Energy and carbon emission assessments of acetylene-based vinyl chloride manufacturing process

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Abstract:

The manufacturing process of vinyl chloride monomer (VCM) through acetylene and hydrogen chloride is seldom used in the world except China. More than 70% capacity of VCM is produced in China by this process which is closely related to low-rank coal-based calcium carbide process. In this study, acetylene-based VCM manufacturing process was established and simulated on the basis of the patent CN 1884241A. The characteristics of the energy utilization, exergy loss distribution as well as carbon emission of this process were researched. The results show that the energy consumption of this process is 66.14 $kgce/t_{VCM}$. The VCM distillation unit is the biggest energy consumer with consuming 52.93% of all the process energy consumption. Through exergy analysis, 0.94 GJ/t_{VCM} exergy is lost in the main reactor unit. These losses pay the maximum part of thermodynamic cost of the whole system. Correspondingly, the carbon footprint of this process was also studied. The calculating results show that the direct and indirect carbon emissions of the process are 59.02 $kgCO_2e/t_{VCM}$ and 429.62 $kgCO_2e/t_{VCM}$, respectively. Proposed from different aspects of view, some hints about how to decrease the energy consumption and reduce the carbon dioxide emission could be obtained. For example, the reaction heat could be used to produce steam to heat other materials. By this way, the energy consumption of the process can be decreased to 26.60 $kgce/t_{VCM}$. The indirect carbon emission can be reduced to 2771.57 $kgCO_2e/t_{VCM}$ accordingly.

Keywords:

Carbon Emission, Low-Rank Coal, Thermodynamic Analysis, Vinyl Chloride Manufacturing.

1. Introduction

Polyvinyl chloride (PVC), which is prepared from vinyl chloride monomer (VCM), is the second most produced and used plastic. Because of its low cost and excellent physical and mechanical properties, PVC is used widely and diversely, ranging from everyday products to highly specialized

applications. The building and construction sector (piping, guttering, window profiles, wall plates) makes the broadest use of PVC [1].

PVC was first industrially produced in Germany by acetylene hydrochlorination method in 1929 [2]. And then, the PVC industry developed gradually. In 1960s, with the large-scale oxychlorination of ethylene to 1, 2-dichloroethane technology developed, this acetylene-based process was replaced by ethylene-based process in the Western World [3].

Today, VCM is mainly manufactured by the ethylene process and acetylene process. The ethylene process takes up about 80% capacity through the whole world [2]. Although there are some other processes such as ethane process and combined process, they take little market shares [4]. In China, it is a very different situation. China now is the world largest PVC production country [5], and over 70% of its PVC production is derived from acetylene hydrochlorination method [6]. Chinese standard [7] specifies the norm of energy consumption of PVC to restrict the high energy consumption enterprises to accessing the sector. In academic studies of acetylene hydrochlorination method, there are few studies reported in the Western World now, and most Chinese researchers focus on exploring non-mercury catalysts with high activity and long stability, such as [8,9]. The properties of energy utilization, exergy loss distribution as well as the carbon footprint of the process have not been reported before. In this paper, the acetylene hydrochlorination process was simulated by Aspen Plus software. Based on reliable simulation results, the Sankey diagrams for enthalpy flow, exergy flow and carbon footprint were obtained. Finally, optimization was executed to decrease the energy consumption and reduce the carbon emission of this process.

2. Process description and simulation

2.1. Process description

The acetylene hydrochlorination process used in this study is from Inner Mongolia Haiji Chlor-Alkali Chemical Co. Ltd [10, 11]. This process was imported from Dutch John and Brown Company initially, and was renovated appropriately before applied. The process is consisted of four important units: U1-main reaction unit, U2-VCM cooling and compression unit, U3-recycle reaction unit, and U4-VCM distillation unit. The simulation process flowsheet was shown in Fig. 1. The detailed process is described as follows.

Qualified acetylene (C_2H_2) and hydrogen chloride (HCl) gases are mixed with equivalent moles in MIXER-1. The mixed gas is fed into the main reactor REACTOR1 after preheated to 100℃ in the preheater HEATER-1. The acetylene hydrochlorination reaction occurs in REACTOR1 at 150℃ to produce crude VCM. The conversion of C_2H_2 is about 85%. The reaction products are mixed with the recycled materials which come from U3 and U4 and then enter into U2. The mixture flows through COOLER1, COMP-1, COOLER2, COND-1, and COND-2 successively and flashes in TANK-1.

