

รายการอ้างอิง

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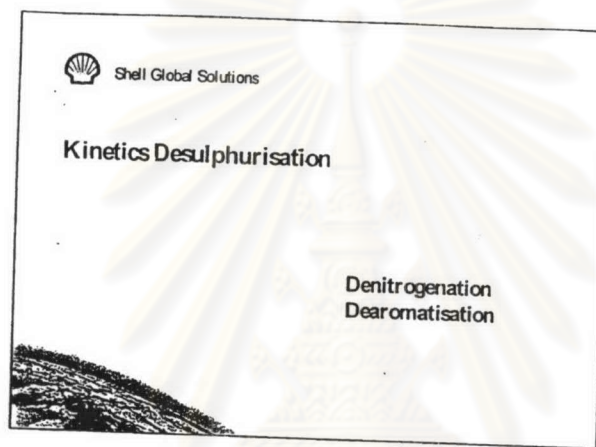
ภาคผนวก

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ภาคผนวก ก

ที่มาของสมการจลศาสตร์ในหัวข้อ 2.3 นั้นมาจากเอกสารดังต่อไปนี้

- 1) จากหนังสือ M-142 Hydrotreater and Hydrodesulfurization Course โดย Shell Global Solution (Confidential)



Reaction kinetics

First order $S_p = S_r \cdot e^{-k \cdot t}$

Second order $1/S_p - 1/S_r = k \cdot t$

What is practice for S?

| | |
|---------------------|-------|
| Vapour phase | : 1 |
| Trickle phase < 90% | : 2 |
| Trickle phase > 90% | : 1.5 |

Explanation ?
Sulphur speciation !

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Effect of processing rate

For continuous flow reactor

$$\text{Reaction time} \sim \frac{1}{\text{Space Velocity}}$$

$$\text{Space Velocity} = \frac{\text{Feed flow rate (t/h)}}{\text{Catalyst (m}^3\text{)}}$$

$$\text{Reaction time} \sim \frac{1}{\text{WHSV (t/m}^3\text{.h)}}$$

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Kinetics deep HDS

$$\frac{d(S)}{dt} = \frac{k \cdot \text{ppH}_2^m \cdot C \cdot F \cdot S^n}{(1 + A_{\text{H}_2\text{S}} \cdot \text{ppH}_2\text{S})}$$

in which:

- S: component to be converted
- k: reaction rate constant
- m: reaction order pH₂
- n: reaction order Sulphur components
- C: catalyst characterisation factor
- A: correction term effect (ppH₂S *)
- F: feed characterisation factor:
MABP, Density, T95, type

* term is dependent on Temperature

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Vapour phase reaction

first order
reaction

$$\ln \left[\frac{S_i}{S_p} \right] = \frac{P}{\text{WHSV}} k_0 \cdot \exp(-E_a / RT)$$

$$E_a = 30,000 \text{ (kcal/kmole)}$$

$$R = 1.987 \text{ (kcal/kmol/K)}$$

• severity

T = Average bed temperature (K)

WHSV = Weight Hourly Space Velocity (1/m².h)

P = $\sqrt{pH_2}$

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Trickle flow reaction

For conversion levels below 90%

pseudo
second order

$$\left(\frac{1}{S_p} - \frac{1}{S_i} \right) = \frac{F.M.P}{\text{WHSV}} k_0 \cdot \exp(-E_a / RT)$$

$$E_a = 27,000 \text{ (kcal/kmol)}$$

Correction factors

F = feedstock factor

M = boiling range factor

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Deep HDS conversion

For conversion levels above 90%

mixed order
reaction

$$\frac{1}{n-1} \left(\frac{1}{S_p^{n-1}} - \frac{1}{S_f^{n-1}} \right) = \frac{F.M.P}{WHSV} k_0 \exp(-E_a/RT)$$

Reaction order:

| | |
|------------------|-------------|
| down to 1000 ppm | n = 2 |
| down to 500 ppm | n = 1.5 |
| down to 50 ppm | n = 1.2-1.4 |

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2) จากหนังสือ Hydrotreater and Hydrodesulfurization Process Guide โดย Shell Global Solution (Confidential)

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HT/HDS/HG Process Guide

December 1995

3.2 MAIN OPERATING VARIABLES - VAPOUR PHASE HYDROTREATING

All kinetic correlations in this paragraph are based on irreversible pseudo first order reactions. At very low levels of sulphur, nitrogen and olefins the accuracy of data is low due to analytical problems. For desulphurisation and hydrodenitrogenation the prediction has therefore been limited to 0.5 ppmwt in the product. For olefins saturation actual product quality is often limited by thermodynamics rather than kinetics.

