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Carbon Footprint for the Petrochemical Industry in Qatar:
A Case Study for the VCM Process

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Dr. Gregory T. Papanikos
President
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Abstract

Qatar has experienced an unprecedented development over the past decade as a main result of its fast growing oil and gas industry. It has the third confirmed reserve on natural gas in the world. With 55.4 tonnes of carbon dioxide per person, Qatar has the highest carbon footprint globally, about 10 times the global average. Against this background, there have been attempts to investigate ways to reduce carbon emissions since CO_2 was deemed to be one of the major green house gases. Power generation is by far the biggest contributor to anthropogenic (man-made) carbon emissions. The carbon emission mitigation methods currently considered include "end of pipe" solutions and "at source" solutions. The techniques currently identified to capture carbon emissions from point sources from industrial activities include post combustion capture, precombustion capture and oxyfuel based capture. These techniques are currently at various stages of development. In this paper, a typical petrochemical process, namely the Vinyl Chloride Monomer (VCM) process has been selected for carbon footprinting. The process primary fossil fuel equivalents which in turn will be turned into CO_2 emissions using combustion processes were identified. Industrial standard simulation software HYSYS was used to carry out the calculations on the heat duties of the entire plant. Energy intensive sections in the VCM process were identified and their associated CO_2 footprint determined. The total CO_2 emissions from VCM plant with a capacity of 300,000MT/yr was estimated to be 95659.2 MT/yr which means that for each 1 ton VCM produced 0.32 ton of CO_2 is emitted.

Key words: Carbon footprints, Combustion, Gas turbine, Brayton cycle, CO_2 emissions, VCM process

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Introduction

As a result of the global industrial revolution, the atmospheric concentration of CH_4, N_2O and specifically CO_2 has undergone a dramatic increase, which has consequently enhanced the heat trapping capability of the earth through what is known as the "greenhouse effect". This increase was associated amongst other phenomena, with the various combustion processes performed in the power plants and petrochemical complexes that utilize fossil fuel as a prime source of energy. Against this background, the discovery of the third largest oil/gas field located at the North of Qatar has indeed boosted the global petrochemical industry and yet even further contributed in emitting CO_2 gas to the atmosphere. This fact has stimulated Qatar to find methods to manage the emission of greenhouse gasses, particularly CO_2. Globally, there have been a number of investigation methods that attempt to specifically reduce the magnitude of CO_2 emissions since CO_2 was recognized to be one of the major greenhouse gases. These methods have included the alternatives of improving the energy efficiency , utilizing more environmentally friendly less carbon intensive fuels (carbon free – low carbon energy sources) and increase the use of renewable energy sources (e.g: nuclear , biomass, solar, wind). A relatively new concept to manage the carbon emissions is the Carbon dioxide sequestration, which considers the technical capturing of the generated CO_2 in industrial processes and long term isolation and storage. The techniques currently identified to capture carbon emissions from point sources from industrial activities include post combustion capture [small fraction of CO_2, typically 3-15% by volume], pre-combustion capture [high fraction of CO_2; typically 15-60%] and oxyfuel based capture [very high fraction of CO_2; more than 80% by volume]. These techniques are currently at various stages of development. Against this background of state of the art in carbon capture approaches for greenhouse gas mitigation, it is important to first obtain reasonably accurate CO_2 emissions. Whilst this may not be a major problem in fossil fuel power plants for domestic electricity generation, it is significantly different in chemical plants, namely, petrochemical complexes where the carbon footprint is estimated from several sources that utilize fossil fuel as its primary energy supply.