In TANK-1, unreacted C_2H_2 and HCl gases are separated from VCM liquid and heated to 100℃ in HEATER2 before entering into the recycle reactor REACTOR2. In REACTOR2, C2H2 and HCl gases continue the reaction in order to ensure a high C_2H_2 conversion ratio. The reaction product outputs from REACTOR2 and flows into COOLER3 and COND-3 sequentially. Then uncondensed gas, N_2 and a few amount of unreacted C_2H_2 and HCl gases, are separated from condensate and exhausted to the subsequent off gas treatment unit. The condensate is recirculated back to MIXER-2 in U1.
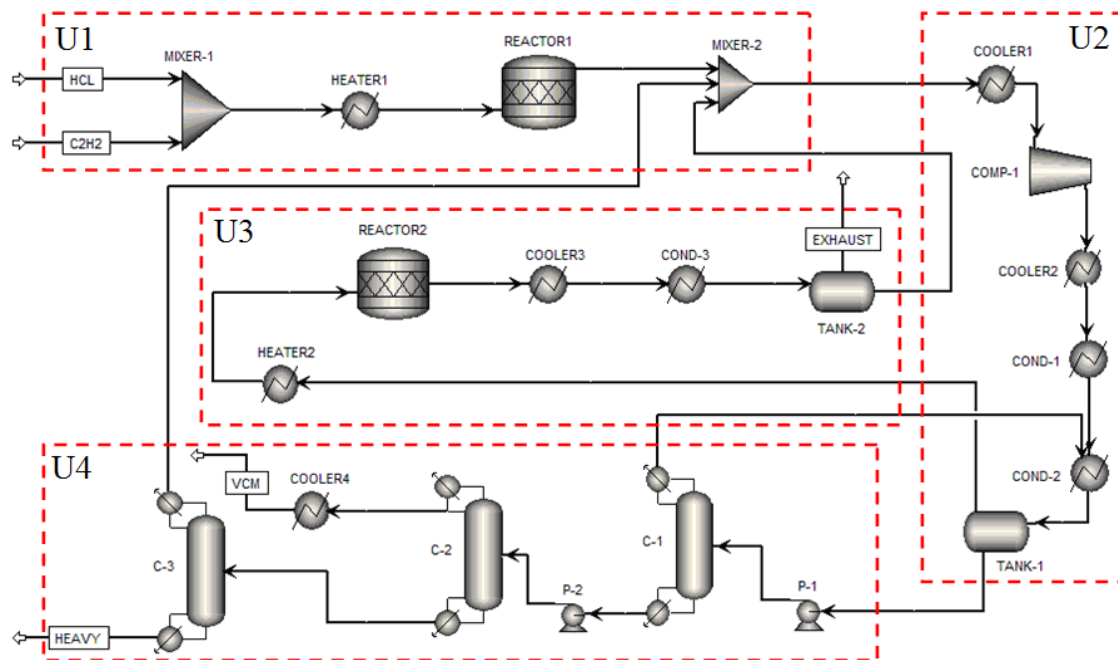
Fig. 1. Simulation flowsheet of the acetylene-based VCM manufacturing process. U1-main reaction unit; U2- VCM cooling and compression unit; U3- recycle reaction unit; U4- VCM distillation unit.

The crude VCM liquid from TANK-1 is pumped into gas stripping device C-1. Light components mainly consist of C_2H_2 and HCl get rid of the liquid here and recycle back to COND-2. Crude VCM flows into VCM distillation column C-2 to get purified VCM product withdrawn at the top of C-2. Then the purified VCM is cooled to ambient temperature and could be used as feed of PVC device. The heavy bottoms out of C-2 are submitted to the heavy ends column to strip back VCM component to MIXER-2 in U1. Heavy component is sent out of the device for further use or for incineration.

2.2. Process simulation

According to the characteristics of the process, some assumptions supposed during the simulation are as follows:

1) Impurities in feed consist of water (H_2O) and nitrogen (N_2), no other components contained.

2) The byproduct of acetylene hydrochlorination reaction is 1,1-dichloroethane only.

3) The temperature in the reactor is uniform.

In consideration of that there are trace amount of H_2O in the system, HCl is in gas state, and liquid phase predominantly contains VCM and 1,1-dichloroethane, RK-Soave equation is employed to describe the material and energy balance in the process.

