

CHAPTER IV PROCESS MODEL

The process for study in this thesis is the hydro-desulphurisation process, which control the amount of sulphur left in the middle distillate from the continuous reactor. This process is an irreversible exothermic reaction. The study part of the processes is show in the figure 4.1.

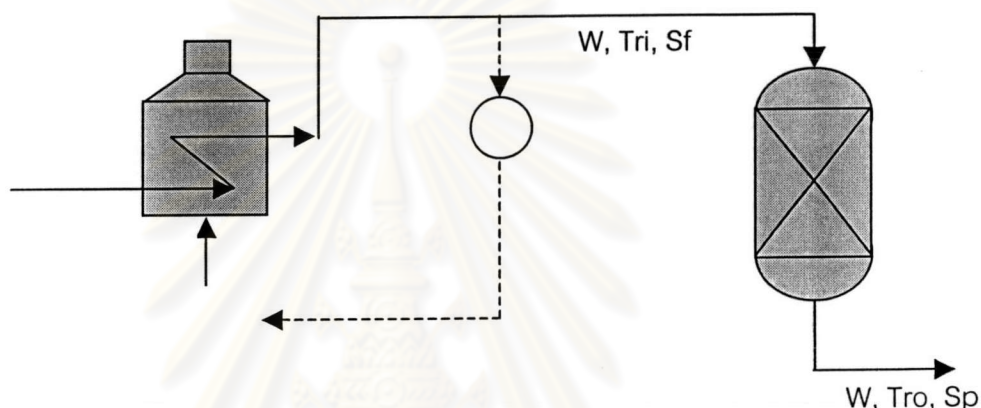


Figure 4.1 The hydro-desulphurisation process for this study

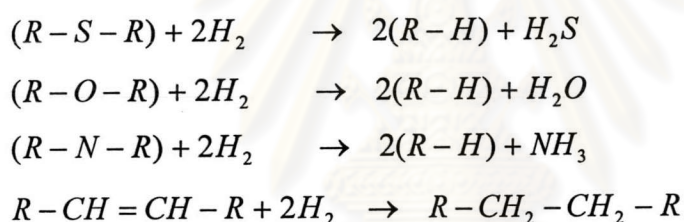
The hydro-desulphurisation process for this study is the trickle phase type, which the feed is mixed with the excess reactant, combined fresh hydrogen and recycles. The mixed feed will be heated in the feed heat exchanger in which exchanges heat from the reactor effluent. The heat exchanger outlet feed will be further heated by the furnace F1 until reaching the desired temperature before entering the reactor R1 which fully contains catalyst. The reactor operating temperature is in range 300-380 degree Celsius and pressure is around 30-60 atmospheres. Sulphur and Nitrogen in feed will be transformed to Hydrogen Sulfite and Ammonia respectively. The existing paraffin will also be transform to paraffin and part of the Aromatic will react to be Naphtene. The reacted product from the reactor is cooled down by the heat exchanger and will be further cooled down until the temperature is around a flash temperature, 270

degree Celsius. At this state gas and liquid will be separated. Gas will be recycle back to feed via the compressor while the liquid phase will be depressured and be further fed to a distillation column. For this thesis, separation parts are not covered.

4.1 Sulphur Model

For the hydro-desulphurisation process trickle phase type, the required hydrogen partial pressure in the reactor. The pressure is kept at a constant pressure.

The reaction is taking place on the catalyst surface, which is cobalt-molybdenum type. The occurred reactions are as follow:



In this thesis, we are only interested the first reaction, which is for getting rid off sulphur content. Based on assumption that ppH_2 is a constant, the reaction order and desulphurization kinetic for conventional desulphurization can be written in the form:

$$r_s = \frac{dS}{dt} = -\sqrt{ppH_2} kS^n \quad (4.1)$$

Although intrinsic desulphurization kinetics always show first order kinetics for single components, it is well known that mixtures of components result in an overall pseudo second order kinetics ($n=2$), as is of application for conventional HDS conditions, i.e. say below 90% HDS. In this description the constant M, F and C represent the feed boiling range factor, the feed refractiveness factor and the catalyst activity factor, respectively. The reaction rate form can be written as below:

$$r_s = \frac{dS}{dt} = -M \cdot F \cdot C \cdot \sqrt{ppH_2} k S^2 \quad (4.2)$$

The feed boiling range factor M is derived from the ASTM D86 distillation curve and the average molal boiling point (T_b), (Process Guide for Hydrotreating, Hydrodesulphurisation, Hydrogenation, 1995)

The catalyst activity factor is defined using the Criterion C424 and C448 activity as reference ($C=1.0$) for NiMo and CoMo catalysts, respectively.

The feed refractiveness factor F , is defined with ME and African straight run feed stocks as reference ($F=1.0$).