Industrial Case Study: Vinyl Chloride Monomer (VCM) Process

 To fulfill the purpose of this study, VCM process was selected to illustrate the carbon foot printing procedure in the absence of available data. Vinyl Chloride Monomer VCM process is counted to be one of the highly developed petrochemical industries worldwide, which is in fact highly interrelated with the continuous dynamic development of Polyvinyl Chloride PVC industry. A modern Vinyl Chloride Monomer VCM production process is mainly divided into three reactive sections which are: direct chlorination, oxychlorination and EDC cracking, and two purification sections which are EDC purification and VCM purification (see Figure 1). The first two reactive sections are used to produce the ethylene dichloride EDC, which is the required intermediate compound to be further processed in the third reactive section which is the EDC cracking. In the EDC cracking, the highly purified EDC from the EDC purification section is sent to a direct – fired furnace at which the non- catalytic gas phase reaction shown below takes place at elevated temperature and pressure (490°C – 11 bar). The EDC is thermally cracked to VCM, HCl and several other heavy chlorinated hydrocarbons that are sent to the VCM purification section for final purification and product storage.

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$$
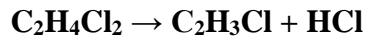
The thermal energy in the EDC furnace is provided by the mean of natural gas combustion with air in the radiation section of the furnace, and by this the EDC cracking furnace is considered to be the first major CO_2 contributor in the process.

The fact that there are significant amounts of light/heavy chlorinated hydrocarbon byproducts produced in the three reactive sections requires a safe treatment for the compounds before the final discharge. In VCM process, the treatment of all vent gasses along with the chlorinated hydrocarbons occurs usually in hazardous incineration unit (multi task operational unit for vapor/liquid/solid treatment). In the incineration unit, the vent gasses that consist of inert gases (e.g. N_2 , CO_2, CH_4) and small fraction of the un-reacted material (e.g. ethylene) along with all the light/heavy chlorinated hydrocarbons produced in the reactors undergo combustion process which further produces CO_2 and thus, the incineration unit is counted to be the second major CO_2 contributor in the VCM process.

The third source of CO_2 in the VCM process arises from the use of gas turbine to drive the refrigeration compressors. A main gas turbine is used for the HCl column's refrigerant compressor in the VCM purification section. The compressor is needed as an integral part of the refrigeration cycle to compress the refrigerant that is required to cool the HCl product at the top of the HCl distillation column and recycle it back to the oxychlorination section. After identifying the main energy intensive sections in VCM process which has high CO_2 emission contribution, it is essential to quantify CO_2 emissions by translating the thermal required duty for a unit operation into the equivalent amount of the fuel required and then performing the combustion reactions and material balance to estimate the CO_2 emissions.

Figure 1. Simplified VCM Process Block Diagram
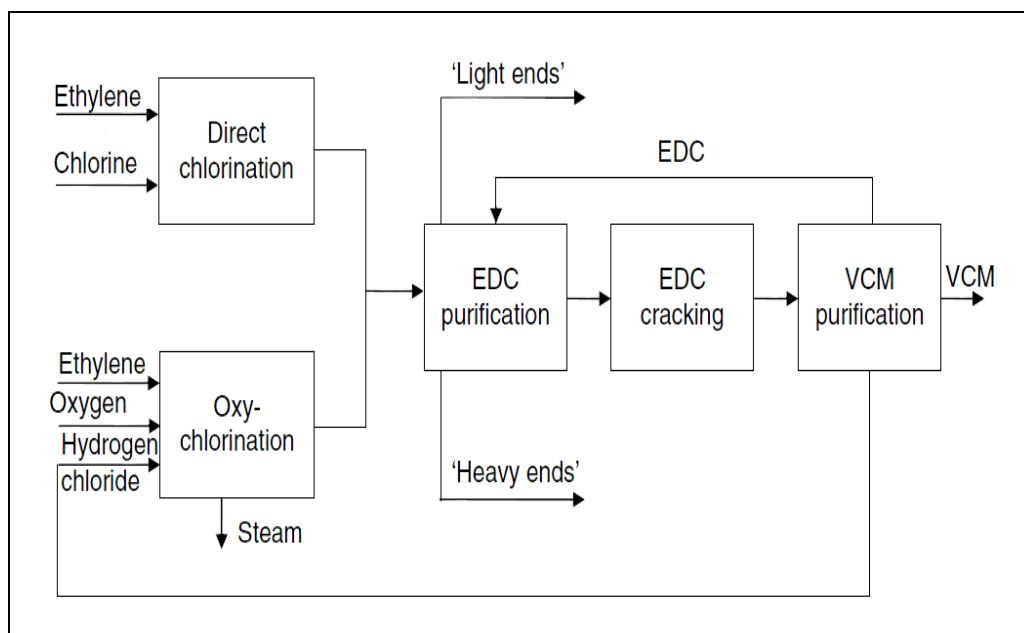
Methodology

