HEFAT2014
10th International Conference on Heat Transfer, Fluid Mechanics and Thermodynamics
14 – 16 July 2014
Orlando, Florida

Effect of Cooling Rate on Improving the Performance of the Catalytic PVC Reactor in Egyptian Petrochemical Company

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Abstract

This work investigates the possibility of improving the performance of poly vinyl chloride (PVC) reactor in Egyptian Petrochemical Company(EPC) by enhancing the rate of heat transfer via increasing the cooling rate of the reactant. two booster pumps have been installed for the four reactors to increase the flow rate of the cooling water in the reactor jacket by a factor of 1.25. Different cooling rates were investigated under different batches of the process. In addition a comparison between theoretical and actual results obtained was carried out. It was found that increasing the cooling rate has increased the PVC productivity of each batch to 23.3 ton/batch by a percentage of 115% of the design capacity; Decreasing the time of the reaction from 6 hr to 4.5 hr. The overall capacity of PVC plant increased by 25% more than the design capacity. In addition a reduction in the operation hours of the agitators i.e saving in energy consumption; Finally increasing the lifetime of the reactor by reducing the frequency of the process of chemical cleaning that has side effect on the reactor life time.

Keywords

PVC reactor, heat transfer, fouling, cooling rate

1. Introduction

Scale formation is the essential drawback of PVC suspension polymerization. Scale on the wall causes a fatal damage on the heat transfer capacity. Contamination of scale into PVC causes fish-eye of product. So perfect reactor cleaning is needed to attain heat transfer capacity and also product quality. Even after the development of high-pressure water cleaning devices, reactor cleaning needs big manpower and long operation time and was the main obstacle for development of large reactor technology. There are few literatures, which are proposing the mechanism of scale formation and scale prevention [1-4]. Bilgic and Savasci [1] summarized the mechanism of scale formation as follows. The exact cause of scale formation is not completely understood; however, the process appears to occur in two steps. The first is the adsorption and subsequent polymerization of vinyl chloride monomer (VCM) on the wall. The second is the deposition of PVC formed in the bulk of the reactor onto the formerly existing scale layer. Many attempts have been done for scale formation prevention and control such as using different materials of construction for the reactor surface. Different methods such as chemical coating and polymeric coating on reactor wall, addition of chemicals during polymerization, cleaning of inner surface of reactor during polymerization, using special agitator or scraper, and others were used to decrease the affinity to VCM, or decrease adhesive strength to PVC deposit [4]. On the other hand heat removal technology represent an important issue in PVC reactor, which attracted the interest of many researchers[5-24] such as, Increasing the heat transfer area by putting jacket on the upper elliptical head; Increasing the number of baffles with water cool system is also effective to increase heat transfer area but for number of baffles there is a limitation, which comes from homogeneous agitation and difficulty of scale prevention or cleaning. Adoption of coolant, chilled water of around 10^{o}C cooled by ice machine can attain almost double of heat removal capacity compared with cooling tower water of around 30^{o}C in the case of polymerization at 50^{o}C but the cost of machine and running cost of electricity for ice machine is very expensive. There is a technology to adopt coolant, such as ammonium or Freon directly into jacket or baffle this technology has also the drawback of high cost. Reflux condenser, by adoption of reflux condenser the latent heat of vaporization of VCM can be removed from the reaction media by evaporation of VCM. Evaporated VCM gas is then cooled at the condenser tube and condensed to the liquid VCM, which returns to the reaction media. Others used inner cooling jacket as there is another significant difference in the jacket side thin film coefficient. In the case of conventional jacket, to improve the jacket side thin film coefficient, special nozzle or baffles of jacket are developed to keep cooling water in contact with the wall moving as much as possible. But the improvement by these attempts is not sufficient mainly because of some leakage of cooling water through clearance of jacket baffles. In contrast to these insufficient cooling water circulation of the conventional jacket, the channel of cooling water of the inner jacket is perfectly closed by welding. Then it is possible to improve the jacket side thin film coefficient significantly by increasing velocity of cooling water circulation in the case of inner jacket reactor. There are several patents filed in this new field [20,21]. Sumitomo Heavy Industry developed a new type inner jacket reactor, which has a structure of cooling water channel isolated from the outside reactor wall [22,23]. This new type inner jacket reactor has been already adopted for the new commercial line in Japan [24].