Processing of feedstocks containing other contaminants as phenols, ethers etc. has been limiting operations in a few incidents. Insufficient information is currently available to allow a kinetic description.

3.2.1 HDT kinetics and operating conditions

3.2.1.1 Desulphurisation kinetics

For feedstocks, processed in vapour phase, such as naphtha, naphtha minus and kerosene minus fractions, in general the desulphurisation requirements are not the limiting parameter. A WHSV of 4 tons/m³.hr, as usually designed for, has shown to be ample to meet sulphur specifications, in particular for platformer feedstocks. In actual practice, however, a higher space velocity could be applied by not filling the reactor completely with catalyst.

More recently, however, with increasing coprocessing of cracked feedstocks, this picture is changing due to increasing sulphur levels in feed as well as a reduced reactivity of the sulphur containing species in feed.

Desulphurisation reactions under vapour phase conditions are described with first order kinetics:

$$\ln \frac{S_f}{S_p} = \frac{k_1 \cdot e^{-E/RT}}{\text{WHSV}} \quad (\text{eq. 3.2.1.1})$$

where:

| | | |
|------------|---|--|
| S_f, S_p | = | sulphur contents of feed and product (%w) |
| T | = | average reactor temperature (K) |
| WHSV | = | space velocity (tons/m ³ . h) |
| k_1 | = | reaction rate constant (tons/m ³ . h) |
| E | = | activation energy (30,000 kcal/k mole) |
| R | = | gas constant (1.986 kcal/k mole.K) |

Thus eq. 3.2.1.1 is used to assess catalyst activity, as based on testrun data, or to predict temperature, or space velocity, requirements given the desulphurisation targets defined. With above equation being used, i.e. without correction for actual hydrogen partial pressure and/or feedstock effects the reference value for k_1 should be determined per unit and per type of feedstock processed through fitting on a testrun data or operating summary, preferably at SOR conditions (fresh catalyst).

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3.3 KINETICS AND MAIN OPERATING VARIABLES - HYDRODESULPHURISATION UNDER TRICKLE FLOW CONDITIONS

3.3.1 Introduction

Using the theoretical concepts for hydrodesulphurisation and related reactions, as described in Ch. 1, in this chapter the selection/optimisation of the main operating variables are described. To this end a full kinetic description is given of the main reactions as occurring under trickle flow desulphurisation conditions, i.e. Hydrodesulphurisation (HDS) and Hydrodenitrogenation (HDN) at conventional as well as deep-desulphurisation conditions. In addition, to allow an improved estimate of the chemical hydrogen consumption (CCH₂), plots to read off extra hydrogen consumption data due to Aromatics saturation (HDA), will be given for straight run as well as cracked feedstocks and have been extrapolated into deep desulphurisation conditions (PPH₂ up to 50 bar).

As main operating variables will be considered the pressure level, i.e. hydrogen and hydrogen sulphide partial pressure, space velocity and temperature. Catalyst and feedstock effects are included as well. Finally new catalyst deactivation correlations have been developed now valid for conventional as well as deep-HDS conditions.

3.3.2 Kinetic description for HDS, HDN and HDA reactions

3.3.2.1 Hydrodesulphurisation (HDS)

Reaction order and desulphurisation kinetics for conventional desulphurisation

Although intrinsic desulphurisation kinetics always show first order kinetics for single components [2], 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 (eq. 3.3.2.1) the constants M, F and C represent the

$$k_0(\text{HDS}) = \frac{\text{WHSV}}{M * F * C * \sqrt{\text{PPH}_2}} * S_f * \left(\frac{1}{S_p} - \frac{1}{S_f} \right) * \exp\left(\frac{E_a}{RT} \right) \quad (\text{eq. 3.3.2.1})$$

feed boiling range factor, the feed refractiveness factor and the catalyst activity factor, respectively. The space velocity WHSV is defined in tons feed per m³ catvolume per hr (t/m³.hr) while S_f and S_p represent the sulphur in feed and product, respectively, in %w. E_a represents the activation energy in cal/mol and R the gas constant (1.986 cal/mol.*K)

