The kinetic parameters and safe operating conditions of nitroglycerine manufacture in the CSTR of Biazzi process

Kai-Tai Lu [a,*], Kuo-Ming Luo [b], Tsao-Fa Yeh [a], Peng-Chu Lin [a]

[a] Department of Applied Chemistry, Chung Cheng Institute of Technology, National Defense University, Taoyuan, Taiwan, ROC
[b] Jen-Te Junior College of Medicine, Nursing and Management, Miaoli, Taiwan, ROC

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ABSTRACT

Nitroglycerine has been widely used as an ingredient of explosives and propellants for a long time. It is produced by the glycerine nitration reaction. Many fire and explosion incidents have occurred during its manufacturing process owing to its severe thermal instability in both the nitration reaction and the purification processes. The kinetic parameters of this reaction and the criteria for stable production have not so far been clearly identified. In this investigation, we estimate its reaction kinetic parameters from the experimental results obtained using a tubular flow reactor by a numerical analysis method. These reaction kinetic parameters are then used to evaluate the safe operating conditions in a CSTR for the Biazzi continuous nitroglycerine production. The results are important and useful in the production process of nitroglycerine.

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1. Introduction

Nitroglycerine (NG), also known as glycerol trinitrate, is usually produced from the glycerine nitration. Its nomenclature is 1,2,3-propanetriol trinitrate, chemical formula is $C_3H_5(ONO_2)_3$, and molecular weight is 227 g/mol. The industrial product is a yellowish oily liquid having a density of 1.591 g/cm^3 at 25 °C. Nitroglycerine has explosive properties and has been widely used as ingredient of explosives and propellant for more than a hundred years. It is the main component of high explosives such as dynamites, as well as an ingredient in most mining explosives. It was used extensively in smokeless powder and together with nitrocellulose as a so-called double base propellant, or with nitrocellulose and nitroguanidine as a triple base propellant, which are used in larger calibre projectiles. Furthermore, it has been used as ingredient of the solid propellant in rockets.

Nitroglycerine has very high impact sensitivity and thermal instability. Thus, many accidents have occurred during its manufacture and transport. According to Biasutti (1985), 500 major accidents occurred in the explosive industry worldwide during the period from 1769 to 1980. Among these accidents, 121 involved nitroglycerine which is approximately 24.2% of the total. Han et al. (1988a) show that there were 43 industrial accidents involving nitroglycerine in the period from 1954 to 1982. Obviously, the manufacturing process of nitroglycerine is more dangerous than other chemical processes.

The manufacturing technique for nitroglycerine includes both batch and continuous processes. Typical examples of the batch method are the Nobel process from 1862 and the Nathan, Thomson and Rintoul process from 1908. A continuous method was first developed by the Schmid process in 1927 followed by the Biazzi process in 1935. Subsequently Nilssen and Brunnberg developed a new injection nitration process in 1950. In 1978 the Hercules Company in U.S.A. designed another new tubular process (Urbanski, 1965; Kaye, 1978a).

Although the manufacture of nitroglycerine has been developed for over 140 years, the dangerous industrial procedures involved have almost remained the same. These procedures include preparing of mixed acid, nitration of glycerine, separation of product and wastes, washing of product, filtration of waste, recycling of nitroglycerine from waste acid and treating of waste acid. Most of industrial accidents have occurred during the glycerine nitration stage or the separation stage (approximately 50.4%, Biasutti, 1985). Therefore, improvements in manufacturing procedures and

Nomenclature

A	pre-exponential factor of the Arrhenius equation
C	concentration
C_P	molar heat capacity of individual component $(kJ\,mol^{-1}\,K^{-1})$
C_v	heat capacity of reactant $(kJ\,l^{-1}\,K^{-1})$
ΔC_{Pd}	specific heat of mixed acid at standard state $(kJ\,mol^{-1}\,K^{-1})$
E	activation energy $(kJ\,mol^{-1})$
h	overall heat transfer coefficient of ambient cooling medium $(kJ\,m^{-2}\,K^{-1}\,min^{-1})$
H	enthalpy $(kJ\,mol^{-1})$
ΔH_d	heat of dilution, $kJ\,mol^{-1}$
ΔH_r	heat of reaction $(kJ\,mol^{-1})$
k	reaction rate constant; dimension depends on kinetics
m	reaction order of nitric acid
M	initial concentration ratio of nitric acid to glycerine
n	reaction order of glycerine
Q_g	dimensionless heat generation rate; definition in Eq. (61)
Q_r	dimensionless heat removed rate; definition in Eq. (62)
r	reaction rate; dimension depends on kinetics
R	universal constant $(kJ\,kg^{-1}\,mol^{-1}\,K^{-1})$
R_F	weight ratio of mixed acid to glycerine
R_N	percentage of nitric acid in anhydrous mixed acid
R_W	percentage of water in mixed acid
S	the external surface area of cooling coils (m^2)
T	temperature (K)
v_o	flow rate of reacted solution
V	volume of reactor (l)
W_{m0}	inflow weight of mixed acid in reactor (g)
$\dot{W}_{m0}$	inflow weight rate of mixed acid in reactor $(kg\,min^{-1})$
W_{mf}	outflow weight of mixed acid in reactor (g)
$\dot{W}_{mf}$	outflow weight rate of mixed acid in reactor $(kg\,min^{-1})$
x	fractional conversion of component

Greek symbols

β	dimensionless ambient temperature in cooling system; definition in Eq. (50)
ε	definition in Eq. (57)
ϕ_0	definition in Eq. (55)
ϕ_1	definition in Eq. (56)
φ	definition in Eq. (52)
θ	definition in Eq. (51)
θ_o	definition in Eq. (53)
θ_{ref}	definition in Eq. (54)
τ	resident time

Subscripts

a	in coolant system
f	final condition
G	$C_3H_5(OH)_3$
j	index of components
N	HNO_3
NG	$C_3H_5(ONO_2)_3$
o	initial condition
ref	standard state
S	H_2SO_4
W	H_2O

the development of safety control techniques are important requirements for this reaction.

The kinetic parameters of the nitroglycerine reaction and the operating conditions for its industrial manufacture are not found in the open literature, presumably because of its military importance. In this investigation, we have estimated the kinetic parameters of the nitroglycerine reaction from the experimental results obtained in a tubular flow reactor by a numerical analysis method. Furthermore, we evaluate the safe operating conditions in a CSTR of the Biazzi continuous process using these kinetic parameters.