Nomenclature

A	m^2	Area of heat transfer
Cp	kJ/kg.K	Heat capacity
D_o	m	Outside heat transfer coefficient
G	kg/m^2.hr	Mass velocity
h_o	kJ/m^2.hr.K	Outside heat transfer coefficient
K_f	kJ/m.hr.K	Thermal conductivity
m	kg/hr	Mass flow rate
U	kJ/m^2.hr.K	Overall heat transfer coefficient
ΔH_r	kJ/kg	Heat of reaction
ΔT	K	Temperature difference
ΔTm	K	Logmean temperature difference
μ_f	kg/m.s	Solution viscosity
ζ		Conversion factor

2. Process description

There are two independent lines in the PVC Plant and each line has Two specific reactors each reactor has 70m^3 capacity to produce 80,000 Ton PVC/Year. The design productivity is 20 Ton PVC/Batch. Each Batch needs 5 hr for complete reaction in each reactor. The reaction inside the reactor is an exothermic reaction therefore the heat of the reaction must be removed by using cooling water through the jacket of the reactor (200-220m^3/hr) and using chilled water through four baffles inside the reactor (90 m^3/hr) as shown in figure 1. This system controls temperature in the reactor by removing heat using cooling water in the jacket and then using chilled water in the baffles depending on the heat of the reaction. The maximum water flow rate in both jacket and baffles represent the maximum heat removal capabilities of the polymerizes , termed maximum economic flow rate.

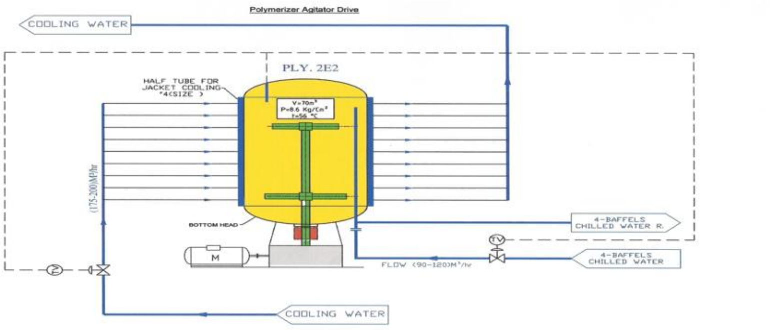


Figure 1: Schematic diagram of PVC reactor.

2.1. Problem Definition

The flow rate of cooling water in the jacket decreased to 175-200 m^3 /hr which is ascribed to a thick layer of deposits (0.5 cm) was found in the jacket which is composed of half pipe; 4in diameter, schedule 40 carbon steel", as a result of these deposits the cooling capacity was decreased and heat transfer through the reactor wall and the cooling medium became low efficiency.

The productivity of each batch reduced to 17-18 ton PVC and the number of batches increased per day "15 batches" and the reaction time increased to "6hrs". Increasing the consumption of chemicals " Shortstop" to control the reaction in case of excessive heat generation and high temperature increase. It also causes an increase in the consumption of electrical power, demiwater, steam and also increasing in the maintenance costs. Increasing of VCM recovery quantity and conversion rate reduced to 70%. Increasing the heat load and the power consumption on the chilled water unit.

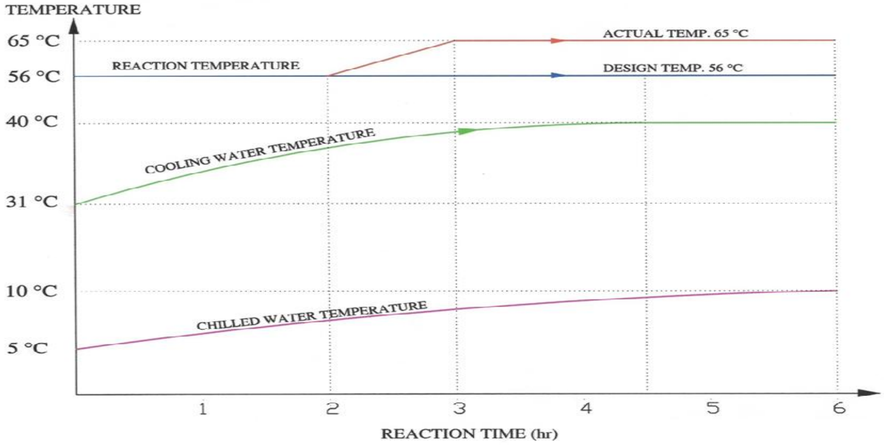


Figure 2: Effect of reaction time on cooling water, Chilled water and reaction temperatures.