The feed boiling range factor M is derived from the ASTM D86 distillation curve and the average molal boiling point (T_B) as defined in eqs. 3.3.2.2 and 3.3.2.3.

$$\log M = -8.8 \log T_B + 24.38 \quad (\text{eq. 3.3.2.2})$$

$$T_B = \left(\frac{\text{ASTM10\%} + \text{ASTM30\%} + \text{ASTM50\%} + \text{ASTM70\%} + \text{ASTM90\%}}{5} - 5.21 * \left(\frac{\text{ASTM90\%} - \text{ASTM10\%}}{80} \right)^{1.18} \right) \quad (\text{eq. 3.3.2.3})$$

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 ranking of other comparable catalyst systems is discussed in paragraph 3.3.3 (Table 3.3.3.1). The feed

refractiveness factor F , discussed in paragraph 3.3.4, is defined with ME and African straight run feedstocks as reference ($F = 1.0$), see also Table 3.3.4.1.

Reaction order deep-desulphurisation

For deep-HDS it is found that the determining conversion of the refractive tail of sulphur species behaves like a less broad mixture of components and thus fits with an overall kinetics of lower reaction order (Figure 3.3.2.1). Thus in our new kinetics formulation for deep-desulphurisation conditions (> 90% HDS), dependent on catalyst type and feedstock, an effective reaction order in sulphur between $n = 1.2$ and $n = 1.5$ is found (Table 3.3.2.1).

Table 3.3.2.1 Kinetic parameters for HDS kinetics (Ref.: eq. 3.3.2.6)

Catalyst: C424 (NiMo)

| Feed | Blend Ratio | m | n | E_a | k_0 | F | k_{0-eff} |
|---------|-------------|---|-----|-------|-------|-----|-------------|
| SRGO | | 1 | 1.2 | 30 | 6.9e9 | 1 | 6.9e9 |
| SR/TCGO | < 50% TCGO | 1 | 1.2 | 30 | 6.9e9 | 0.7 | 4.85e9 |
| | > 50% TCGO | 1 | 1.4 | 30 | 9.0e9 | 0.7 | 6.3e9 |
| SR/LCO | < 30% LCO | 1 | 1.2 | 30 | 6.9e9 | 0.7 | 4.85e9 |
| | > 30% LCO | 1 | 1.4 | 30 | 9.0e9 | 0.7 | 6.3e9 |

*) discontinuities as a consequence of switching to other range of feedstock composition are within the accuracy of the model

**) for multi component mixtures the feedstock effect is simulated as a two component mixture with the contribution of the most refractive component as determining

Catalyst: C448 (CoMo)

| Feed | Blend Ratio | m | n | E_a | k_0 | F | k_{0-eff} |
|---------|-------------|-----|-----|-------|--------|------|-------------|
| SRGO | | 0.8 | 1.5 | 25 | 5.0e8 | 1 | 5.0e8 |
| SR/TCGO | < 50% TCGO | 0.8 | 1.5 | 30 | 2.1e10 | 0.75 | 1.6e10 |
| | > 50% TCGO | 0.8 | 1.5 | 30 | 2.1e10 | 0.7 | 1.5e10 |
| SR/LCO | < 50% LCO | 0.8 | 1.5 | 30 | 2.1e10 | 0.75 | 1.6e10 |
| | > 50% LCO | 0.8 | 1.5 | 30 | 2.1e10 | 0.7 | 1.5e10 |

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แสดงผลลัพธ์ของสมการฝั่งซ้าย ฝั่งขวา และ "อัตราส่วนที่แตกต่าง"กันจากการแทนค่าที่เก็บข้อมูลได้จากกระบวนการผลิต

$$\frac{1}{n-1} \left[\frac{1}{S_p^{n-1}} - \frac{1}{S_f^{n-1}} \right] = \frac{F * M * P}{WHSV} k_0 \cdot \text{Exp} (-E_a/RT)$$