Input C_2H_2 flow rate is 3300.0 kg/h, and HCl flow rate is 4612.5 kg/h. Based on the simulation results, HCl conversion, VCM purity, as well as C_2H_2 and HCl consumption per ton VCM are calculated in order to validate the accuracy of simulation. The calculated results are listed in Table 1. According to the results obtained, the maximum negative error is HCl consumption (-0.85%). Since C_2H_2 and HCl are fed into the system with specify proportion, and their conversions are very high, the tolerances of their consumptions are quite close. In a word, the deviation of the simulation

results and literature values are within an acceptable range. The model established is reliable to simulate the actual acetylene-based VCM manufacturing process.

Table 1.   Comparison of simulation value and literature value.

Item	Lirerature value [10]	Simulation value	Tolerance (%)
HCl conversion (%)	99	98.7	-0.30
VCM purity (%)	99.95	99.99	0.04
C_2H_2 consumption (kg/t)	440	436.3	-0.84
HCl consumption (kg/t)	615	609.8	-0.85

3. Results and discussion

3.1. Thermodynamic analysis

3.1.1. Energy consumption analysis

Based on the simulation results, an energy flow diagram of the process is obtained and shown in Fig. 2. In a normal energy flow diagram, the width of each line stands for the energy amount of the stream. The wider the line is, the more energy the stream has. Since the stream of C_2H_2 brings a large amount of energy, utility stream lines become too narrow to be noticed. This leads to the difficulty in analyzing the energy flow diagram, and also makes the advantage of the Sankey diagram disappeared. In order to hightlight the key effect of utilities during the process, a flexible method is adopted by enlarging the energy amount of utility streams as ten times as their original values (still marked the original values on the diagram). By this way, the energy flow diagram can show us more clearly how the system exchanges energy with utility and can indicate the key point we should pay more attention to. Besides, this change will not affect the dominant position of the material streams.

In Fig. 2, different energy streams are painted by different colors. For example, material flows are painted by dark cyan (except waste, painted by brown); steam lines are colored by red, and so on. For utility streams, their names are marked on the top of the bus line (such as Electricity), and energy amount are written below the bus line (such as 183.93 kW). For input and output material streams, their names are corresponding to the names given in Fig. 1 (such as C2H2), and also their energy amount are written below the streams. Other energy values are written close to the stream in order to be distinguished clearly.
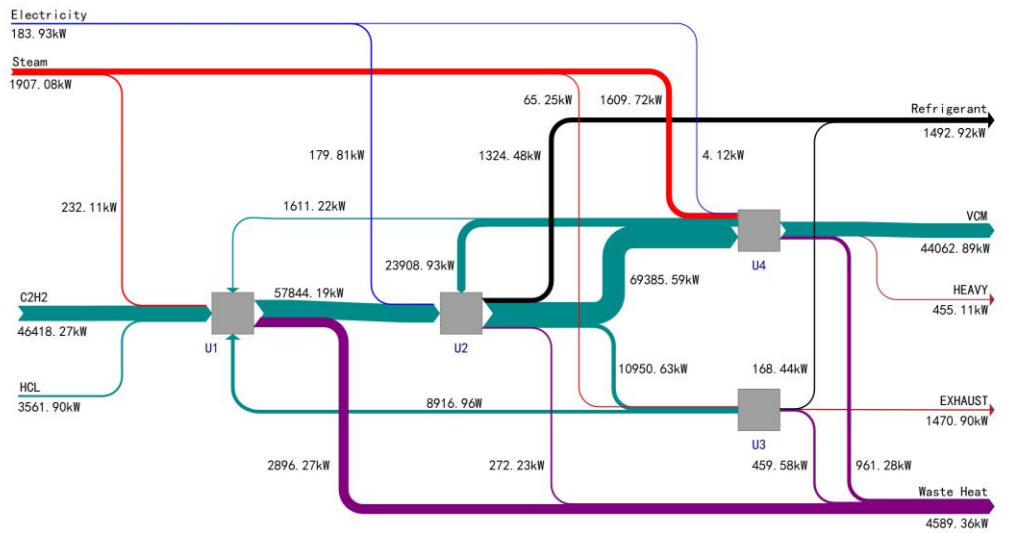
Fig. 2.   Energy flow diagram of the process.

Table 2. Energy consumption of the process.