As shown in figure 2 the reaction temperature increases by increasing the reaction time which is ascribed to the fact that catalyst performance is not homogeneous all over the reaction time; As shown in figure 3 the reaction proceed from very low conversion rate up to an average rate of 0.2 hr^{-1}. consequently, cooling and chilled water temperatures increase.

3. Results and discussions

There are two main solutions considered for the solution of the above problem which can be simplified by the following; first to make chemical cleaning for the jacket and baffles by means of citric acid 10% as it will remove the iron deposits, second is to Increasing the cooling water flow rate for reducing the temperature of the reactor from the actual conditions at 65 ^oC to design temperature at 56^oC. In this study We installed two booster pumps for four reactors to increasing the flow rate of cooling water in the reactor jacket from 200 to 275 m^3/hr, and the new system is now as shown in figure 3.

3.1. Analysis of the situation before and after fouling

For the operation under fouling conditions the reactor temperature increased to 65^oC instead of 56^oC(design temperature) i.e ΔT due to fouling = 65 –56 = 9^oC. The main design parameter for this research work is to calculate the amount of cold water required to reduce the reaction temperature again to 56^oC.

The main source of heat for this system is the heat of reaction that may be calculated using the equation(1).

$$\text{heat of reaction} = Q_r = m_{(VCM)}\,\Delta Hr\,\zeta/t \tag{1}$$

$$Q_r = 25000 * 1600 * 0.8 * \frac{1}{4hr} \quad \text{kJ/hr}$$

$$Q_r = 8000000/4.186 = 1911132 \text{ Kcal/hr}$$

The heat of reaction Q_r is constant for both cases; clean and fouling conditions. The cooling system uses both cold water and chilled water. Chilled water usually used at the end of the process when released heat exceeds certain limits. Thus

$$Q_{avail} = Q_{\text{Cold water}} + Q_{\text{Chilled water}} \quad (2)$$

$$Q_{avail} = (m\,Cp\,\Delta T)_{CW} + (mCp\Delta T)_{Chw} \quad (3)$$

Assume for this stage chilled water exit temperature is constant in both cases at 10^oC and its entrance temperature is 5^oC.

It is determined that for the design conditions approximately no fouling as shown in figure 2 the cooling water inter the system at 31 and exit at 40^oC i.e the temperature difference $\Delta T = 9^oC$ while for chilled water the difference is 5. Thus:

$$Q_{avail} = (200 * 1 * 9 + 90*1 * 5)* 1000 = 2250 * 10^3 \text{ Kcal/hr}$$

i.e the available heat Q_{avail} according to the design is greater than the heat required Q_r which fulfill the requirement.

In case of Fouling a reduction in the amount of heat transfer takes place thus the cooling water exit temperature will be 36^oC instead of 40 ^oC (records of the actual conditions in the plant) i.e the temperature difference of cooling water for this case will be only 5^oC.

$$Q_{avail} = (m\,Cp\,\Delta T)_{CW} + (m\,Cp\Delta T)_{Chw} =$$

$$(200*1*5 + 90*1*5) * 1000$$

$$Q_{avail} = 1450 * 10^3 \quad \text{kcal/hr}$$

In this case the Q_{avail} is less than Q_r because of Fouling.

3.2. Calculation of the required cooling rate to overcome fouling

The cooling water flow rate for the new condition(after fouling) was calculated as follows; Due to fouling part of the heat will not transfer represented by Q_{diff}.

$$Q_{diff} = 1{,}911{,}132 - 1{,}450{,}000 = 461{,}132 \text{ kcal/hr}$$

This amount of heat accumulates inside the reactor which causes the reactor temperature to increase from 56^oC to 65^oC at maximum conditions of catalyst performance. Theoretically we assumed that this extra heat load can be removed by increasing the cooling water flow rate thus, the required extra cooling H_2O was calculated as follows:

$$Q_{diff} = m\,Cp\,\Delta T$$

$$461{,}132 = m * 1 * (T_2 - T_1)$$

Assume T_2 is the average between the exit temperature of cooling water in case of no fouling (40^oC) and the exit temperature in case of fouling (36^oC) i.e exit temperature was considered 38^oC, thus the required flow rate of cooling water is now

$$m = 65876 \text{ kg/hr} = 65.876 \text{ m}^3/\text{hr}$$

Assume safety factor 10% for overcoming fouling

$$m = 65.876 * 1.1 = 72.46 \text{ m}^3/\text{hr},$$

this value was approximated to 75 m^3/hr, then new selected flow rate for cooling water using new booster pump was recommended to be 275 m^3/hr instead of 200 m^3/hr.