สมการฝั่งซ้าย

สมการฝั่งขวา

Calculation value

| Data number | left hand side | right hand side | Diff (ratio) = left/right |
|-------------|----------------|-----------------|------------------------------|
| 1 | 8.086 | 6.317 | 1.280 |
| 2 | 8.284 | 6.877 | 1.205 |
| 3 | 9.059 | 6.867 | 1.319 |
| 4 | 9.352 | 7.411 | 1.262 |
| 5 | 7.257 | 7.310 | 0.993 |
| 6 | 6.249 | 6.719 | 0.930 |
| 7 | 6.937 | 6.717 | 1.033 |
| 8 | 11.024 | 7.934 | 1.389 |
| 9 | 7.896 | 6.624 | 1.192 |
| 10 | 6.900 | 6.120 | 1.128 |
| 11 | 6.852 | 6.447 | 1.063 |
| 12 | 6.686 | 6.361 | 1.051 |
| 13 | 6.955 | 6.067 | 1.146 |
| 14 | 8.283 | 7.146 | 1.159 |
| 15 | 7.034 | 6.425 | 1.095 |
| 16 | 6.768 | 6.167 | 1.097 |
| 17 | 6.653 | 6.280 | 1.059 |
| 18 | 7.374 | 6.893 | 1.070 |
| 19 | 7.855 | 7.207 | 1.090 |
| 20 | 8.966 | 8.518 | 1.053 |
| 21 | 9.305 | 8.600 | 1.082 |
| 22 | 8.309 | 7.709 | 1.078 |
| 23 | 9.205 | 8.235 | 1.118 |
| 24 | 9.411 | 8.293 | 1.135 |
| 25 | 7.564 | 6.891 | 1.098 |
| 26 | 8.942 | 8.089 | 1.105 |
| 27 | 8.561 | 6.673 | 1.283 |
| 28 | 8.205 | 8.954 | 0.916 |
| 29 | 7.138 | 7.420 | 0.962 |
| 30 | 6.551 | 8.636 | 0.759 |
| 31 | 10.953 | 12.196 | 0.898 |
| 32 | 8.627 | 9.238 | 0.934 |
| 33 | 7.307 | 7.977 | 0.916 |

ภาคผนวก ข (ต่อ)

| Data number | left hand side | right hand side | Diff (ratio) = left/right |
|-------------|----------------|-----------------|------------------------------|
| 34 | 9.877 | 10.704 | 0.923 |
| 35 | 6.942 | 7.508 | 0.925 |
| 36 | 6.718 | 8.867 | 0.758 |
| 37 | 6.595 | 7.449 | 0.885 |
| 38 | 7.701 | 8.914 | 0.864 |
| 39 | 8.451 | 9.896 | 0.854 |
| 40 | 6.736 | 7.577 | 0.889 |
| 41 | 9.467 | 10.547 | 0.898 |
| 42 | 8.597 | 11.881 | 0.724 |
| 43 | 8.617 | 11.899 | 0.724 |
| 44 | 7.898 | 10.046 | 0.786 |
| 45 | 7.995 | 10.472 | 0.763 |
| 46 | 10.952 | 12.312 | 0.890 |
| 47 | 8.838 | 11.239 | 0.786 |
| 48 | 9.715 | 13.638 | 0.712 |
| 49 | 6.087 | 7.718 | 0.789 |
| 50 | 10.475 | 11.667 | 0.898 |
| 51 | 11.134 | 13.305 | 0.837 |
| 52 | 8.533 | 10.548 | 0.809 |
| 53 | 7.897 | 10.449 | 0.756 |
| 54 | 9.232 | 13.163 | 0.705 |
| 55 | 7.160 | 9.142 | 0.783 |
| 56 | 9.080 | 13.178 | 0.689 |
| 57 | 9.999 | 13.469 | 0.742 |
| 58 | 8.431 | 10.846 | 0.777 |
| 59 | 7.049 | 8.051 | 0.876 |
| 60 | 5.326 | 7.185 | 0.741 |
| 61 | 6.398 | 8.860 | 0.722 |
| 62 | 7.053 | 10.240 | 0.689 |
| 63 | 9.282 | 13.213 | 0.703 |
| 64 | 9.452 | 11.071 | 0.854 |
| 65 | 7.307 | 10.174 | 0.718 |

