

Evaluation of Industrial Routes to Vinyl Chloride According to Material and Energy Efficiency Green Metrics Analysis

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Abstract

This work presents a detailed analysis of various industrial syntheses of vinyl chloride according to material and energy efficiency green metrics. The routes examined are hydrochlorination of acetylene, oxyhydrochlorination of ethane, and tandem hydrochlorination of ethylene and dehydrochlorination of 1,2-dichloroethane. The green metrics selected are process mass intensity (PMI) and input enthalpy per unit mass of product measured in MJ per ton.

Introduction

Vinyl chloride is a high volume industrial chemical that is primarily used to make polyvinyl chloride.^{1,2} Since World War II, in Western countries vinyl chloride is made via tandem chlorination of ethylene and dechlorination of 1,2-dichloroethane while in Eastern countries, such as India and China, it is made via hydrochlorination of acetylene using mercuric chloride as catalyst. Half of the world's mined mercury ore is destined to manufacture mercury(II) chloride which is used as a catalyst to make vinyl chloride from acetylene and hydrogen chloride.³ China is the leading manufacturer of vinyl chloride by this method since it also has the largest reserves of coal from which acetylene is obtained. As a consequence of this process China is also the highest mercury polluter. In order to mitigate this situation research efforts have been made to replace mercury(II) chloride with gold chloride catalysts in order to carry out the hydrochlorination of acetylene.⁴⁻⁶ In this work we examine the material and energy efficiencies of the following three main industrial routes to vinyl chloride: hydrochlorination of acetylene (route 1), oxyhydrochlorination of ethane (route 2), and tandem hydrochlorination of ethylene and dehydrochlorination of 1,2-dichloroethane (route 3). The balanced chemical reactions are summarized in Figure 1. Based on our prior published algorithms we were able to determine the

process mass intensities (PMIs)^{7,8} and input enthalpies per unit mass of product^{9,10} for all routes. The PMI is defined as the total mass of input materials used per unit mass of product. Processes having low PMI values are considered material efficient. Input enthalpies per unit mass of product were determined by calculating the change in enthalpy of all input materials between state 1 representing ambient conditions of 25°C and 1 atm, and state 2 representing reaction temperature and pressure conditions. Processes having low values for enthalpies per unit mass of product are considered less energy intensive. Data used for all calculations were obtained primarily from experimental procedures given in the patent literature.

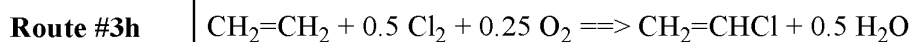
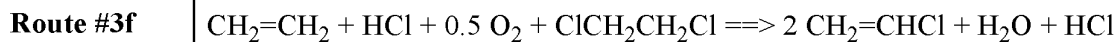
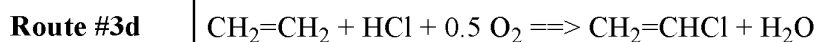
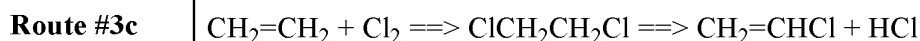
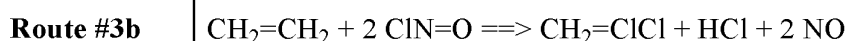
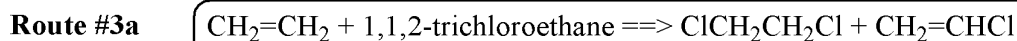
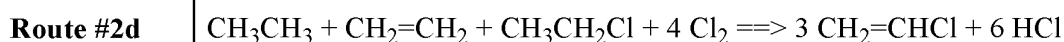
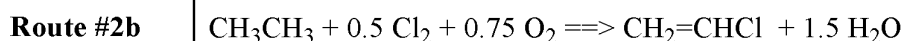
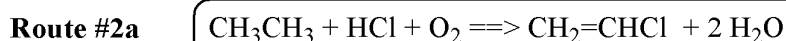
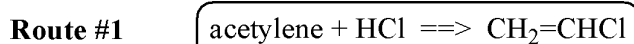


Figure 1 Various industrial routes for the production of vinyl chloride.

Industrial Routes from Acetylene

Table 1 summarizes the PMI and input enthalpy values for hydrochlorination of acetylene.¹¹⁻¹⁸ From these data we observe that the catalytic routes using mercury(II) chloride are both more material and energy efficient compared to the gold chloride routes. The primary reason for the lower performance of the gold-based catalysts is the low reaction yield of 20 % compared to the very high yields of 97+ % using mercury-based catalysts. The best performing gold-based catalyst was the one used in conjunction with cobalt(III) catalysts embedded in spherical activated carbon (SAC). However, despite these efforts, to the best of our knowledge there are no published reports that verify that the gold catalytic route has been proven to work on an industrial scale.