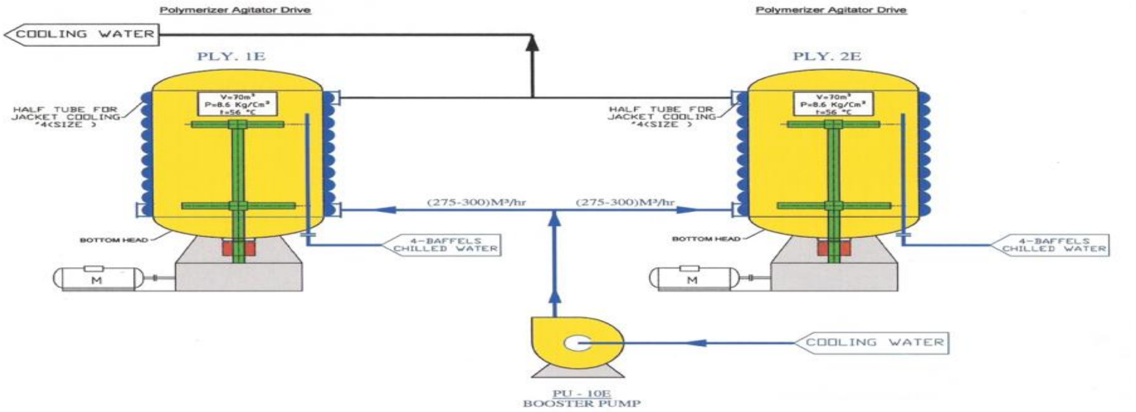
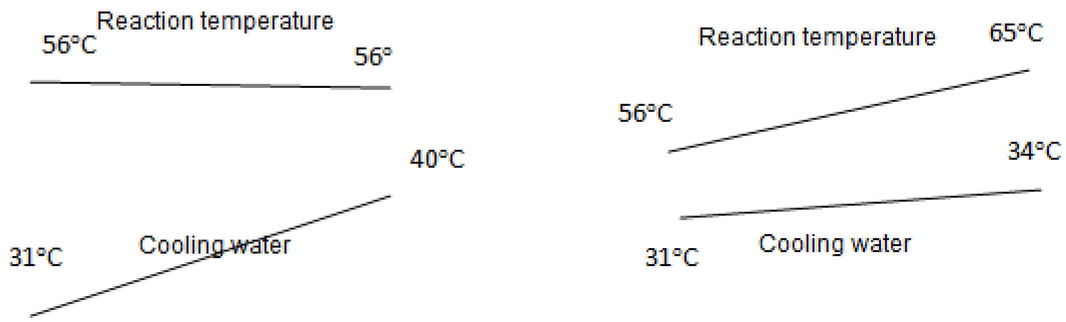


Figure 3: schematic diagram of the new system with one booster pump for each two reactors.

3.3. Effect of changing cooling rate on the heat transfer coefficient



(a) (b)

Figure 4: Temperature distribution for (a) clean surface and (b) after fouling

The real inlet and outlet temperatures of cooling water and that of the reactor measured before and after fouling are shown in figure 4. The driving force for the clean and fouling conditions of the reactor has been changed, from 20 to 27.4^{o}C respectively. Which means that the overall heat transfer coefficients for clean and fouling reactor will change. As the reactor area and generated heat (heat of reaction) are constant, accordingly the ratio

$$\frac{(\mathrm{U\ A\ \Delta Tm\ })\mathrm{clean}}{(\mathrm{U\ A\ \Delta Tm\ })\mathrm{fouling}} = \frac{Q}{Q} = 1 \qquad (4)$$

Thus; $\frac{\mathrm{U\ \ \Delta Tm}_{Clean}}{\mathrm{U\ \ \Delta Tm}_{fouling}} = 1$ and

$$\frac{\mathrm{U}_{\ Clean}}{\mathrm{U}_{\ fouling}} = \frac{\Delta\mathrm{Tm}_{fouling}}{\Delta\mathrm{Tm}_{Clean}} = \frac{27.4}{20} = 1.37$$

Or; $\frac{\mathrm{U}_{\ fouing}}{\mathrm{U}_{\ Clean}} = 0.7299$

in other words the heat transfer coefficient decreased by approximately 27% than the coefficient of the clean surface.