จุฬาลงกรณ์มหาวิทยาลัย

ภาคผนวก ข (ต่อ)

| Data number | left hand side | right hand side | Diff (ratio) = left/right |
|-------------|----------------|-----------------|------------------------------|
| 66 | 6.770 | 8.555 | 0.791 |
| 67 | 7.609 | 8.863 | 0.858 |
| 68 | 8.558 | 10.907 | 0.785 |
| 69 | 8.477 | 10.219 | 0.830 |
| 70 | 6.272 | 7.896 | 0.794 |
| 71 | 9.177 | 12.070 | 0.760 |
| 72 | 5.755 | 7.517 | 0.766 |
| 73 | 9.253 | 10.870 | 0.851 |
| 74 | 7.610 | 9.531 | 0.798 |
| 75 | 8.950 | 11.137 | 0.804 |
| 76 | 7.800 | 10.259 | 0.760 |
| 77 | 8.809 | 12.562 | 0.701 |
| 78 | 7.267 | 10.737 | 0.677 |
| 79 | 9.213 | 13.006 | 0.708 |
| 80 | 7.507 | 11.287 | 0.665 |
| 81 | 7.993 | 12.017 | 0.665 |
| 82 | 8.549 | 12.946 | 0.660 |
| 83 | 7.619 | 11.747 | 0.649 |
| 84 | 7.862 | 12.337 | 0.637 |
| 85 | 10.075 | 14.417 | 0.699 |
| 86 | 9.533 | 14.029 | 0.680 |
| 87 | 7.179 | 11.378 | 0.631 |
| 88 | 10.900 | 17.659 | 0.617 |
| 89 | 9.512 | 15.684 | 0.606 |
| 90 | 9.127 | 14.890 | 0.613 |
| 91 | 6.321 | 10.389 | 0.608 |
| 92 | 11.375 | 20.715 | 0.549 |
| 93 | 10.142 | 21.399 | 0.474 |
| 94 | 10.739 | 19.521 | 0.550 |
| 95 | 11.830 | 21.170 | 0.559 |
| 96 | 6.799 | 14.075 | 0.483 |
| 97 | 11.355 | 23.146 | 0.491 |
| 98 | 9.569 | 21.622 | 0.443 |
| 99 | 9.048 | 20.733 | 0.436 |
| 100 | 7.956 | 17.470 | 0.455 |
| 101 | 9.440 | 20.337 | 0.464 |

ภาคผนวก ค

ผลการคำนวณคุณสมบัติของเครื่องมือและปริมาณกำมะถันในผลิตภัณฑ์เมื่อใช้สมการแบบจำลองคณิตศาสตร์ที่หาได้

