Cl$	3729.42	-71	-
$3Cl_2 + 3C_2H_4$ --> $3HCl + 3C_2H_3Cl$	5658.33	-39	-
$2Cl_2 + 2C_2H_4 + 2C_2H_2$--> $4C_2H_3Cl$	-85.84	-90	-
$2Cl_2 + 2C_2H_4 + C_2H_2$--> $HCl + 3C_2H_3Cl$	1843.31	-58	-
$Cl_2 + 2HCl + C_2H_4 + 3C_2H_2$--> $4C_2H_3Cl$	-3900.62	51	23
$Cl_2 + HCl + O_2 + C_2H_4$-->$2H_2O + 3C_2H_3Cl$	-1370.1563	-	-
$2HCl + O_2 + 2C_2H_4$-->$2H_2O + 2C_2H_3Cl$	-3904.2663	-66	-
$2Cl_2$+HCl +O_2 +$4C_2H_4 + C_2H_2$->$2H_2O$ +$5C_2H_3Cl$	-2060.96	-	-
Cl_2+3HCl +O_2+$3C_2H_4$ +$2C_2H_2$->$2H_2O$+ $5C_2H_3Cl$	-5875.98	-	-
$5Cl_2 + 5C_2H_4 + 2C_2H_2$-->$3HCl + 7C_2H_3Cl$	5572.73	-129	-
$4Cl_2 + 4C_2H_4 + 4C_2H_2$--> $8C_2H_3Cl$	-171.2	-180	-

Mean available energy (or exergy) dissipation of the synthetic routes, $(\overline{\Delta\epsilon_o})$ is -46.48Kcal/g-mol. The standard deviation of the available energy or exergydissipation of the synthetic routes of from the mean $(\delta_{\Delta\epsilon_o})$ is 3367.62. While, variance of exergy dissipation of the synthetic routes $(L\Delta\epsilon_o)$ is -3414.1.

From the results, route1, 2, 3, 4, 5, 6, 7, 8, 10, 13 and 14 are considered for further assessment in terms of potential profit criteria since theirnegative difference between it's $\Delta\epsilon_o$ and $\Delta\epsilon_o$ values is $(-\delta_{\Delta\epsilon_o})$ or greater,while 9, 11 and 12 are eliminated. Also, synthetic route 8with potential profit greater than zero ($\Delta\varsigma_i > 0$) is further assessment in terms of toxicity indices, while synthetic routes 1, 2, 3, 4, 5, 6, 7, 10, 13 and 14 are eliminated.Toxicity index of synthetic route 8 is obtained as 23, showing that the toxicity index of synthetic route 16 is low and hence sustainable.

CONCLUSION

This methodology for process route selection of vinyl chloride manufacture can be applicable to any chemical process to assess their sustainability potential. Also, process routes can be assessed further in regards to other criteria such as environmental and ecological impacts, social concerns, and regulatory constraints as they become sufficiently quantifiable.

REFERENCES

Achour M. H., Haroun A. E., Schlt C. J., and Gasem K. A. M, (2005). 'A New Method to Assess the Environmental Risk of a Chemical Process'. *Chemical Engineering Processing, 44: 901-909.*

EdwardsD. W. andCave, S. R., (1997) 'Chemical Process Route Selection Based on Assessment of Inherent Environmental Hazards'. *Computers Chemical Engineering 21: S965-S970.*

Edwards and Lawrence, (1993). 'Assessing the inherent safety of chemical process routes: Is there a relation between plant cost and inherent safety?' *Transaction on IChemE, 71(B), 252-258.*

Edwards, D. W.and Gunasekera, M. Y., (2006). 'Assessing the inherent atmospheric environmental friendliness of Chemical process routes: An unsteady state distribution approach for a catastrophic release'. *Compt. Chem. Eng. 30 (4); 744-757*

EdwardsD. W.and M. Y. Gunasekera, (2006), 'Chemical Process Route Selection based upon the potential toxicity impact on the aquatic, terrestrial and atmospheric environments'. *Journal of loss Prevention in Process Industries 19(1): 60-69.*

FanL. H, Tengyan Zhang, Jiahong Liu, and John R. Schlup(2007), 'Assessment of Sustainability-potential: Hierarchical Approach'. *Ind. Chem. Res, 46: 4506-4516.*

Graveland A. J. G. G. & E. Gisolf, (1998), 'Exergy analysis: An efficient tool for process optimization and understanding'. *Computers Chem. Engng Vol. 22: pp S545-S552.*

Lakshmanan A. & Beigler L. T. (1997). A case study for Reaction Network Synthesis: The vinyl chloride process. *Comput. Chem Eng. 21, S785-S790.*

Palaniappan, C., Srinivasan, R., Tan, R. (2002), 'Expert System for the Design of Inherently Safer Processes. 1. Route Selection Stage'. *Ind. Eng. Chem. Res., Vol. 41, pp. 6698-6710.*

Tyler, B. J., Thomas A. R., Doran P., Greig F. R., (1996). 'A Toxicity hazard Index'. *Chem. Health Safety 19-25*

Xiangping Zhang, Chunshan Li, Chao Fu, and Suojiang Zhang, (2008), 'Environmental Impact Assessment of Chemical Process using the Green degree method'. *Journal of Ind. Eng. Chem. Res. 47: 1085-1094*.

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