In order to quantify the emission of CO_2 for a certain VCM process, it is essential first to decide on the production rate for the VCM process to be analyzed. By investigating the different VCM processes, a medium production rate of 300,000 MT/year was chosen which in fact suits the VCM production in a region like Qatar. Establishing the VCM production rate, the following stage was the analysis; evaluation and selection of the best feasible technology among the several commercialized VCM technologies that fits the study's vision. A comprehensive analysis based on many crucial decisions criterions was carried out; accordingly a hybrid between Vinnolit and Toyo Soda technologies was selected as the best appropriate technology. Following, the material balance was performed on the addressed sections based on the developed PFD taking into consideration all the various constrains and assumptions in order to quantify the required feed streams for HYSYS simulation. The compositions of the Ethylene, Chlorine and Oxygen streams that are considered to be the raw materials in the process were obtained through communications with the industry (Qatar Vinyl Company) along with the product specification. The feeds compositions and the product specifications are presented in Tables 1 and 2 respectively.

Table 1. Feed Compositions of Chlorine, Ethylene and Oxygen

Feed Composition Vol.%			
Chlorine stream	Cl_2	98.55	%
	O_2	0.75	%
	CO_2	0.30	%
	N_2	0.40	%
Ethylene stream	C_2H_4	99.87	%
	CH_4	650	ppm
	C_2H_6	650	ppm
O2 stream	O_2	100	%

Table 2. Product (VCM) specification

Product Specification Wt.%	
VCM product	100%

The material balance approach on the VCM plant was initiated by conducting the backward calculation starting from the cracking section in which mass conservation law was applied.

Mass Conservation Law for any component in the system:

Input+Generation-Output-Consumption=Accumulation (Eq-1)

For any continues process where the variables are steady with time, the accumulation term is canceled and mass conservation law is reduced to:

Input+ Generation= Output+ Consumption (Eq-2)

In the case where no chemical reactions are taking place and the species of the system undergoes a separation process or a phase change process, both generation and consumption terms are canceled and the mass conservation law is reduced to:

Input= Output   (Eq-3)

The results of the material balance on the VCM process were as shown in Table 3 below.

Table 3. Material balance results on VCM process

Component	Chemical Formula	Inlet to the Plant (Kg /hr)	Outlet from the Plant(Kg /hr)
Chlorine	Cl_2	21413.01	0.00
Oxygen	O_2	73.54	73.54
Carbon dioxide	CO_2	34.34	226.53
Nitrogen	N_2	40.46	34.34
Ethylene	C_2H_4	16768.21	254.06
Methane	CH_4	6.24	6.24
Ethane	C_2H_6	11.70	11.70
Water	H_2O	0.00	5373.44
Chloroform	$CHCl_3$	0.00	93.22
Carbon tetrachloride	CCl_4	0.00	90.09
1,1,1,2-Tetrachloroethane	$C_2H_2Cl_4$	0.00	140.09
Tetrachloroethylene	C_2Cl_4	0.00	97.13
Trichloroethylene	C_2HCl_3	0.00	43.61
Chloroethane	C_2H_5Cl	0.00	64.23
Vinyl trichloride	$C_2H_3Cl_3$	0.00	507.05
VCM	C_2H_3Cl	0.00	35612.89
Chloroprene	C_4H_5Cl	0.00	187.20
1,4-Dichlorobut-2-ene	$C_4H_6Cl_2$	0.00	330.36
Total		43255.83	43255.83

The methodology followed to quantify the CO_2 emissions involves the use of modern industrial engineering software "Aspen HYSIS". Aspen HYSIS software was utilized in simulations of various sections in the VCM process and obtaining the required equipment thermal duties. The fluid package that was used in Aspen HYSYS simulation is Peng Robinson since it best represents the behavior of chlorinated hydrocarbons in the absence of water which was the case in the three addressed energy intensive sections. By applying the basic concept of energy balance, the

utilities requirements for the major equipments in the VCM process were identified. Table 4 below shows the expected consumption figures for the utilities to produce 300,000 MT/year of VCM product.