| Data number | Cf | New Right hand side value | Diff left/right | การคำนวณคุณสมบัติของเครื่องมือ | | การคำนวณปริมาณกำมะถันในสารผลิตภัณฑ์ | | การคำนวณปริมาณกำมะถันในสารผลิตภัณฑ์ | | การคำนวณปริมาณกำมะถันในสารผลิตภัณฑ์ | |
|-------------|-------|---------------------------|-----------------|--------------------------------|------|-------------------------------------|-------|-------------------------------------|---------------------|-------------------------------------|-----------|
| | | | | Predicted WABT using Cf | DegC | Actual WABT | DegC | Difference between | Predict Sp using Cf | % wt | Actual Sp |
| 1 | 1.123 | 7.093 | 1.140 | 351 | 347 | 4.0 | 0.037 | 0.031 | 0.006 | | |
| 2 | 1.091 | 7.503 | 1.104 | 353 | 349 | 3.1 | 0.034 | 0.030 | 0.004 | | |
| 3 | 1.112 | 7.635 | 1.187 | 355 | 349 | 5.3 | 0.033 | 0.028 | 0.007 | | |
| 4 | 1.095 | 8.113 | 1.153 | 356 | 352 | 4.4 | 0.031 | 0.025 | 0.006 | | |
| 5 | 1.037 | 7.581 | 0.957 | 350 | 351 | -1.3 | 0.035 | 0.037 | -0.002 | | |
| 6 | 1.001 | 6.725 | 0.929 | 346 | 348 | -2.2 | 0.041 | 0.045 | -0.004 | | |
| 7 | 1.003 | 6.736 | 1.030 | 349 | 348 | 0.9 | 0.041 | 0.039 | 0.002 | | |
| 8 | 1.115 | 8.844 | 1.247 | 360 | 353 | 6.9 | 0.028 | 0.020 | 0.008 | | |
| 9 | 1.030 | 6.821 | 1.158 | 350 | 345 | 4.5 | 0.041 | 0.033 | 0.008 | | |
| 10 | 1.064 | 6.513 | 1.059 | 346 | 345 | 1.8 | 0.043 | 0.040 | 0.003 | | |
| 11 | 1.035 | 6.674 | 1.027 | 347 | 346 | 0.8 | 0.042 | 0.041 | 0.001 | | |
| 12 | 1.024 | 6.512 | 1.027 | 346 | 345 | 0.8 | 0.044 | 0.042 | 0.002 | | |
| 13 | 1.082 | 6.566 | 1.059 | 347 | 345 | 1.7 | 0.043 | 0.040 | 0.003 | | |
| 14 | 1.088 | 7.777 | 1.065 | 352 | 350 | 2.0 | 0.034 | 0.031 | 0.003 | | |
| 15 | 1.083 | 6.958 | 1.011 | 349 | 349 | 0.3 | 0.040 | 0.039 | 0.001 | | |
| 16 | 1.022 | 6.301 | 1.074 | 346 | 344 | 2.2 | 0.046 | 0.042 | 0.004 | | |
| 17 | 1.006 | 6.317 | 1.053 | 346 | 344 | 1.6 | 0.046 | 0.043 | 0.003 | | |
| 18 | 1.050 | 7.237 | 1.019 | 351 | 351 | 0.6 | 0.038 | 0.037 | 0.001 | | |
| 19 | 1.063 | 7.664 | 1.025 | 351 | 350 | 0.8 | 0.035 | 0.034 | 0.001 | | |
| 20 | 1.065 | 9.070 | 0.989 | 356 | 357 | -0.4 | 0.028 | 0.028 | 0.000 | | |
| 21 | 1.054 | 9.063 | 1.027 | 357 | 356 | 0.8 | 0.028 | 0.027 | 0.001 | | |
| 22 | 1.030 | 7.939 | 1.047 | 353 | 352 | 1.4 | 0.034 | 0.031 | 0.002 | | |
| 23 | 1.077 | 8.868 | 1.038 | 357 | 356 | 1.2 | 0.029 | 0.027 | 0.002 | | |
| 24 | 1.042 | 8.638 | 1.090 | 358 | 355 | 2.7 | 0.030 | 0.026 | 0.004 | | |
| 25 | 1.015 | 6.992 | 1.082 | 352 | 350 | 2.4 | 0.040 | 0.036 | 0.004 | | |
| 26 | 1.038 | 8.397 | 1.065 | 357 | 355 | 2.0 | 0.031 | 0.028 | 0.003 | | |
| 27 | 1.017 | 6.787 | 1.261 | 356 | 349 | 7.2 | 0.042 | 0.030 | 0.012 | | |
| 28 | 0.968 | 8.665 | 0.947 | 356 | 358 | -1.7 | 0.030 | 0.033 | -0.003 | | |
| 29 | 0.992 | 7.363 | 0.969 | 350 | 351 | -1.0 | 0.039 | 0.041 | -0.002 | | |
| 30 | 0.899 | 7.760 | 0.844 | 350 | 355 | -5.3 | 0.036 | 0.045 | -0.010 | | |
| 31 | 0.782 | 9.532 | 1.149 | 367 | 363 | 4.5 | 0.025 | 0.021 | 0.005 | | |
| 32 | 0.993 | 9.176 | 0.940 | 351 | 353 | -1.9 | 0.028 | 0.031 | -0.003 | | |
| 33 | 1.003 | 8.000 | 0.913 | 352 | 354 | -2.9 | 0.034 | 0.039 | -0.005 | | |