Unit	Block		Load (kW)	Utility	Utility amount	Energy consumption (kgce/t$_{VCM}$)		Ratio (%)	
U1	HEATER		232.11	0.3MPa steam	386.17 kg/h	4.81	9.50	7.28	14.37
	REACTOR1		2896.27	Cooling water	248.25 t/h	4.69		7.09	
U2	COOLER1		78.88	Cooling water	6.76 t/h	0.13	17.71	0.19	26.76
	COMP-1		179.81	Electricity	179.81 kW	2.92		4.42	
	COOLER2		193.35	Cooling water	16.57 t/h	0.31		0.47	
	COND-1		897.31	Refrigerant	598.21 kW*	9.72		14.69	
	COND-2		427.17	Refrigerant	284.78 kW*	4.63		6.99	
U3	HEATER2		65.25	0.3MPa steam	108.56 kg/h	1.35	3.92	2.05	5.94
	REACTOR2		398.81	Cooling water	34.18 t/h	0.65		0.98	
	COOLER3		60.77	Cooling water	5.21 t/h	0.10		0.15	
	COND-3		168.44	Refrigerant	112.29 kW*	1.82		2.76	
U4	P-1		0.49	Electricity	0.49 kW	0.01	35.01	0.01	52.93
	C-1	Condenser	-	-	-	-		-	
		Reboiler	592.00	0.3MPa steam	984.93 kg/h	12.28		18.56	
	P-2		3.63	Electricity	3.63 kW	0.06		0.09	
	C-2	Condenser	901.06	Cooling water	77.23 t/h	1.46		2.21	
		Reboiler	995.79	0.3MPa steam	1656.74 kg/h	20.65		31.22	
	COOLER4		60.22	Cooling water	5.16 t/h	0.10		0.15	
	C-3	Condenser	-	-	-	-		-	
		Reboiler	21.92	0.3MPa steam	36.47 kg/h	0.45		0.69	
Summation			8173.29	-	-	66.14		100.00	

*Converted to electricity consumption.

According to Fig. 2, cooling water takes away a lot of energy (4589.36 kW). Most of the energy comes from U1 where the main reaction occurs. The energy becomes waste heat finally and could not be used again. Steam is used to heat the column reboilers in U4, which consumes 1609.72 kW steam heat out of 1907.08 kW in total. There are 1492.92 kW energy transfered to refrigerant from U2 and U3. The electricity needed is only 183.93 kW; it contributes the smallest of the total energy transfered between the system and utilities.

In consideration of the differences of different utilities, the utilities consumption and also their coal equivalent consumption of each unit and each block are calculated and listed in Table 2. During the calculation, the temperature difference between cooling water inlet and outlet is assumed to be 10℃. And the coefficient of performance for refrigeration is assumed to be 1.5.

The results show that the total coal equivalent consumption of the process is 66.14 kgce/t_{VCM}. Energy consumption of U1, U2, U3 and U4 is 9.50 kgce/t_{VCM}, 17.71 kgce/t_{VCM}, 3.92 kgce/t_{VCM} and 35.01 kgce/t_{VCM}, respectively. As to blocks, C-2 consumes the maximum part (20.65 kgce/t_{VCM}, 31.22% of the total) of energy consumption because of its enormous need for 0.3MPa steam. The second consumer is C-1 which also needs a lot of 0.3MPa steam. U4 takes the biggest part (52.93%) of the energy consumption due to the contributions of C-2 and C-1 blocks. As a contrast, the biggest energy source U1, which needs cooling water to take away reaction heat to keep constant temperature, consumes 4.69 kgce/t_{VCM} that only account for 7.09% of the total consumption.