Table 1 Summary of reaction conditions and metrics for the production of vinyl chloride from acetylene (route 1).

catalyst	% yield	T(rxn)/p(rxn)/			PMI	E(MJ/ton)	Reference
		deg C	atm				
HgCl ₂	97.3	250	1	1.04	271	11	
HgCl ₂ /CeCl ₃ /activated carbon	98.5	100	1	1.03	84	12	
HgCl ₂ /activated carbon	98.7	120	1	1.35	126	13	
HAuCl ₄ /activated carbon/silicon carbide	20	185	0.5	16.11	>2435	14	
melamine/activated carbon	67.3	250	1.18	2.37	573	15	
Au/Co(III)/SAC (spherical activated carbon)	91.5	150	1.18	1.23	>165	16	
HgCl ₂ /activated carbon	81	185	0.51	1.26	226	17	
HgCl ₂ /CeCl ₃ /activated carbon	98.5	100	1	1.07	86	18	

Examination of the common methods to prepare the respective catalysts reveals the following results. Mercury(II) chloride is obtained from cinnabar in a two-step process involving first roasting the ore in air at

500°C to obtain elemental mercury (98 % yield)^{19,20} followed by treatment with chlorine gas at 85°C (74 % yield).²¹ The overall process has a PMI of 114 and an input enthalpy of 29,400 MJ/ton. On the other hand, chloroauric acid is obtained from gold ore in a two-step process involving the traditional cyanidation process at 25°C to obtain elemental gold (80 % yield)²² followed by treatment at 70°C with chlorine gas generated *in situ* by reacting potassium permanganate with hydrochloric acid (50 % yield).²³ The overall process has a PMI of 191,000,000 and an input enthalpy of 33,900 MJ/ton. It is clear that the major drawback in using the gold catalyst is the extremely high PMI. This high value arises from the fact that in order to obtain 6.24 g of pure gold from 499 tonnes of ore by the cyanidation process, 472 kg of potassium cyanide, 21 kg of zinc, and 535 tonnes of water are needed. The spent water and ore tailings are of course contaminated and need further treatment to remove traces of potassium and zinc cyanide and potassium hydroxide by-products before they can be released back to the environment. For the sake of argument, if we omit entirely the water consumption in the cyanidation process, the PMI drops down by about 50 % to 92,500,000. Based on all of these findings it makes no economic or environmental sense to pursue a strategy of replacing the mercury catalyst for a gold catalyst in the hydrochlorination of acetylene. Therefore, a route to vinyl chloride that is both efficient in terms of materials usage and energy consumption, including production of catalysts, and also has less environmental impact than either mercury or cyanide, must begin from a different starting material other than acetylene.

Industrial Routes from Ethane

Tables 2 to 5 summarize the PMI and input enthalpy values for oxyhydrochlorination of ethane according to route 2a²⁴⁻²⁸, route 2b^{29,30}, route 2c³¹, and route 2d³². Among these routes, route 2a involving K₂O/Fe₂O₃/beta-Al₂O₃ catalyst and route 2c involving Cr-Al₂O₃ catalyst have the best PMI and energy consumption profiles. However, these routes have PMI values that are 6 to 10 times larger than the mercury catalyzed acetylene route. They also have input enthalpy values that are 20 to 40 times larger than the mercury catalyzed acetylene route.

Table 2 Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $\text{CH}_3\text{CH}_3 + \text{HCl} + \text{O}_2 \Rightarrow \text{CH}_2=\text{CHCl} + 2 \text{H}_2\text{O}$ (route 2a).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
KCl/CuCl/CuCl ₂	10.2	439.82	468	1	119260	24
CuCl ₂ /CeCl ₃ /LiCl/MnCl ₂ /Al ₂ O ₃	27.9	28.78	425	1	10504	25
Fe ₂ O ₃ /alpha-Al ₂ O ₃	23.1	23.37	550	1	12224	26
K ₂ O/Fe ₂ O ₃ /beta-Al ₂ O ₃	41.4	13	500	1	6110	27
CuCl ₂ /Al ₂ O ₃ /K ₃ PO ₄	74.5	43.96	600	1	>23201	28

Table 3 Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $\text{CH}_3\text{CH}_3 + 0.5 \text{Cl}_2 + 0.75 \text{O}_2 \Rightarrow \text{CH}_2=\text{CHCl} + 1.5 \text{H}_2\text{O}$ (route 2b).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
CuCl ₂ /ZnCl ₂ /KCl/celite	70.4	18.19	500	1	8183	29
NaY zeolite/Ag ₂ O/MnO	14.5	50.59	400	1	>16563	30

Table 4 Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $\text{CH}_3\text{CH}_3 + \text{S} + \text{HCl} \Rightarrow \text{CH}_2=\text{CHCl} + \text{H}_2\text{S} + \text{H}_2$ (route 2c).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
Cr-Al ₂ O ₃	46.7	6.09	621	0.34	>3329	31