2. Evaluation of kinetic parameters of glycerine–nitric acid reaction system from the experimental results in a tubular flow reactor

The elemental reaction of producing nitroglycerine is esterification reaction of glycerine and nitric acid. This chemical reaction can be expressed as:

$$C_3H_5(OH)_3 + 3HNO_3 \xrightarrow{H_2SO_4} C_3H_5(ONO_2)_3 + 3H_2O \tag{1}$$
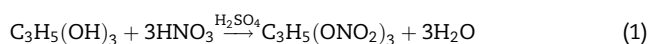
In this chemical reaction, the mixed feed acid contains both HNO_3 and H_2SO_4. The reagent H_2SO_4 acts as a dehydrating agent (Ren, 1994). Therefore, only the HNO_3 participates in this reaction. The chemical consumption can be expressed by

$$C_G = C_{G,0}(1 - x_G) \tag{2}$$

and

$$C_N = C_{N,0} - 3C_{G,0}x_G = C_{G,0}(M - 3x_G) \tag{3}$$

where C_G and C_N denote the concentration of glycerine and nitric acid, respectively. x_G represents the fractional conversion of glycerine and M is the initial concentration ratio of $C_{N,0}$ to $C_{G,0}$. Assuming the reaction is n order in the glycerine and m order in the nitric acid and that the reaction rate constant can be expressed as Arrhenius form, where A and E denote the frequency factor and activation energy, respectively. Then, the reaction rate of glycerine and nitric acid can be expressed as

$$-r_G = kC_G^n C_N^m = A\,e^{-E/RT}C_G^n C_N^m$$
$$= A\,e^{-E/RT}C_{G,0}^{n+m}(1 - x_G)^n(M - 3x_G)^m \tag{4}$$

2.1. Mass and energy balance in a tubular flow reactor

Four experimental data points during the production of nitroglycerine in a tubular flow reactor as shown in Fig. 1, have been measured by Han et al. (1988b). These include inflow compositions and operating conditions and are listed in Table 1. We can evaluate the kinetic parameters of the reaction using these experimental data.
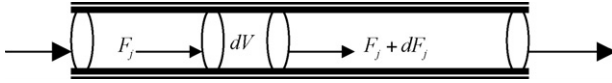
Fig. 1 – The tubular flow reactor of producing nitroglycerine.

If we consider this reaction system in a tubular flow reactor as Fig. 1, the mass balance can be expressed as

$$F_{G,0}\, dx_G = (-r_G)\, dV \tag{5}$$

where $F_{G,0}$ represents the molar flow rate of glycerine and V is the volume of tubular flow reactor, respectively. Substituting Eq. (4) into Eq. (5), we can express the equation of mass balance in terms of fractional conversion of glycerine as

$$\frac{dx_G}{d\tau} = A\, e^{-E/RT} C_{G,0}^{n+m-1} (1 - x_G)^n (M - 3x_G)^m \tag{6}$$

where $\tau = V/\nu_o$ is the space time and ν_o is the volumetric flow rate of reactants.

The energy balance in a tubular flow reactor is

[Accumulation of heat] = [Enthalpy flow in]

$$- \text{[Enthalpy flow out]} \tag{7}$$

At steady state, there is no heat accumulated in this reactor. Thus, we can express the above term as

$$0 = \left[\sum_{j=1}^{S} h_j(T) F_j\right]_V - \left[\sum_{j=1}^{S} h_j(T) F_j\right]_{V+dV} \tag{8}$$

where h is the enthalpy of reactant which can be expressed as function of temperature and F is the molar flow rate of reactant, respectively. Subscript j represents the reactants of $C_3H_5(OH)_3$, HNO_3, H_2SO_4, $C_3H_5(ONO_2)_3$ and H_2O in the reaction system, respectively. Eq. (8) is divided by dV and for $dV \rightarrow 0$ it can be expressed as

$$\frac{d}{dV}\left[\sum_{j=1}^{S} h_j(T) F_j\right] = 0 \tag{9}$$

or

$$\sum_{j=1}^{S}\left[h_j(T)\frac{dF_j}{dV} + F_j\frac{dh_j(T)}{dT}\frac{dT}{dV}\right] = 0 \tag{10}$$

where $dF_j/dV = r_j$ represents the reaction rate of reactant and $dh_j(T)/dT = C_{P,j}$ is the heat capacity of reactant in the reaction system. The subscript j of Eq. (10) can be replaced by reactant. We can rearrangement to obtain

$$(r_G)h_G(T) + (r_N)h_N(T) + (r_{NG})h_{NG}(T) + (r_W)h_W(T)$$
$$+ \frac{dT}{dV}(F_G C_{P,G} + F_N C_{P,N} + F_{NG} C_{P,NG} + F_W C_{P,W} + F_S C_{P,S}) = 0 \tag{11}$$

The subscript G, N, NG, W and S represent reactants $C_3H_5(OH)_3$, HNO_3, $C_3H_5(ONO_2)_3$, H_2O and H_2SO_4, respectively. The correlation of reaction rate for above components from Eq. (1) is

$$-r_G = -\frac{1}{3}r_N = \frac{1}{3}r_W = r_{NG} = r \tag{12}$$

Combining Eqs. (11) and (12) one obtains

$$- rh_G(T) - 3rh_N(T) + rh_{NG}(T) + 3rh_W(T)$$
$$+ \frac{dT}{dV}(F_G C_{P,G} + F_N C_{P,N} + F_{NG} C_{P,NG} + F_W C_{P,W} + F_S C_{P,S}) = 0 \tag{13}$$

or

$$r(\Delta H) + \frac{dT}{dV}(F_G C_{P,G} + F_N C_{P,N} + F_{NG} C_{P,NG} + F_W C_{P,W} + F_S C_{P,S}) = 0 \tag{14}$$

The generation heat in the glycerine–nitric acid reaction system includes the heat of reaction and heat of dilution (Kaye, 1978b), which can be expressed as

$$\Delta H = \Delta H_r + \Delta H_d \tag{15}$$

where ΔH_r represents the heat of reaction and ΔH_d represents the heat of dilution, respectively. The heat of reaction also can be expressed as

$$\Delta H_r = \Delta H_{r,T_{ref}} + \Delta C_P(T - T_{ref}) \tag{16}$$

$$\Delta C_P = C_{P,NG} + 3C_{P,W} - C_{P,G} - 3C_{P,N} \tag{17}$$

where T_{ref} and $\Delta H_{r,T_{ref}}$ are the temperature and heat of reaction at standard state. Table 2 shows the values of heat capacities and heat of formation at standard state for each component in this reaction. Substituting Eq. (16) into Eq. (15) we can obtain

$$\Delta H = \Delta H_r + \Delta H_d = \Delta H_{r,T_{ref}} + \Delta C_P(T - T_{ref}) + \Delta H_d$$
$$= \Delta H_o + \Delta C_P(T - T_{ref}) \tag{18}$$

where $\Delta H_o = \Delta H_{r,T_{ref}} + \Delta H_d$. The molar flow rates of $C_3H_5(OH)_3$, HNO_3, $C_3H_5(ONO_2)_3$, H_2O and H_2SO_4 can be correlated as the conversion of $C_3H_5(OH)_3$ with the following terms:

Table 1 – The experimental data of the glycerine–nitric acid reaction system in a tubular flow reactor [Han et al. (1988b)]							
Test code	Inflow compositions					Operating conditions		
	Glycerine	Mixed acid				Inflow temperature T_0 (K)	Outflow temperature T_f (K)	Reaction time τ (s)
	$C_3H_5(OH)_3$ (g)	HNO_3 (g)	H_2SO_4 (g)	H_2O (g)	Amount (g)			
a	32.72	160.48	562.08	77.44	800	283.15	307.65	1.8
b	33.60	192.96	516.17	94.87	804	282.95	303.05	2.1
c	33.17	124.96	567.28	107.76	800	282.15	301.15	6.6
d	22.80	68.34	445.14	86.52	600	282.35	299.35	14.0