3.1.2. Exergy analysis

As is shown in Fig. 3, an exergy flow diagram of the process is obtained based on the simulation results. The diagram is treated like Fig. 2. The exergy amounts of utility streams are enlarged as twenty times as their original values. Figure 3 is like Fig. 2 in most parts. The biggest difference between them is that there are internal exergy loss lines, which are colored by light coral, added in Fig. 3. Besides, energy flows from the system to refrigerant in Fig. 2, while exergy flows from refrigerant to the system in Fig. 3. In order to analyze the characteristics of the process exergy loss, each ratio of branch to bus line is calculated and showed in the diagram. For example, the internal exergy loss of U1 is 1974.77 kW, and it accounts for 54.04% of the total internal exergy loss. The total internal exergy loss, 3653.97 kW, accounts for 65.24% of the total exergy loss of the process.
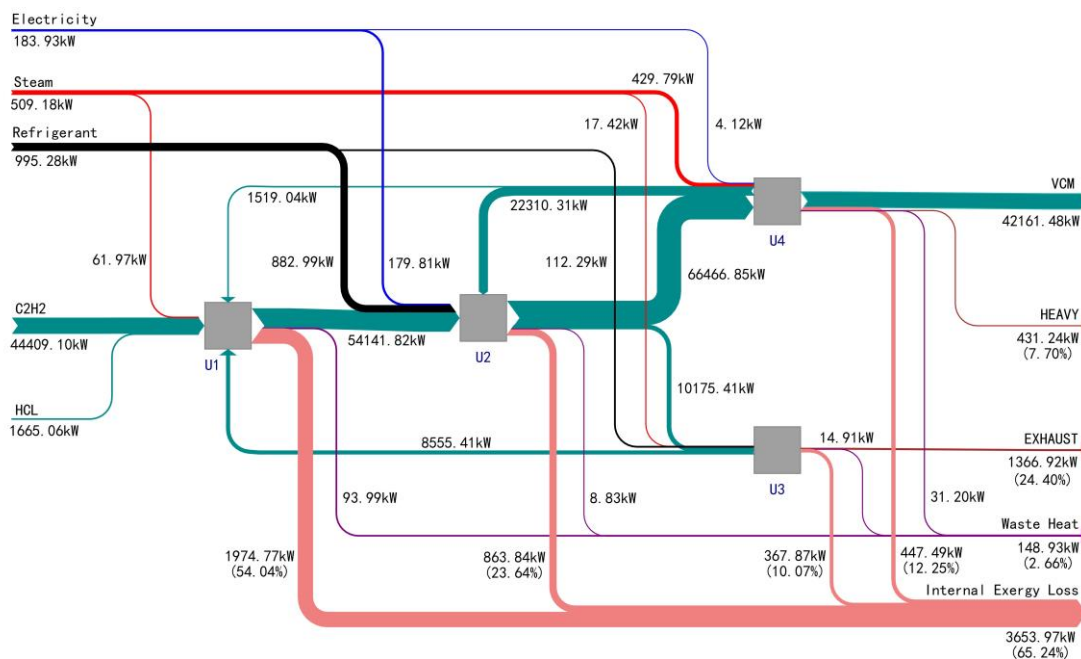

Fig. 3.   Exergy flow diagram of the process.

The total exergy loss consists of external and internal exergy losses. In the process, external exergy loss contains exergy taken away by materials (HEAVY and EXHAUST) and cooling water (Waste Heat). Internal exergy loss is the summation of the internal exergy loss of each unit. According to Fig. 3, the exergy taken away by materials is 1798.16 kW in total. It accounts for 32.10% of all the exergy loss. These exergy could be used by combustion or material reusing. Its use needs trade-off decisions since it needs additional equipments. Cooling water takes away only 148.93 kW exergy. But looking back to Fig. 2, it takes away 2896.27 kW reaction heat, which is the largest part of energy transferred between the system and utilities. This means that energy transferred to the cooling water directly is not appropriate. It leads to enormous exergy loss. The internal exergy loss, 3653.97 kW, accounts for 65.24% of all exergy loss. It indicates that the process has a relatively high irreversibility. And exchanging heat with cooling water is a main reason for the high thermodynamical irreversibility.

In the view of internal exergy loss, loss in U1 is 1974.77 kW (0.94 GJ/t_{VCM}), 54.04% of total internal exergy loss. This loss is from REACTOR1 mostly. As the reaction proceeding, a lot of chemical energy transforms into heat and the heat is transferred into cooling water then. This process makes huge irreversibility. Loss in U2 is 863.84 kW, 23.64% of the total internal exergy loss. It is mainly caused by condensation process in COND-1 and COND-2. Because of high quality electricity is used to produce cold energy, it leads to a lot exergy lost. As to U4, although it consumes the biggest part of energy consumption, its internal exergy loss is only 447.49 kW. Since it uses lower quality steam rather than electricity or chemical energy to heat the materials, thermodynamical irreversibility of this unit is lower than U1 and U2, correspondingly. The last one is U4 whose internal exergy loss is 367.87 kW, 10.07% of the total loss. Although there are reactor and condenser in U4, its low processing capacity (about 1/5 of U1) leads to low exergy loss and also causes low irreversibility.