Table 5 Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $\text{CH}_3\text{CH}_3 + \text{CH}_2=\text{CH}_2 + \text{CH}_3\text{CH}_2\text{Cl} + 4 \text{Cl}_2 \Rightarrow 3 \text{CH}_2=\text{CHCl} + 6 \text{HCl}$ (route 2d).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
CuCl/CuCl ₂ /KCl	40.6	230.42	474	1	64210	32

Industrial Routes from Ethylene

Tables 6 to 13 summarize the PMI and input enthalpy values for tandem hydrochlorination of ethylene and dehydrochlorination of 1,2-dichloroethane according to route 3a³³, route 3b³⁴, route 3c^{35,36}, route 3d^{37,38}, route 3e³⁹, route 3f⁴⁰, route 3g⁴¹, and route 3h⁴². Route 3e using calcium sulphate catalyst has the lowest PMI value of 2.45 and the second lowest input enthalpy of 1137 MJ/ton. Route 3h using sand//CuCl₂/KCl/ThCl₄/silica gel catalyst has the second lowest PMI value of 4.03 and the lowest input enthalpy of 930 MJ/ton. Both routes are on average 2 to 4 times less material efficient and consume 6 to 7 times more energy than the mercury catalyzed acetylene route.

Table 6. Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $\text{CH}_2=\text{CH}_2 + 1,1,2\text{-trichloroethane} \Rightarrow \text{ClCH}_2\text{CH}_2\text{Cl} + \text{CH}_2=\text{CHCl}$ (route 3a).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
CuCl ₂ /ZrOCl ₂ /KCl/silica gel	17.8	22.53	350	1	>17164	33

Table 7 Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $2 \text{ClN}=\text{O} + \text{CH}_2=\text{CH}_2 \Rightarrow \text{CH}_2=\text{ClCl} + \text{HCl} + 2 \text{NO}$ (route 3b).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
silica	17.5	15.09	480	1	6362	34

Table 8 Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $\text{CH}_2=\text{CH}_2 + \text{Cl}_2 \Rightarrow \text{ClCH}_2\text{CH}_2\text{Cl} \Rightarrow \text{CH}_2=\text{CHCl} + \text{HCl}$ (route 3c).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
none	95.8	3.04	380	0.34	1448	35
none	80	7.98	451	1	5745	36

Table 9 Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $\text{CH}_2=\text{CH}_2 + \text{HCl} + 0.5 \text{O}_2 \Rightarrow \text{CH}_2=\text{CHCl} + \text{H}_2\text{O}$ (route 3d).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
KCl/CuCl/CuCl ₂	36.2	4.83	420	1	2017	37
CuO/firebrick	50	4.51	425	1	>1809	38

Table 10 Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $\text{ClCH}_2\text{CH}_2\text{Cl} + \text{CH}_2=\text{CH}_2 \Rightarrow \text{CH}_2=\text{CHCl} + \text{CH}_3\text{CH}_2\text{Cl}$ (route 3e).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
CaSO ₄	97	2.45	260	20.4	1137	39

Table 11 Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $\text{CH}_2=\text{CH}_2 + \text{HCl} + 0.5 \text{O}_2 + \text{ClCH}_2\text{CH}_2\text{Cl} \Rightarrow 2 \text{CH}_2=\text{CHCl} + \text{H}_2\text{O} + \text{HCl}$ (route 3f).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
FeCl ₂ /RhCl ₃ /ZnCl ₂ /LiCl/Al ₂ O ₃	38.9	6.21	350	1	>2798	40

Table 12 Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $\text{CH}_2=\text{CH}_2 + \text{Cl}_2 + \text{ClCH}_2\text{CH}_2\text{Cl} \Rightarrow 2 \text{CH}_2=\text{CHCl} + 2 \text{HCl}$ (route 3g).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
none	95	8.87	540	27.2	5424	41

Table 13 Summary of reaction conditions and metrics for the production of vinyl chloride from ethane via $\text{CH}_2=\text{CH}_2 + 0.5 \text{Cl}_2 + 0.25 \text{O}_2 \Rightarrow \text{CH}_2=\text{CHCl} + 0.5 \text{H}_2\text{O}$ (route 3h).

catalyst	% yield	PMI	T(rxn)/	p(rxn)/	E(MJ/ton)	Reference
			deg C	atm		
sand//CuCl ₂ /KCl/ThCl ₄ /silica gel	91.7	4.03	500; 400	3; 2.8	930	42

Conclusion

Overall, the best performing industrial routes to manufacture vinyl chloride based on PMI and input enthalpy performances, and weighed against potential environmental impacts, begin from ethylene as the starting material. Routes 3e and 3h are ranked highest among all routes examined. The next best options are routes 2a and 2c that involve oxyhydrochlorination of ethane. Though hydrochlorination of acetylene produces the lowest PMI and lowest input enthalpy overall compared to the other routes, its potential environmental impact with respect to catalyst manufacture and usage makes it relatively unfavourable. Of particular note, the replacement of gold- for mercury-based catalysts in that process does not appear to be justified from a green principles perspective based on the analysis reported in this work.

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