As the reaction kinetic varied with operating temperature, Arrhenius equation is applied to kinetic rate constant, k . Therefore, the reaction rate form can be rewritten as:

$$r_s = \frac{dS}{dt} = -M \cdot F \cdot C \cdot \sqrt{ppH_2} k_0 e^{-E/RT} S^2 \quad (4.3)$$

or

$$r_s = \frac{dS}{dt} = -\alpha k_0 e^{-E/RT} S^2 \quad (4.4)$$

where

$$\alpha = M \cdot F \cdot C \cdot \sqrt{ppH_2} \quad (4.5)$$

and	k	Reaction rate constant
	k_0	Reaction rate constant at reference temperature
	M	Feed boiling range factor
	F	Feed refractiveness factor
	C	Catalyst activity factor
	E	Activation energy, for hydro-desulphurisation (kcal/kmol)
	R	Gas constant (1.986 kcal/kmol.K)

T Reaction temperature (K)

In practice, the reactor outlet temperature should always be kept to the minimum at which the required specifications are met. Higher temperatures will increase the rate at which undesirable side reactions, like coke formation, occur resulting in decrease of catalyst activity. In addition, for gasoil hydro-desulphuriser, the liquid feed evaporated will increase with temperature to such an extent that it will become more difficult to attain the desired hydrogen partial pressure, while fuel consumption will also be increased.

For kinetics the weighted average bed temperature (WABT) of the reactor is used.

For processing gasoil feedstock in a single bed reactor the average temperature can be found fairly accurately by adding 2/3 of the temperature rise to the reactor inlet temperature (Process Guide for Hydrotreating, Hydro-desulphurisation, Hydrogenation, 1995).

Based on the temperature profile the WABT for single bed operation can be calculated as follows:

$$WABT = \frac{1}{3}T_{ri} + \frac{2}{3}T_{ro} = T_{ri} + \frac{2}{3}\Delta T \quad (4.6)$$

where

T_{ri}	Reactor inlet temperature
T_{ro}	Reactor outlet temperature
ΔT	Difference of reactor inlet and outlet temperature

As a result the equation (4.5) can be written in the form:

$$r_s = \frac{dS}{dt} = -\alpha k_0 e^{-E/RWABT} S^2 \quad (4.7)$$

When we consider mass of sulphur balance around the reactor, we got:

$$\frac{dS_p}{dt} = \frac{WS_f}{\rho V_r} - \frac{WS_p}{\rho V_r} + r_s \quad (4.8)$$

or

$$\frac{dS_p}{dt} = \frac{WHSV}{\rho} (S_f - S_p) - \alpha k_0 e^{-E/RWABT} S_p^2 \quad (4.9)$$

where

W	mass flow rate (ton/hr)
V_r	catalyst volume in reactor (m^3)
S_f, S_p	sulphur content in feed and product (%wt)
$WHSV = \frac{W}{V_r}$	weight hourly space velocity ($t/hr.m^3$)
ρ	bulk density (t/m^3)
r_s	sulphur rate of reaction (%wt/hr)

We can see from equation (4.9) that the reaction rate is depend on sulphur content in feed, weight hourly space velocity and reaction temperature in the reactor. But for a continuous process for this thesis, the sulphur content in feed and weight hourly space velocity is as the effluent from the predecessor units. For control, these parameters act as disturbances. The only handle to control reaction is WABT. However, a limitation is at the reactor outlet temperature. It needs to be limited to 380 °C maximum due to coke formation on catalyst surface.

The reactions in the reactor are all exothermic reaction. The total heat release from reactions can be written in the form:

$$Q_r = -\Delta H_S r_S \quad (4.10)$$

$$Q_r = -\Delta H_S k_{0S} e^{-E_S/RWABT} S^2 \quad (4.11)$$

4.2 Reactor Heat Transfer Model

The heat balance equation can be written as below:

$$\rho V_r C_p \frac{dT_{ro}}{dt} = WC_p (T_{ri} - T_{ro}) + Q_r \quad (4.12)$$

$$\boxed{\frac{dT_{ro}}{dt} = \frac{WHSV}{\rho} (T_{ri} - T_{ro}) + \frac{Q_r}{\rho V_r C_p}} \quad (4.13)$$

4.3 Furnace Heat Transfer Model

Because the reactor inlet temperature is controlled by furnace firing adjustment, the amount of energy balance in furnace tubes can be written in the form below:

$$\rho V_{tube} C_p \frac{dT_{ri}}{dt} = -WC_p (T_{ri} - T_{risp}) \quad (4.14)$$

$$\boxed{\frac{dT_{ri}}{dt} = -\frac{W}{\rho V_{tube}} (T_{ri} - T_{risp})} \quad (4.15)$$

where V_f represent a pseudo volume to counter balance the firing dynamic and lower level controller action.

The model parameters were taken from ARC HDS process engineer, ShedSim [Computer file] , Rayong: ARC, 1999. and identification to fit the model with the process which they are defined in the table 4.1.

Table 4.1 Process parameters of Hydro-desulphurisation process for this thesis

No.	Variable	Description	Value	Unit
1	k_0	Rate of reaction	14e8	%w/hr
2	$\alpha = MFC\sqrt{ppH_2}$	Reaction rate factor	48.49	-
3	ΔH	Heat of reaction	-45437	kJ/%w
4	E	Activation energy	27000	cal/mole
5	R	Gas constant	1.986	cal/mole.K
6	C_p	Heat capacity	75.31	kJ/ton.K
7	ρ	Bulk density	0.78	ton/m ³
8	S_f	Sulphur content in feed	1.43	%w
9	S_p	Sulphur content in product	0.04553	%w
10	V_f	Pseudo volume for furnace dynamic	30	m ³
11	W	Mass flow rate	600	ton/hr
12	V_r	Reactor volume	50.813	m ³

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