3.2. Carbon footprint assessment

Depending on the input and output materials and utilities, carbon emission of the process is calculated using the calculation methods recommended by [12]. The results are shown in Fig. 4. Carbon emission contains direct carbon emission (DCE) and indirect carbon emission (ICE), drawn in the upside and downside of the picture respectively. ICE drawn in Fig. 4 is seperated detailedly to four different parts according to different utilities used. For example, the lines in red stand for ICE produced by using 0.3MPa steam, and the lines in blue stand for ICE produced by using electricity. Generally, ICE consists of two parts. One is the carbon emission produced by utilities used during the process. The other one is the carbon emission discharged in pretreating raw materials. According to [13] and [14], ICE by raw materials pretreating is 2558.89 kgCO$_2$e/t_{VCM}. It is the biggest part of carbon emission during VCM manufacturing. But, in fact, it has little relationship with the process studied; it is not drawn in Fig. 4.

In the process, DCE occurs in TANK-2 (in U3) and C-3 (in U4), and is 59.02 kgCO$_2$e/t_{VCM} as a total. It accounts for 12.08% of the carbon emission during the process. Most DCE is discharged in U3 (44.75 kgCO$_2$e/t_{VCM}, 75.82% of all DCE). ICE is 429.62 kgCO$_2$e/t_{VCM}, 87.92% of the total process carbon emission. ICE caused by using 0.3MPa steam to heat is 255.86 kgCO$_2$e/t_{VCM}. It is the biggest part of ICE, followed by ICE caused by refrigerant and cooling water using. In the view of units, U4 makes the biggest part of ICE. This is caused by using too much steam. When considering the measures for reducing carbon emission, the way to decrease the consumption of 0.3MPa steam is very important, and U4 is an available starting point.
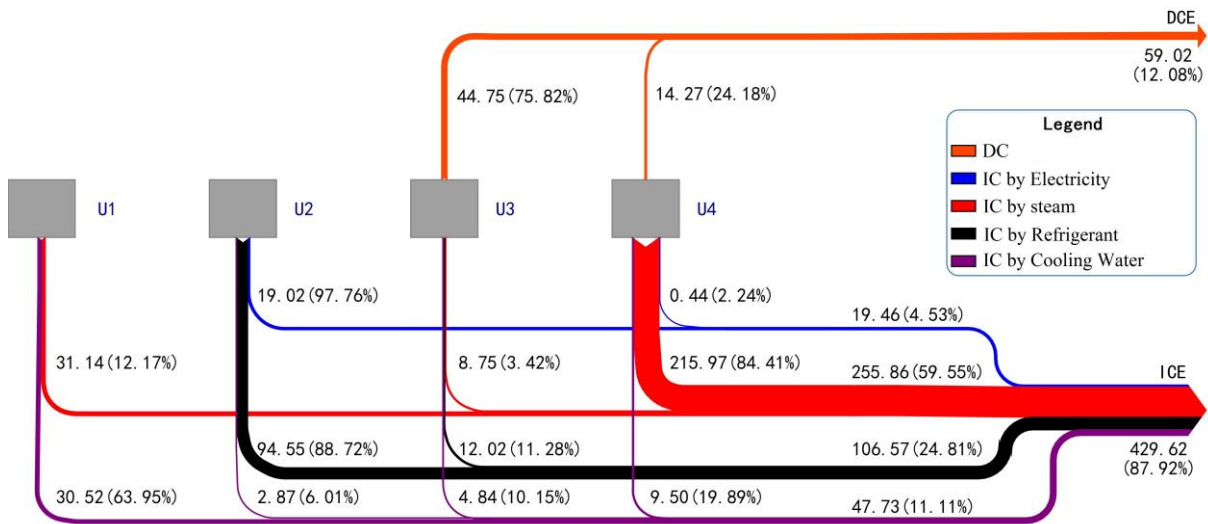
Fig. 4. Carbon footprint diagram of the process, kgCO₂e/t$_{VCM}$.