Table 2 – Heat capacities and heat of formation in the glycerine–nitric acid reaction system					
Property	Chemical				
	$C_3H_5(OH)_3$	HNO_3	H_2SO_4	$C_2H_5(ONO_2)_3$	H_2O
$H_{f,T_{ref}}$ (kJ/mol)	−665.925	−173.008	−810.399	−368.462	−285.838
C_P (kJ/mol K)	0.214	0.125	0.140	0.339	0.075
$\Delta C_P = -0.025$ kJ/mol K, $\Delta H_{r,T_{ref}} = -41.027$ kJ/mol.					

$$F_G = F_{G,0}(1 - x_G) \tag{19}$$

$$F_N = F_{N,0} - 3F_{G,0}x_G \tag{20}$$

$$F_{NG} = F_{NG,0} + F_{G,0}x_G \tag{21}$$

$$F_W = F_{W,0} + 3F_{G,0}x_G \tag{22}$$

$$F_S = F_{S,0} \tag{23}$$

Then, substituting Eq. (5) and Eqs. (18)–(23) into Eq. (14), we can obtain

$$
\frac{dT}{\Delta H_o + \Delta C_P(T - T_{ref})}
$$
$$
= -\frac{F_{G,0}\,dx_G}{(F_{G,0}C_{P,G} + F_{N,0}C_{P,N} + F_{NG,0}C_{P,NG} + F_{W,0}C_{P,W} + F_{S,0}C_{P,S})}
$$
$$
\quad + F_{G,0}x_G(-C_{P,G} - 3C_{P,N} + C_{P,NG} + 3C_{P,W})
$$
$$
= -\frac{C_{G,0}\,dx_G}{(C_{G,0}C_{P,G} + C_{N,0}C_{P,N} + C_{NG,0}C_{P,NG} + C_{W,0}C_{P,W} + C_{S,0}C_{P,S})}
$$
$$
\quad + C_{G,0}x_G(-C_{P,G} - 3C_{P,N} + C_{P,NG} + 3C_{P,W}) \tag{24}
$$

Let us define

$$C_v = C_{G,0}C_{P,G} + C_{N,0}C_{P,N} + C_{NG,0}C_{P,NG} + C_{W,0}C_{P,W} + C_{S,0}C_{P,S} \tag{25}$$

Then, substituting Eq. (25) into Eq. (24) and integrating it, we can obtain

$$\int_{T_0}^{T} \frac{dT}{(\Delta H_0/\Delta C_P) + (T - T_{ref})} = -\int_0^{x_G} \frac{dx_G}{(C_v/C_{G,0}\,\Delta C_P) + x_G} \tag{26}$$

If it is assumed that the heat capacities and heat of reaction are constant, then, the fractional conversion of glycerine can be expressed as a function of reaction temperature. Integrating results in

$$x_G = -\frac{C_v(T - T_0)}{C_{G,0}\,\Delta H} \tag{27}$$

Finally, substituting Eq. (27) into Eq. (6) and integrating it, we can obtain an equation for glycerine and nitric acid reaction system as Eq. (28).

$$
\tau = \frac{C_{G,0}^{-(n+m)}C_v}{A(-\Delta H)} \int_{T_0}^{T_f} \frac{dT}{e^{-E/RT}[1 + (C_v/C_{G,0}\,\Delta H)(T - T_0)]^n} \\
\times [M + 3(C_v/C_{G,0}\,\Delta H)(T - T_0)]^m \tag{28}
$$

In general, the relationship between the fractional conversion of reactant and the reaction temperature in an adiabatic reactor can be expressed as $x = (T - T_0)/(T_f - T_0)$ on condition that the reactant is entirely reacted during the reaction (Westerterp et al., 1995a). But in this case, the reactant is not entirely reacted during the reaction. Accordingly, we derive the relationship between fractional conversion and reaction temperature for this reaction system as Eq. (27), which can substitute into Eq. (6) to obtain Eq. (28). The data used in the calculation for Eq. (28) are listed in Table 3.

2.2. Analysis of heat of dilution of mixed acid

The heat produced during the reaction of the glycerine–nitric acid system is not only due to the heat of reaction, but also due to the heat of dilution of the acids by the water produced in the reaction. The heat of dilution is large enough to influence the reaction temperature. Therefore, it cannot be ignored in calculating the total enthalpy (ΔH). The heat of dilution can be determined from:

$$\Delta H_d = \frac{W_{mf}H_{df} - W_{m0}H_{d0}}{M_{NG}} \tag{29}$$

$$H_{d0} = H_{d,T_{ref}} + \Delta C_{Pd}(T_0 - T_{ref}) \tag{30}$$

$$H_{df} = H_{d,T_{ref}} + \Delta C_{Pd}(T_f - T_{ref}) \tag{31}$$

where W_{m0} and W_{mf} are, respectively, the inflow and outflow masses of mixed acid in reactor. H_{d0} and H_{df} are the relative enthalpies of inflow and outflow for mixed acid, and M_{NG} represents the number of moles of nitroglycerine after the system has reacted. $H_{d,T_{ref}}$ and ΔC_{pd} are relative enthalpy and specific heat of mixed acid at standard state ($T_{ref} = 25$ °C). The values of relative enthalpy and specific heat of mixed acid

Table 3 – The operating conditions of glycerine–nitric acid reaction system in a tubular flow reactor							
Test code	Reaction time (τ) (s)	Inflow concentration (mol/l)		Outflow concentration		$M = (C_{N,0})/(C_{G,0})$	C_v (kJ/l K)
		$C_3H_5(OH)_3$ ($C_{G,0}$)	HNO_3 ($C_{N,0}$)	$C_3H_5(OH)_3$ ($C_{G,f}$)	HNO_3 ($C_{N,f}$)		
a	1.8	0.6258	4.5274	0.0063	2.6689	7.2347	2.7029
b	2.1	0.6163	5.2209	0.0062	3.3904	8.4711	2.7176
c	6.6	0.6346	3.5265	0.0063	1.6417	5.5570	2.8182
d	14.0	0.5948	2.6297	0.0059	0.8632	4.4213	2.8738

Table 4 – The relative enthalpy and specific heat of mixed acid for various compositions at standard state (T_{ref} = 298.15 K) [Mckinley and Brown (1942)]

$\dfrac{H_2O}{HNO_3 + H_2SO_4 + H_2O}$ (R_W)	$\dfrac{HNO_3}{HNO_3+H_2SO_4}$ (R_N)	Relative enthalpy (kJ/kg)	Specific heat (kJ/kg K)
30/100	10/100	−246.648	2.039
	20/100	−239.530	2.094
	30/100	−229.029	2.207
	40/100	−219.407	2.290
	50/100	−204.606	2.315
20/100	10/100	−213.617	1.884
	20/100	−205.485	1.926
	30/100	−198.079	2.010
	40/100	−187.858	2.064
	50/100	−173.995	2.123
15/100	10/100	−181.322	1.830
	20/100	−173.187	1.872
	30/100	−167.141	1.901
	40/100	−159.010	1.943
	50/100	−146.704	2.010
10/100	10/100	−134.122	1.729
	20/100	−127.348	1.792
	30/100	−123.282	1.813
	40/100	−119.731	1.884
	50/100	−113.371	1.926
0/100	10/100	−30.670	1.453
	20/100	−26.483	1.537
	30/100	−24.389	1.578
	40/100	−22.296	1.620
	50/100	−19.574	1.645

The enthalpies of pure H_2SO_4, HNO_3 and H_2O are assumed as zero.

solution for various compositions were obtained from Mckinley and Brown (1942) and are listed in Table 4. We can express the relative enthalpy, $H_{d,T_{ref}}$ and the specific heat, ΔC_{pd} as functions of the weight percentage of water in mixed acid R_W and the weight percentage of nitric acid in anhydrous mixed acid R_N by means of least square mathematical curve fitting approach and obtain the following equations as:

$$H_{d,T_{ref}} = -29.39 - 1276.08R_W + 1689.96R_W^2 + 0.92R_N$$
$$+ 296.24R_WR_N + 42.74R_N^2 \tag{32}$$

$$\Delta C_{Pd} = 1.4286 + 2.0398R_W + 0.5496R_N \tag{33}$$

We can use Eqs. (32) and (33) to calculate the values of the relative enthalpy and the specific heat in the ranges of $0 \leq R_W \leq 0.3$ and $0.1 \leq R_N \leq 0.5$. The heat of dilution for four experiments in a tubular flow reactor are calculated and listed in Table 5. It is found that the experiment 'a' has a larger heat of dilution than other experiments, which leads to higher outflow temperature of reactant and shorter time of reaction in this experiment.