Table 4.Utility requirements in the VCM process plant

Utility Type	Utility Requirement	
Fuel	3.23×10^3	Kg/hr
Electricity	3.98×10^4	kW
HP steam	1.55×10^4	Kg/hr
MP steam	1.1×10^4	Kg/hr
LP steam	4.97×10^4	Kg/hr
BFW	6.50×10^4	Kg/hr

Results and Discussion

The EDC cracking furnace and the gas turbine requires external fuel in order to operate, whiles in the incineration unit, no external fuel is required and the quantity of hydrocarbons sent to the unit are enough to operate the combustion reactions. The amounts of hydrocarbons sent to incineration were obtained by performing material balance on the different process sections. Thus, no simulation required for the incineration unit.

EDC Cracking Furnace

The fuel is introduced to the furnace with enough air to be combusted to provide heat to process the endothermic reaction. The fuel used in the cracking furnace was chosen to be natural gas with the following compositions in Table 5, which were provided by Qatar Vinyl Chloride Company (QVC). The duty as obtained from HYSYS was recorded to be 2.91 kW, yet this duty is translated into fuel requirement assuming 90% furnace efficiency and a heating value of 1030 BTU/SCF (approximately equivalent to 53538.69 kJ/kg). And thus, the natural gas requirement for the cracking furnace was calculated to be 2174.12 kg/hr.

Table 5. Composition of fuel utilized in the cracking furnace.

Component	Vol%

N_2	3.95
CO_2	0.82
CH_4	93.51
C_2H_6	1.68
C_3H_8	0.04
Total	100

Gas Turbine:

The compressor used in the refrigeration cycle of the HCl column is driven by gas turbine assumed to operate according to the Brayton cycle with an efficiency of 45%. The gas turbine utilizes natural gas that has the same compositions of the fuel used in the cracking furnace. The compressor's duty was assumed to be the condenser's duty in the HCl distillation column. Thus, the HCl column was simulated and a condenser duty of 7042 kW was recorded. Consequently the amount of fuel to run the gas turbine was calculated to be 1052.25 kg/hr.

Carbon Footprinting

Having obtained the natural gas equivalents for EDC cracking furnace and the gas turbine, along with the available information of the fuel composition, the CO_2 footprint is estimated by performing combustion processes. The combustion reactions were also performed on the hazardous incineration unit using the material balance results. The CO_2 footprint is performed on each section individually as this would indicate the section with the highest CO_2 contribution.

EDC Cracking furnace:

The combustion reactions that take place in the cracking furnace are tabulated in Table 3 where complete combustion reactions were assumed. Besides, the amount of the emitted CO_2 is evaluated by using the stiochiometry.

Table 6. Combustion reactions and CO_2 emitted in cracking section

Combustion Reaction	Emitted CO_2 [kg/hr]
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	5575.24
$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$	200.64
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	7.04
Total Amount of CO_2	5831.78[1]

Gas Turbine:

Since the fuel utilized to run the gas turbine is assumed to have the same composition of that used in the cracking furnace, both will have the same combustion reactions. Table 4 presents the combustion reactions along with the amount of CO_2 emitted.

Table 7. Combustion reactions and CO_2 emissions in gas turbine

Combustion Reaction	Emitted CO_2 [kg/hr]
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	2698.08
$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$	96.96
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	3.43
Total Amount of CO2	2822.16 [2]

Hazardous Byproduct of Incineration:

All the vent gases and waste chlorinated hydrocarbons in VCM process are sent to incineration unit. By performing material balance on each section in the VCM plant, the amounts of hydrocarbons sent to this unit were obtained as presented in Table 3. The waste/vent streams undergo combustion reactions with oxygen in the air and by assuming complete combustion, the CO_2 emissions were evaluated. The incineration receives streams mainly from three process sections; oxychlorination, direct chlorination, and EDC purification, thus the combustion reactions were performed on each vent/waste stream. The results of CO_2 emissions are presented in Tables 8, 9, and 10.