By the new conditions the cooling water flow rate increased by 37.5% than the design value (no fouling). For studying the effect of increasing the cooling rate on the heat transfer coefficient the following equation can be used for flow outside tube[25]

$$\frac{h_O D_O}{K_F} = \frac{a_O}{F_S}\left(\frac{D_O G_S}{\mu_f}\right)^{0.6}\left(\frac{C_P \mu}{K}\right)^{0.33} \qquad (5)$$

As all parameters are approximately constant except the mass velocity which has been changed from 200 to 275 m^3/hr for same area of the cooling surface. Accordingly the above equation(5) can be approximated to be:

$$\frac{h_{oNew}}{h_{o\ Design}} = \left(\frac{G_{sNew}}{G_{sDesign}}\right)^{0.6}$$

$$\frac{h_{oNew}}{h_{o\ Design}} = 1.21$$

Which shows that the heat transfer coefficient for the shell side approximately increased by 21% by increasing the water flow rate from 200 to 275 m^3/hr. the difference between both values of fouling reduction 27% and cooling water enhancement 21% is compensated by the reduction in fouling layer thickness due to turbulences generated by increasing the cooling water flow rate.

3.5. Effect of changing the cooling rate on the overall reactor performance

As shown in figures 5 and 6 the results show that conversion of VCM increased from 80% in design condition to 92% in new design, which increase the plant capacity from 80000 ton/yr (design) to 100,000 ton/yr. In addition increasing the conversion save the amount of demiwater used by minimizing the amount blown down with lower conversion, which improves the process economy . In addition it is worthy to mention that the change in cooling amount was calculated based on using excess of cooling water and not from chilled water, i.e saving in chilled H_2o is expected which improves the economy of the process. Also presence of chilled water as back up for Temperature increase reduced the possibilities of using short stop chemical that increase the conversion of VCM and hence increase the productivity. Table1 shows the main changes that took place due to the booster pump installation and increasing the cooling water flow rate.

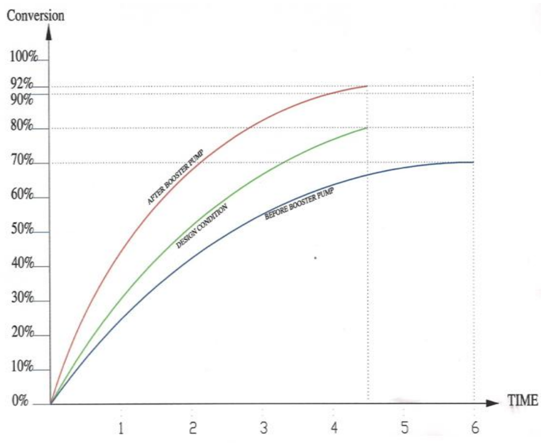


Figure 5: comparison between VCM conversion before and after installing the booster pump.

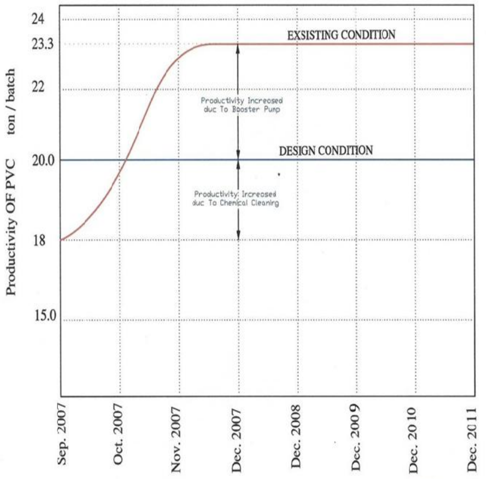


Figure6: productivity of PVC with time before and after changing to the existing conditions

Table1: main improvements considered by installation of the booster pump.