3.3. Optimization for energy saving and carbon emission reducing

Based on the previous analyses, in order to make the VCM manufacturing process consume less energy and reduce carbon emission, the key is to cut down the steam consumption of the process. With the reduction of 0.3MPa steam, energy consumption and ICE of the process will be decreased simultaneously. In consideration of the characters of the system, to cut down the steam consumption is feasible. From the simulation results, the main reactor released 2896.27 kW heat during reaction, and the heat is transferred into cooling water and became worthless waste heat. The temperature of the main reactor is 150℃, while the outlet temperature of preheater is 100℃, and the highest temperature in U4 is 84.4℃. Therefore, the reaction heat could be used to produce 0.3MPa steam (saturation temperature is 133.6℃), and then these steam could be used to heat other streams. There are 4.8 t/h steam produced if the reaction heat were all used. These steam can fully meet the needs of heating (only 3.2 t/h steam is needed in the process).
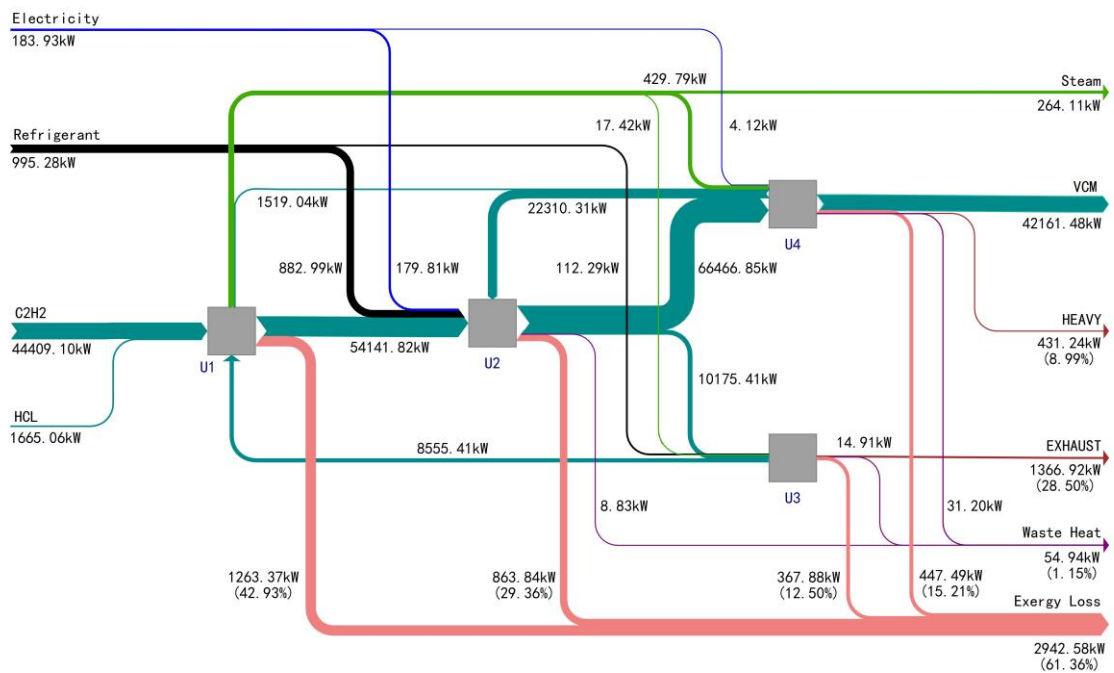

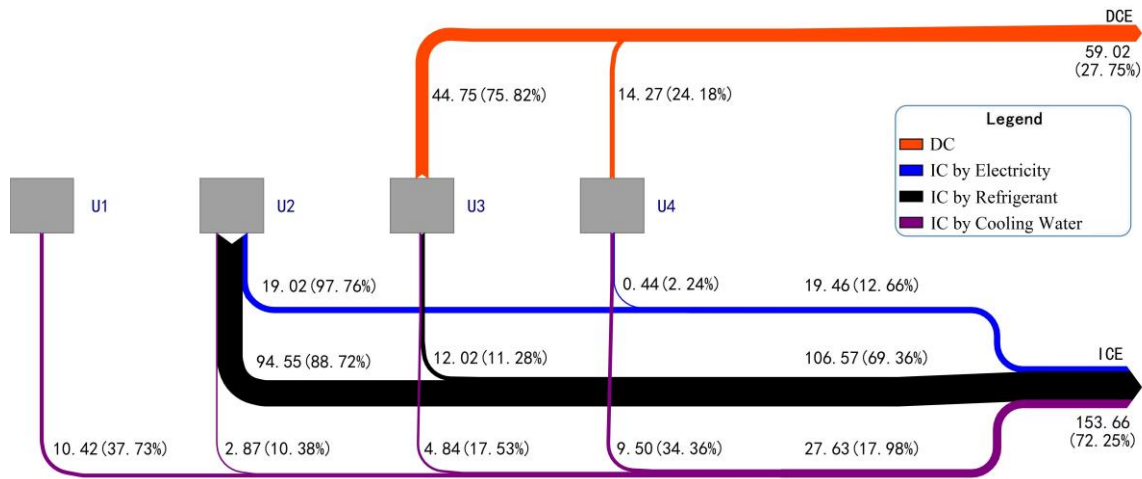*Fig. 5. Exergy flow diagram of the reformed process.*