Table 8. Combustion reactions and CO_2 emissions from direct chlorination vent gases

Combustion reaction	CO_2 Emission (kg/hr)
$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	263.12
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	8.80
$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$	17.60
Total CO_2	466.4 [4]

Table 9. Combustion reactions and CO$_2$ emissions from oxychlorination vent gases

Combustion reaction	CO$_2$ Emission (kg/hr)
$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	255.2
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	8.36
$C_2H_6 + \dfrac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$	16.72
Total CO$_2$	330[3]

Table 10. Combustion reactions and CO$_2$ emissions from EDC purification wastes

Combustion reaction	CO$_2$ Emission (kg/hr)
$4CHCl_3 + 5O_2 \rightarrow 4CO_2 + 6Cl_2 + 2H_2O$	34.32
$CCl_4 + O_2 \rightarrow CO_2 + 2Cl_2$	25.96
$C_2Cl_4 + 2O_2 \rightarrow 2CO_2 + 2Cl_2$	51.92
$4C_2HCl_3 + 9O_2 \rightarrow 8CO_2 + 6Cl_2 + 2H_2O$	29.04
$2C_2H_2Cl_4 + 5O_2 \rightarrow 4CO_2 + 2H_2O + 4Cl_2$	73.04
$4C_2H_5Cl + 13O_2 \rightarrow 8CO_2 + 2Cl_2 + 10H_2O$	87.56
$4C_2H_3Cl_3 + 11O_2 \rightarrow 8CO_2 + 6H_2O + 6Cl_2$	334.4
$4C_4H_5Cl + 21O_2 \rightarrow 16CO_2 + 10H_2O + 2Cl_2$	369.6
$2C_4H_6Cl_2 + 11O_2 \rightarrow 8CO_2 + 6H_2O + 2Cl_2$	464.64
Total CO$_2$	1470.48

Thus, the total CO$_2$ emissions from the hazardous incineration unit are recorded to be 2040.28 kg/hr. Table 11 shows the total amount of CO$_2$ emissions from the three addressed sections.

Table 11. Amount of CO$_2$ emitted in the three sections

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Section	CO_2 emission (kg/hr)
EDC Cracking Furnace	5831.78
Gas Turbine	2822.16
Hazardous Byproduct Incineration	2266.68
Total Emissions	10920.82

Total CO_2 emissions from VCM plant with a capacity of 300,000MT/yr was estimated through calculations to be 10920.82 kg/hr (95659.2 MT/yr) which means that for each 1 ton VCM produced 0.32 ton of CO_2 is emitted.

Conclusion

This study highlighted the direct emissions of carbon dioxide from a typical petrochemical plant; VCM in which a quantitative analysis was conducted to evaluate the amount of CO_2 emitted in the different sections of the process. Fuel combustion in the cracking furnace, which is used to drive the endothermic cracking of EDC into VCM contributed to the largest CO_2 emissions when compared to the other addressed sections with estimated CO_2 emissions of 5831.78 kg/hr (49126.91 MT/year). The second highest contributor to the CO_2 emissions was found to be the fuel combustion used to run the gas turbine, which was estimated to be 2822.16 kg/hr (23773.88 MT/year). On the other hand, CO_2 emissions from the hazardous byproducts incineration of the vent gases of the direct chlorination and Oxychlorination reactors as well as the EDC purification wastes were the lowest with total CO_2 emissions of 2266.68 kg/hr (19094.51 MT/year). Accordingly, the production of 300,000 MT/year of VCM results in an overall CO_2 emissions of 10920.82 kg/hr (95659.2 MT/year), which translates to 0.32 ton of CO_2 emitted for each 1 ton of VCM produced. Moreover, the contribution of additional parameters to the overall CO_2 emissions from the VCM process, such as the number of stuff, and the use of AC will be further investigated in the second phase of this study. In addition, potential solutions for the captured CO_2 from the VCM process will be investigated and introduced.

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