2.3. Determination of kinetic parameters

The kinetic parameters n, m, A and E of the glycerine–nitric acid reaction in Eq. (4) can be determined from the experimental data and operating conditions presented in Tables 1 and 3 according to Eq. (28). The heat of dilution calculated and presented in Table 5 is used to reduce the number of unknowns in Eq. (28) to 4. The results from the four experiments are used to determine the four unknown parameters with the integral equations being solved by trial and error using Mathematica 4.1 software (Wolfram Research, Inc.). The values of the four kinetic parameters n, m, A and E have been determined to be 0.9350, 1.117, 1.630×10^{21} (l^{1-n-m}/mol^{1-n-m} s) and 122.0 (kJ/g mol), respectively.

The rate of glycerine nitration to produce nitroglycerine is determined by the concentrations of glycerine and nitric acid, and the reaction temperature. The temperature of the reaction is increased by both the heat of reaction and the heat of dilution of the mixed acid, since water is produced during the nitration. Sometimes, the heat of dilution exceeds the heat of reaction. The heat of dilution varies with the reaction conditions, which thus affect the rate of reaction. In this

Table 5 – The dilution heat of four experiments in a tubular flow reactor

| Test code	Inflow compositions of mixed acid					Outflow compositions of mixed acid					ΔH_d (kJ/mol NG)
	HNO₃ (g)	H₂SO₄ (g)	H₂O (g)	R_W (%)	R_N (%)	HNO₃ (g)	H₂SO₄ (g)	H₂O (g)	R_W (%)	R_N (%)	
a	160.48	562.08	77.44	9.68	22.25	94.33	562.08	96.78	12.85	14.37	−64.6104
b	192.96	516.17	94.87	11.8	27.25	125.03	516.17	114.73	15.18	19.50	−47.5252
c	124.96	567.28	107.76	13.47	18.05	57.50	567.28	127.37	16.93	9.20	−43.2737
d	68.34	445.14	86.52	14.42	13.31	21.97	445.14	100.00	17.63	4.70	−42.0429
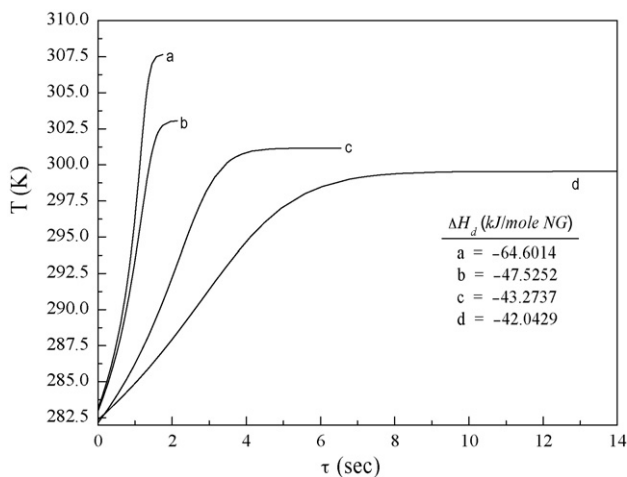
Fig. 2 – The relationships between reaction temperature and reaction time at various reaction conditions for the glycerine–nitric acid system.
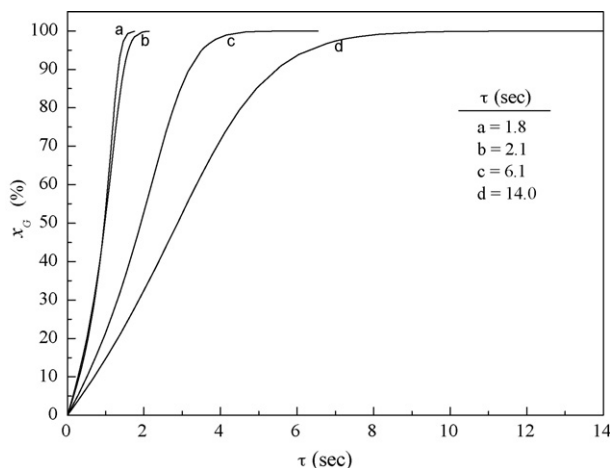

Fig. 3 – The relationships between fractional conversion and reaction time at various reaction conditions for the glycerine–nitric acid system.

investigation, the heat of dilution was only one determinant of the overall heat. The relationships between both reaction temperature and fractional conversion, and reaction time obtained from the four experiments can be calculated using the values of reaction kinetic parameters obtained above. These are plotted in Figs. 2 and 3, respectively. Fig. 2 indicates that reaction temperature varies more quickly when the heat of dilution is larger, in all four experiments performed in a tubular flow reactor. The variation in fractional conversion is similar to that in Fig. 3. The numerically simulated reaction

times are consistent with the known experimental data obtained from four experiments, which indicates that the kinetic mode of derivation in this investigation is reasonable for a glycerine–nitric acid reaction system.

3. Safe operating conditions of nitroglycerine manufacture in Biazzi continuous process

Although nitroglycerine has been produced and used by many countries for a long time, the production process is still very dangerous. Numerous thermal runaway incidents and explosion disasters have occurred. Unfortunately, its reactive hazard has not been clearly identified. Therefore, operators must carefully maintain the entire reaction system under proper operating conditions to prevent any runaway of the reaction system during production. The Biazzi continuous process is one of the most common methods for nitroglycerine manufacture. Two factories use the Biazzi continuous process to produce nitroglycerine in Taiwan. Fig. 4 shows a general sketch of the production process (Biazzi NG Plant, 1973). The stable reaction criteria and safe operating conditions in this continuous stirred tank reactor (CSTR) during the Biazzi continuous process are determined below.

3.1. Derivation of balance equations

In the first place, we will derive the mass and energy balance equations in the CSTR for glycerine–nitric acid reaction system. The transient mass balance equation for the production of nitroglycerine in the CSTR system can be expressed as follows:

$$V\frac{dC_G}{dt} = v_0 C_{G,0} - v_0 C_{G,f} - V(-r_G) \tag{34}$$

where $-r_G$ is the reaction rate of glycerine which can be expressed as negative sign for its consumption. The v_0 and V are the flow rate of reacted solution and volume of reactant respectively. $C_{G,0}$ and $C_{G,f}$ are inflow and outflow concentrations of glycerine in this CSTR.