Fig. 6.   Carbon footprint diagram of the reformed process, kgCO₂e/t_VCM.

After reforming, new exergy flow diagram and carbon footprint diagram are obtained and shown as Fig. 5 and Fig. 6. Figure 5 and Fig. 3, as well as Fig. 6 and Fig. 4, are similar in their structures.

In contrast with Fig. 3, some lime green lines are added in Fig. 5 and steam streams in red are disappeared. These new added lines stand for the 0.3MPa steam produced by reaction heat. As is seen in Fig. 5, most part of the exergy carried by the produced steam is used in the system itself. Furthermore, there is 264.11 kW exergy could supply to external needs. Because of heat transferred to steam rather than cooling water, the internal exergy loss of U1 is decreased from 1974.77 kW to 1263.37 kW. Exergy loss is decreased by 711.40 kW, which accounts for 12.70% of original total exergy loss. The energy efficiency of the process has increased. As the steam needed is produced by the system itself, energy consumption decreases from 66.14 kgce/t$_{VCM}$ to 26.60 kgce/t$_{VCM}$. Obvious energy saving effect is achieved.

Comparison with Fig. 4, the biggest difference in Fig. 6 is that ICE produced by using 0.3MPa steam was gone. And ICE by refrigerant takes the lion's share of all ICE. U2 replaces U4 to be the largest carbon emission unit as a consequence. After reforming, carbon emission of the system is decreased from 488.64 kgCO₂e/t$_{VCM}$ to 212.68 kgCO₂e/t$_{VCM}$, and the total carbon emission of VCM manufacturing is 2771.57 kgCO₂e/t$_{VCM}$. The reforming makes a significant effect of carbon emission reduction.

4. Conclusion

This paper focuses on the thermodynamic properties of the acetylene-based VCM manufacturing technology. A reliable simulation with less than 1% error was built on the basis of the process of Inner Mongolia Haiji Chlor-Alkali Chemical Co. Ltd. The energy consumption characters, exergy loss distribution, as well as the carbon footprint of the process were analyzed based on the simulation results. The energy flow diagram was drawn and the energy consumption properties were obtained. The main reaction unit releases a lot reaction heat; the VCM cooling and compression unit needs cold energy primarily; The VCM distillation unit needs steam to supply heat; and the recycle reaction unit consumes the least energy because of its low processing capacity. The energy consumption of the process is 66.14 kgce/t$_{VCM}$ in total, and U4 consumes 52.93% of all because its enormous needs for 0.3MPa steam.

The internal and external exergy losses were obtained based on the exergy flow diagram of the process. It turns out that the internal exergy loss accounts for 65.24% of the total loss. The internal

exergy loss of U1, 1974.77 kW, is the biggest part of all, followed by U2, U4 and U3. The external exergy loss is 1947.09 kW, accounts for 34.76% of the total loss. Reaction heat transferred to cooling water leads to a large number of exergy loss.

The carbon footprint flow diagram shows that the direct and indirect carbon emissions are 59.02 $kgCO_2e/t_{VCM}$ and 2988.51 $kgCO_2e/t_{VCM}$, respectively. In the indirect carbon emissions, that caused by materials pretreating is 2558.89 $kgCO_2e/t_{VCM}$, dominating the total carbon emissions. Indirect carbon emission caused by utility consumption in the system is 429.62 $kgCO_2e/t_{VCM}$, most of which is caused by using 0.3MPa steam.

After reforming, the reaction heat is recovered to produce 0.3MPa steam. Through this way, energy consumption of the process is decreased from 66.14 $kgce/t_{VCM}$ to 26.60 $kgce/t_{VCM}$, and the total carbon emission is reduced to 2771.57 $kgCO_2e/t_{VCM}$. The reforming makes a significant energy saving and carbon emission reduction effect.

Acknowledgements

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