Specification	**Before Booster Pump**	**After Booster Pump**
Reaction Time (hr.)	6	4.5
Cooling water flow rate (m3/hr.)	200	275
VCM Fresh Ton / Batches	*18.5*	*23.5*
VCM Recovery Ton / Batches	*7*	*2*
Heat Capacity M kcal/hr	*2.88*	*3.68*

Productivity Ton / Batches	*18*	*23.3*
Conversion	*70%*	*92%*
No. of Batches/Day	*15*	*12*
PVC Unit Design Capacity	80,000 ton	100,000 ton

4. Conclusions

Cooling water flow was used for improving the PVC reactor performance in Egyptian Petrochemical Company, Alexandria, Egypt, the flow rate was increased from 200 to 275 m3/hr, which is believed to reduce the fouling effect and enhance the heat transfer through the reactor wall. The following improvements have been proven in the plant operation.

1. The productivity of each batch after increasing the flow rate of the cooling water has been 23.3 ton/batch Minimum, and then decreasing no. of batches per day from 15 to 11 batches.
2. Decreasing the time of reaction from 6 hr. to 4.5 hr.
3. The Design capacity of PVC plant increased by 25 % (100,000 ton PVC/year), in Jan 2009 we produced actual 10,000 tons PVC.
4. Protect the body of the reactors to repeat the process of chemical cleaning that has side effect.
5. Reduce the operation hours of the Agitators, saving in the spare parts, saving in chemicals and demiwater, saving in energy consumption.

References

1. T. Bilgic, O.T. Savasci, Polym Plast Technol Eng. 33(3)(1994)381–390.
2. Meinel L, Behrens H. Plaste Kautschuk 1982;29(11):643–646.
3. M. Ravey, J. Appl. Polym. Sci. 21(1977)839–840.
4. Japanese Examined Patent Sho45-30,835, assigned to Shinetsu Chemical; 1970.
5. R.H. Burgess, Suspension polymerisation of vinyl chloride. In: Burgess RH, editor Manufacture and processing of PVC. London: Applied Science Publishers; (1980)1-38
6. L.F. Albright, C.G. Bild, Chem Eng.; Sep 15(1975)121–8.
7. T. Imanaka, M. Kikuchi , Kagaku Sochi;37 (8) (1995)71–9.
8. Japanese Examined Patent Sho45-20,297, assigned to Shinetsu Chemical; 1970.
9. Japanese Unexamined Patent Hei6-199,912, assigned to Shinetsu Chemical; 1994.
10. Japanese Unexamined Patent Hei5-320,206; Hei5-320,207; Hei5-320,208; Hei5-320,209, assigned to Shinetsu Chemical; 1993.
11. Japanese Unexamined Patent Sho58-32,606, assigned to Toa Gosei Chemical; 1983.
12. Japanese Unexamined Patent Sho56-47,410, assigned to Denki Kagaku; 1981.
13. Japanese Unexamined Patent Sho55-157,607, assigned to Ryonichi; 1980.
14. Japanese Unexamined Patent Hei5-320,213, assigned to Shinetsu Chemical; 1993.
15. Japanese Examined Patent Hei3-4,249; 1991, USP 4,552,724, assigned to Kureha Chemical and Shinko Pantec.
16. K. Inoue, Kagaku Sochi, 34(2) (1992)15–19.
17. T. Shinkai, Shinko Pfaudler Tech Rep,32(3)(1988)21–6.
18. T. Emura, T. Suzuki, Preprint of No. 51 Poly Vinyl Chloride Forum in Osaka, (2000)6–11.
19. Y. Saeki, T. Emura, Technical progresses for PVC production, Prog. Polym. Sci. 27 (2002) 2055–2131
20. Japanese Unexamined Patent Sho55-82,289, assigned to Hoechst.
21. US Patent 5,027,971 and 5,150,831, assigned to B.F. Goodrich.
22. Japanese Unexamined Patent Hei11-276,869, assigned to Sumitomo Heavy Industries; 1999.
23. H. Nishimi, T. Inoue, M. Wada, M. Mishima. Kagaku Kogaku, 62(1998)102–104.

24. Japanese Unexamined Patent Hei8-73,509, assigned to Mitsubishi Chemical.
25. M.S. Peters and K.D. Timmerhaus, Plant Design and Economics for Chemical Engineeers, 4th edn., Mc Graw Hill, 1991.