At steady state, i.e. $dC_G/dt = 0$, dividing Eq. (34) by v_0 and defining the resident time $\tau = V/v_0$, we can express this equation in the CSTR as

$$0 = C_{G,0} - C_{G,f} - \tau(-r_G) \tag{35}$$

Substituting Eqs. (2) and (4) into Eq. (35) we can obtain the mass balance in the CSTR at steady state as

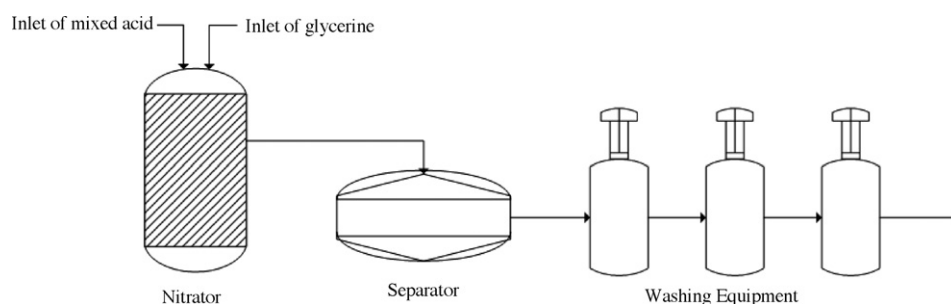$$x_G = \tau A\, e^{-(E/RT_f)} C_{G,0}^{n+m-1}(1 - x_G)^n (M - 3x_G)^m \tag{36}$$

Fig. 4 – The general sketch out of the Biazzi apparatus (according to Biazzi NG Plant, 1973).

where T_f is the reaction temperature in the CSTR. The correlation of reaction rate for $C_3H_5(OH)_3$, HNO_3, $C_3H_5(ONO_2)_3$ and H_2O is listed in Eq. (12), hence the outflow concentration of $C_3H_5(OH)_3$, HNO_3, $C_3H_5(ONO_2)_3$, H_2O and H_2SO_4 can be expressed as

$$C_{G,f} = C_{G,0} - \tau r \tag{37}$$

$$C_{N,f} = C_{N,0} - 3\tau r \tag{38}$$

$$C_{NG,f} = C_{NG,0} + \tau r \tag{39}$$

$$C_{W,f} = C_{W,0} + 3\tau r \tag{40}$$

$$C_{S,f} = C_{S,0} \tag{41}$$

The energy balance in the CSTR is

[rate of accumulation of heat within CSTR]

   = [rate of heat flow into CSTR]

     − [rate of heat flow out of CSTR]

     + [heat generation rate by chemical reaction]

     − [heat removed from ambient of CSTR]   (42)

At steady state, there is no heat accumulated in the CSTR. Thus, the above term can be expressed as

$$0 = v_0(C_{G,0}H_{G,T_0} + C_{N,0}H_{N,T_0} + C_{NG,0}H_{NG,T_0} + C_{W,0}H_{W,T_0} + C_{S,0}H_{S,T_0})$$
$$- v_0(C_{G,f}H_{G,T_f} + C_{N,f}H_{N,T_f} + C_{NG,f}H_{NG,T_f} + C_{W,f}H_{W,T_f} + C_{S,f}H_{S,T_f})$$
$$+ V(-\Delta H_r - \Delta H_d)r - hS(T_f - T_a) \tag{43}$$

where $H_{G,T_0}, H_{N,T_0}, H_{NG,T_0}, H_{W,T_0}$ and H_{S,T_0} are the inflow enthalpies of components $C_3H_5(OH)_3$, HNO_3, $C_3H_5(ONO_2)_3$, H_2O and H_2SO_4, respectively. $H_{G,T_f}, H_{N,T_f}, H_{NG,T_f}, H_{W,T_f}$ and H_{S,T_f} are the outflow enthalpies of the above five components, respectively. h represents the convective heat transfer coefficient of the cooling medium, S denotes the external surface area of cooling coils, T_a is the inlet temperature of cooling medium. Substituting Eqs. (37)–(41) into Eq. (43) and rearrangement to obtain

$$C_{G,0}(H_{G,T_0} - H_{G,T_f}) + C_{N,0}(H_{N,T_0} - H_{N,T_f}) + C_{NG,0}(H_{NG,T_0} - H_{NG,T_f})$$
$$+ C_{W,0}(H_{W,T_0} - H_{W,T_f}) + C_{S,0}(H_{S,T_0} - H_{S,T_f})$$
$$- (H_{NG,T_f} + 3H_{W,T_f} - H_{G,T_f} - 3H_{N,T_f})\tau r$$
$$+ (-\Delta H_r - \Delta H_d)\tau r - hS(T_f - T_a)/v_0 = 0 \tag{44}$$

Assuming the heat capacity of each component is setting a reference temperature at standard state as T_{ref}, thus we can express the inflow and outflow enthalpies of each component as

$$H_{j,T_0} = C_{P,j}(T_0 - T_{ref}) \tag{45}$$

$$H_{j,T_f} = C_{P,j}(T_f - T_{ref}) \tag{46}$$

The heat of reaction is expressed as

$$\Delta H_r = \sum H_{j,T_{ref}} + \sum (H_{j,T_f} - H_{j,T_{ref}}) = \Delta H_{r,T_{ref}} + \Delta C_P(T_f - T_{ref}) \tag{47}$$

where $\Delta H_{r,T_{ref}} = H_{NG,T_{ref}} + 3H_{W,T_{ref}} - H_{G,T_{ref}} - 3H_{N,T_{ref}}$ and $\Delta C_P = C_{P,NG} + 3C_{P,W} - C_{P,G} - 3C_{P,N}$.

Substituting Eqs. (45)–(47) and (25) into Eq. (44) to obtain

$$C_v(T_0 - T_f) - (2\Delta H_r + \Delta H_d)\tau r - hS(T_f - T_a)/v_0 = 0 \tag{48}$$

Substituting Eqs. (4), (12) and (47) into Eq. (48), we can express the energy balance in the CSTR at steady state as

$$C_v(T_0 - T_f) - [2\Delta H_{r,T_{ref}} + 2\Delta C_P(T_f - T_{ref})$$
$$+ \Delta H_d]\tau A\,e^{-(E/RT_f)}C_{G,0}^{n+m}(1 - x_G)^n(M - 3x_G)^m$$
$$- hS(T_f - T_a)/v_0 = 0 \tag{49}$$

To analyze the equations of energy and mass balance in a more simple form, the dimensionless group can be used as following definitions

$$\beta = \frac{RT_a}{E} \tag{50}$$

$$\theta = \frac{E}{RT_a^2}(T_f - T_a) \tag{51}$$

$$\varphi = \tau A C_{G,0}^{n+m-1} \exp\left(-\frac{1}{\beta}\right) \tag{52}$$

$$\theta_0 = \frac{E}{RT_a^2}(T_0 - T_a) \tag{53}$$

$$\theta_{ref} = \frac{E}{RT_a^2}(T_{ref} - T_a) \tag{54}$$

$$\phi_0 = \frac{-(2\Delta H_{r,T_{ref}} + \Delta H_d)\tau A \exp(-1/\beta)C_{G,0}^{n+m}}{C_v\beta^2(E/R)} \tag{55}$$

$$\phi_1 = \frac{-2\Delta C_P\tau A \exp(-1/\beta)C_{G,0}^{n+m}}{C_v} \tag{56}$$

$$\varepsilon = \frac{hS}{v_0 C_v} \tag{57}$$

From the above definitions of Eqs. (50)–(57), Eqs. (36) and (49) can be simplified into the following equations

$$x_G = \varphi \exp\left(\frac{\theta}{\beta\theta + 1}\right)(1 - x_G)^n(M - 3x_G)^m \tag{58}$$

$$(\phi_0 + \phi_1\theta - \phi_1\theta_{ref})\exp\left(\frac{\theta}{\beta\theta + 1}\right)(1 - x_G)^n(M - 3x_G)^m$$
$$= (\varepsilon + 1)\theta - \theta_0 \tag{59}$$

Eqs. (58) and (59) are the dimensionless mass and energy balance equations in the CSTR. The left hand side and right hand side terms in Eq. (59) represent the heat generation and heat removed rate, respectively, which can be expressed as

$$Q_g = (\phi_0 + \phi_1\theta - \phi_1\theta_{ref})\exp\left(\frac{\theta}{\beta\theta + 1}\right)(1 - x_G)^n(M - 3x_G)^m \tag{60}$$

and

$$Q_r = (\varepsilon + 1)\theta - \theta_0 \qquad (61)$$

Thus, Eq. (59) can also be written as

$$Q_g = Q_r \qquad (62)$$

In general, we can use average values of molar heat capacity C_p and reaction heat ΔH_r to derive the energy balance equation for a CSTR. We can take either, C_p averaged over the feed composition in the temperature range inlet to outlet conditions and ΔH_r at outlet temperature, or C_p averaged over the product composition in the same temperature range and ΔH_r at inlet temperature (Westerterp et al., 1995b). But in this research, we derive the energy balance equation for a CSTR using the molar heat capacity of each reactant and the heat of reaction varies with the reaction temperature, which is close to the actual condition of the reaction system compared with above mode of derivation. Although this energy balance equation is a more complicated form, we use the dimensionless groups to reduce the number of parameters. This dimensionless energy balance equation can aid the analysis of safe operating conditions for the glycerine–nitric acid system in the CSTR.

3.2.   Verification of reaction kinetic parameters

The reaction kinetic parameters are estimated from the experimental results for a tubular flow reactor using the previously described numerical analysis. The kinetic parameters n, m, A and E were 0.9350, 1.117, 9.780×10^{22} (l^{1-n-m}/mol^{1-n-m} min) and 122.0 (kJ/g mol), respectively. Tables 6 and
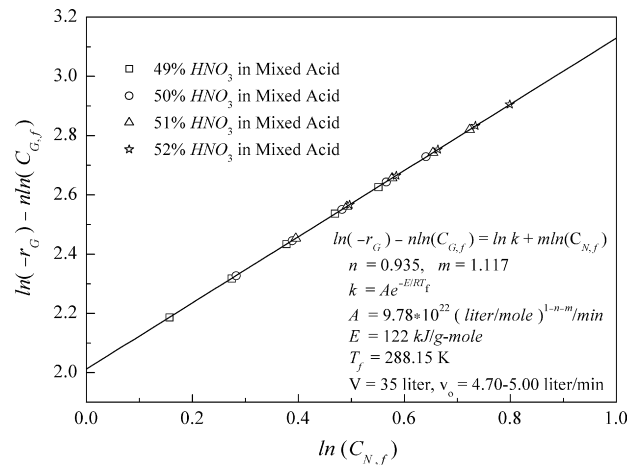

Fig. 5 – The correlation of $\ln(-r_G) - n\ln(C_{G,f})$ and $\ln(C_{N,f})$ for glycerine–nitric acid reaction system in a CSTR of Biazzi continuous process.

7 present the operating conditions of the glycerine–nitric acid reaction system in a CSTR using the Biazzi continuous process (Klassen and Humphrys, 1953; Biazzi NG Plant, 1973). They can be used to verify the values of the kinetic parameters determined above. Fig. 5 plots $\ln(-r_G) - n\ln C_{G,f}$ versus $\ln C_{N,f}$ under various operating conditions. This plot yields the best linear correlation by curve fitting. The slope and point of intersection on the vertical axis of the line equals m and $\ln k$, respectively, where $k = A\,e^{-E/RT_f}$ is the kinetic constant of the reaction at $T_f = 288.15$ K. The values of m and $\ln k$ are 1.117 and 2.0122, respectively, which correspond to the results of the analysis in the preceeding section. Accordingly, the kinetic

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Table 6 – The operating conditions of glycerine–nitric acid reaction system in Biazzi continuous process (I)

R_F	R_N	Inflow compositions (kg/min)			Outflow compositions (kg/min)		Contents of spent acid (wt.%)		Fractional conversion of $C_3H_5(OH)_3$
		$C_3H_5(OH)_3$	Mixed acid		$C_3H_5(ONO_2)_3$	Spent acid	HNO$_3$	$C_3H_5(ONO_2)_3$	
			HNO$_3$	H$_2$SO$_4$					
4.8	49%	1.06	2.4931	2.5949	2.5957	3.5429	4.80	4.52	0.9885
	50%	1.06	2.5440	2.5440	2.6146	3.5261	6.30	3.99	0.9900
	51%	1.06	2.5949	2.4931	2.6405	3.5020	7.90	3.19	0.9912
	52%	1.06	2.6458	2.4422	2.6526	3.4926	9.30	2.94	0.9921
4.9	49%	1.06	2.5451	2.6489	2.6224	3.6286	6.30	3.51	0.9897
	50%	1.06	2.5970	2.5970	2.6410	3.6059	7.80	3.01	0.9909
	51%	1.06	2.6489	2.5451	2.6524	3.5956	9.20	2.78	0.9918
	52%	1.06	2.7009	2.4931	2.6612	3.5854	10.65	2.58	0.9927
5.0	49%	1.06	2.5970	2.7030	2.6420	3.7086	7.65	2.83	0.9906
	50%	1.06	2.6500	2.6500	2.6510	3.7030	9.10	2.60	0.9918
	51%	1.06	2.7030	2.5970	2.6618	3.6916	10.50	2.39	0.9928
	52%	1.06	2.7560	2.5440	2.6747	3.6778	11.83	2.20	0.9933
5.1	49%	1.06	2.6490	2.7571	2.6530	3.8058	8.75	2.55	0.9915
	50%	1.06	2.7030	2.7030	2.6554	3.8023	10.25	2.43	0.9924
	51%	1.06	2.7571	2.6489	2.6706	3.7884	11.60	2.16	0.9930
	52%	1.06	2.8111	2.5949	2.6788	3.7846	12.95	2.04	0.9937
5.2	49%	1.06	2.7009	2.8111	2.6552	3.9092	10.00	2.28	0.9921
	50%	1.06	2.7560	2.7560	2.6639	3.9005	11.40	2.11	0.9931
	51%	1.06	2.8111	2.7009	2.6751	3.8902	12.70	1.98	0.9937
	52%	1.06	2.8662	2.6458	2.6854	3.8804	14.00	1.88	0.9943

(1) R_F: The weight ratio of mixed acid to glycerine. (2) R_N: The weight percentage of nitric acid in mixed acid. (3) The temperature in the nitrator is kept 15 °C by cooling system. (4) The weight of $C_3H_5(ONO_2)_3$ contains about 5.5–6.5 wt.% nitric acid in outflow compositions.

Table 7 – The operating conditions of glycerine–nitric acid reaction system in Biazzi continuous process (II)

R_F	R_N	Weight flow rate of inflow (kg/min)	Volumetric flow rate of inflow (l/min)	Inflow concentrations (mol/l)		Outflow concentrations (mol/l)		Resident time (min)	Reaction rate (mol/l min)
				$C_3H_5(OH)_3$	HNO_3	$C_3H_5(OH)_3$	HNO_3		
4.8	49%	6.148	4.6265	2.4904	8.5535	0.0290	1.1696	7.5650	0.3254
	50%	6.148	4.6472	2.4793	8.6894	0.0250	1.3265	7.5315	0.3259
	51%	6.148	4.6678	2.4683	8.8240	0.0219	1.4847	7.4982	0.3263
	52%	6.148	4.6884	2.4575	8.9574	0.0194	1.6432	7.4652	0.3266
4.9	49%	6.254	4.7054	2.4486	8.5854	0.0253	1.3154	7.4383	0.3258
	50%	6.254	4.7264	2.4377	8.7216	0.0221	1.4747	7.4051	0.3262
	51%	6.254	4.7475	2.4269	8.8566	0.0195	1.6345	7.3723	0.3265
	52%	6.254	4.7686	2.4162	8.9904	0.0175	1.7943	7.3397	0.3268
5.0	49%	6.360	4.7842	2.4083	8.6163	0.0223	1.4585	7.3157	0.3261
	50%	6.360	4.8057	2.3975	8.7528	0.0197	1.6195	7.2830	0.3265
	51%	6.360	4.8272	2.3868	8.8881	0.0176	1.7805	7.2506	0.3268
	52%	6.360	4.8487	2.3763	9.0222	0.0159	1.9412	7.2184	0.3270
5.1	49%	6.466	4.8631	2.3692	8.6461	0.0200	1.5985	7.1971	0.3264
	50%	6.466	4.8850	2.3586	8.7830	0.0179	1.7608	7.1648	0.3267
	51%	6.466	4.9069	2.3481	8.9186	0.0161	1.9227	7.1328	0.3269
	52%	6.466	4.9288	2.3376	9.0531	0.0146	2.0841	7.1011	0.3271
5.2	49%	6.572	4.9419	2.3314	8.6750	0.0182	1.7353	7.0823	0.3266
	50%	6.572	4.9643	2.3209	8.8122	0.0163	1.8984	7.0504	0.3269
	51%	6.572	4.9866	2.3105	8.9481	0.0148	2.0610	7.0188	0.3271
	52%	6.572	5.0090	2.3002	9.0829	0.0135	2.2229	6.9875	0.3273

parameters of the glycerine–nitric acid reaction system can be confirmed.

3.3. Calculation of heat of dilution

The heat of dilution in the CSTR can be assumed to be

$$\Delta H_d = \frac{\dot{W}_{mf}H_{df} - \dot{W}_{m0}H_{d0}}{\dot{M}_{NG}} \tag{63}$$

where $\dot{W}_{m0}$ and $\dot{W}_{mf}$ are weight flow rate of inflow and outflow of mixed acid in reactor, respectively. The $\dot{M}_{NG}$ represents the mole producing rate of nitroglycerine after the system is

reacted. The H_{d0} and H_{df} are inflow and outflow relative enthalpies of mixed acid, respectively, which have been described by Eqs. (30)–(33). We have derived the mass balance equations at steady state in the CSTR and defined as Eq. (36). The fractional conversion of glycerine x_G at various reaction temperature T_f can be calculated using Eq. (36) by means of trial and error technique. Thus, we can obtain the values of dilution heat ΔH_d at various inflow compositions (R_F, R_N), reaction temperatures (T_f) and inflow temperatures (T_0) using Eq. (63) in the CSTR of Biazzi continuous process. Fig. 6 shows the variations of ΔH_d at various T_f, R_N and T_0 with $R_F = 4.8$–5.2 for glycerine–nitric acid reaction system in the CSTR of Biazzi continuous process. The values of ΔH_d increase along the
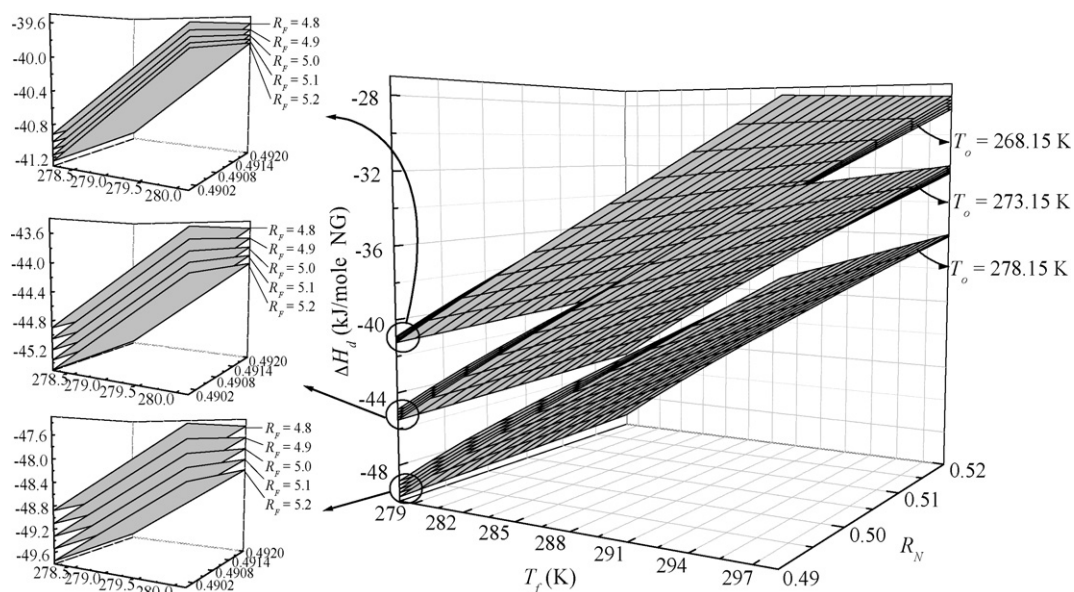

Fig. 6 – The variations of ΔH_d at various T_f, R_N and T_0 with $R_F = 4.8$–5.2 for glycerine–nitric acid reaction system in a CSTR of Biazzi continuous process.

increasing values of T_f, but decrease along the increasing values of T_0. The variations of R_N do not affect the value of ΔH_d. Therefore, the dilution heat of reaction is larger when the temperature of outflow is lower or the temperature of inflow is higher. However, the variations of R_F affect the value of ΔH_d, the dilution heat of reaction is larger when the value of R_F is larger.

3.4. Analysis of optimum operating conditions of cooling system

The rate of chemical reaction is very sensitive to the temperature of an exothermic reaction system. When the rate of generation of heat in the reactive system exceeds the rate of removal of heat from the ambient cooling medium, the whole system very easily accumulates energy and its temperature increases. Then, the reactive system becomes unbalanced and a fast reaction is triggered. As soon as the temperature reaches the critical point, the reactive system enters an unbalance situation or even explodes. Therefore, the heat removal rate of the ambient cooling medium must be controlled to maintain a stable temperature of the reactive system.

The mass and energy balance equations which have been derived in dimensionless form for a glycerine–nitric acid reaction system in the CSTR of the Biazzi continuous process are shown in Eqs. (58) and (59). Tables 6 and 7 present the operating conditions of the glycerine–nitric acid reaction system of the Biazzi continuous process in the CSTR; these can be applied to analyze the optimum operating conditions and its cooling system.

Fig. 7 shows how the fractional conversion of glycerine, x_G is affected by the variations of θ and β for $R_F = 4.9$ and $R_N = 51\%$. It can be seen that the fractional conversion of glycerine increases with increasing values of θ and β, this means that a higher temperature of the reaction system or a higher temperature of the cooling system will lead to higher fractional conversion.

Fig. 8 shows how values of ε which are affected by variations in θ_o and β for $R_N = 49\%$ and $R_F = 4.8$–5.2 when the temperature of reaction system is set at 15 °C. ε is the dimensionless group which reflects the heat transfer capacity of the reactor. It can be seen that ε increases with increasing
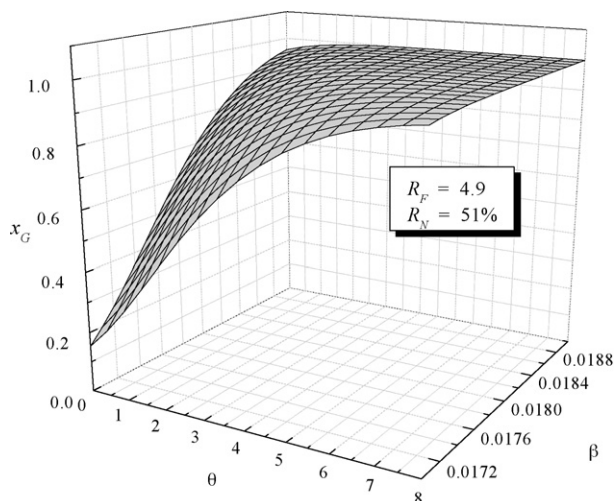

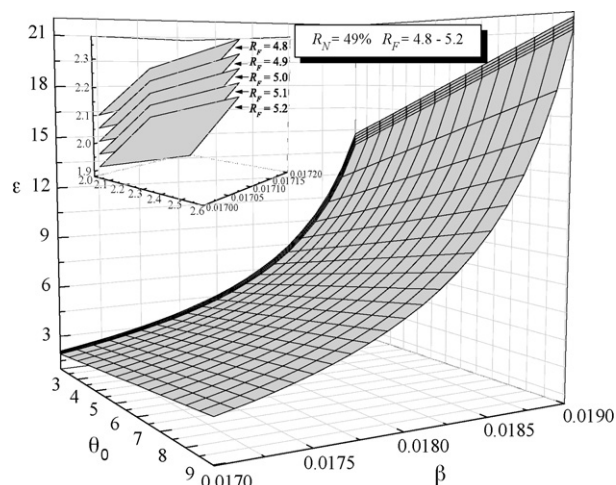Fig. 8 – Relationships of θ_o–β–ε at $R_N = 49\%$ for glycerine–nitric acid reaction system in a CSTR of Biazzi continuous process.
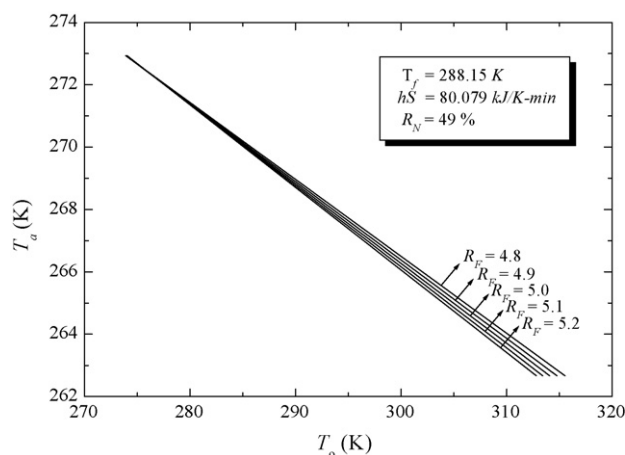

Fig. 9 – Relationships between T_a and T_0 at $R_N = 49\%$ and $R_F = 4.8$–5.2 for glycerine–nitric acid reaction system in a CSTR of Biazzi continuous process.

values of θ_o and β, which means that the use of a higher reactant inlet temperature or a higher temperature in the cooling medium requires higher values of h, the overall heat transfer coefficient or S, the surface area of the cooling coils. The relationships of θ_o–β–ε at other values of R_N are similar, but the value of ε is larger when the value of R_N is larger.

There are two factories which use the Biazzi continuous process to produce nitroglycerine in Taiwan. Their operating conditions are considered from the viewpoints of both safety and economy. The inflow rate of glycerine and mixed acid are controlled at 1.06 and 5.194 kg/min, respectively. The weight ratio of mixed acid to glycerine is 4.9 and the weight percentage of nitric acid in mixed acid is 51%. The temperature of inflow compositions is kept within 18–20 °C. The temperature of the nitrator is maintained at 15 °C by cooling coils fed with brine. The cooling surface and heat transfer coefficient of coils are 1.7 m^2 and 47.104 kJ/K m^2 min (Biazzi NG Plant, 1973), respectively. The inlet temperature of the cooling medium is adjusted within −2 to −5 °C in the nitrator. We can use the above-mentioned system parameters to predict the relationship between the inlet temperature of cooling system, T_a and the inlet temperature of the reactants entering the reactor, T_0

Fig. 7 – Relationships of θ–β–x_G for glycerine–nitric acid reaction system in a CSTR of Biazzi continuous process.

with compositions within R_F = 4.8–5.2 and R_N = 49% from Fig. 8. The result is shown in Fig. 9. The relationships of T_a and T_0 at other values of R_N are similar, but the value of T_a is larger when the value of R_N is smaller under the same value of T_0. From the prediction shown in Fig. 9, we find the inlet temperature of cooling system must be kept within −4.55 to −5.05 °C when the inlet temperature of the reactants T_0 is 18–20 °C. The result of this simulation is close to the actual operating conditions of the reaction system.

4.   Conclusions

From the above calculations and analyses, this research obtains the following conclusions:

1. The reaction rate of glycerine–nitric acid to produce nitroglycerine in the CSTR of Biazzi continuous process can be expressed as $-r_G = 9.78 \times 10^{22}\, e^{-(14674.044/T_f)}\, C_{G,f}^{0.935} C_{N,f}^{1.117}$, which has been verified from several actual operating conditions.
2. The heat of dilution of reaction is varied by operating conditions for glycerine–nitric acid reaction system in the CSTR of Biazzi continuous process. The heat of dilution is larger when the temperature of outflow is lower or the temperature of inflow is higher.
3. The relationship of θ_o–β–ε at various values of R_N and R_F is shown in Fig. 8, which can be used to evaluate the heat transfer coefficient of reactor which is an important parameter for the reactor design of glycerine–nitric acid reaction to produce nitroglycerine.
4. The relationship between inlet temperature of cooling system T_a and temperature of inflow reactants T_0 at various values of R_N and R_F is shown in Fig. 9. These relationships can be used for safe operation in the present factories of Taiwan.

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