ภาคผนวก ค (ต่อ)

| Data number | Cf | New Right hand side value | Diff left/right | Predicted WABT using Cf | | Actual WABT | | Difference betw een Predict WABT-Actual WABT | | Predict Sp using Cf | | Actual Sp | | Difference betw een Predict Sp - Actual Sp | |
|-------------|-------|---------------------------|-----------------|-------------------------|------|-------------|-------|--|-------|---------------------|-------|-----------|--------|--|--|
| | | | | DegC | DegC | DegC | DegC | DegC | DegC | % wt | % wt | % wt | % wt | | |
| 34 | 0.981 | 10.504 | 0.940 | | 362 | 364 | -2.0 | | 0.023 | | 0.025 | | -0.002 | | |
| 35 | 0.981 | 7.368 | 0.942 | | 350 | 352 | -1.8 | | 0.039 | | 0.042 | | -0.003 | | |
| 36 | 0.877 | 7.778 | 0.864 | | 351 | 356 | -4.6 | | 0.036 | | 0.044 | | -0.008 | | |
| 37 | 0.978 | 7.287 | 0.905 | | 350 | 353 | -3.1 | | 0.040 | | 0.046 | | -0.006 | | |
| 38 | 0.948 | 8.449 | 0.912 | | 355 | 358 | -2.9 | | 0.032 | | 0.037 | | -0.005 | | |
| 39 | 0.937 | 9.272 | 0.911 | | 352 | 355 | -2.9 | | 0.028 | | 0.032 | | -0.004 | | |
| 40 | 0.968 | 7.337 | 0.918 | | 350 | 352 | -2.6 | | 0.039 | | 0.045 | | -0.005 | | |
| 41 | 0.962 | 10.146 | 0.933 | | 362 | 364 | -2.2 | | 0.024 | | 0.027 | | -0.003 | | |
| 42 | 0.814 | 9.672 | 0.889 | | 361 | 365 | -3.8 | | 0.026 | | 0.031 | | -0.005 | | |
| 43 | 0.794 | 9.445 | 0.912 | | 362 | 365 | -3.0 | | 0.027 | | 0.031 | | -0.004 | | |
| 44 | 0.865 | 8.691 | 0.909 | | 357 | 360 | -3.0 | | 0.031 | | 0.036 | | -0.005 | | |
| 45 | 0.808 | 8.463 | 0.945 | | 359 | 361 | -1.8 | | 0.032 | | 0.035 | | -0.003 | | |
| 46 | 0.827 | 10.179 | 1.076 | | 370 | 367 | 2.4 | | 0.024 | | 0.022 | | 0.003 | | |
| 47 | 0.998 | 10.088 | 0.876 | | 362 | 366 | -4.3 | | 0.025 | | 0.030 | | -0.006 | | |
| 48 | 0.845 | 11.525 | 0.843 | | 367 | 372 | -5.6 | | 0.020 | | 0.025 | | -0.006 | | |
| 49 | 0.875 | 6.757 | 0.901 | | 348 | 351 | -3.2 | | 0.045 | | 0.052 | | -0.007 | | |
| 50 | 0.828 | 9.658 | 1.085 | | 368 | 366 | 2.6 | | 0.026 | | 0.023 | | 0.003 | | |
| 51 | 0.833 | 11.089 | 1.004 | | 370 | 370 | 0.1 | | 0.021 | | 0.021 | | 0.000 | | |
| 52 | 0.918 | 9.686 | 0.881 | | 361 | 365 | -4.1 | | 0.026 | | 0.032 | | -0.006 | | |
| 53 | 0.899 | 9.394 | 0.841 | | 359 | 365 | -5.6 | | 0.027 | | 0.036 | | -0.008 | | |
| 54 | 0.836 | 10.999 | 0.844 | | 365 | 371 | -5.5 | | 0.021 | | 0.028 | | -0.007 | | |
| 55 | 0.925 | 8.458 | 0.847 | | 356 | 362 | -5.3 | | 0.032 | | 0.042 | | -0.009 | | |
| 56 | 0.855 | 11.281 | 0.806 | | 365 | 372 | -7.0 | | 0.021 | | 0.029 | | -0.008 | | |
| 57 | 0.878 | 11.824 | 0.846 | | 367 | 373 | -5.5 | | 0.019 | | 0.025 | | -0.006 | | |
| 58 | 0.854 | 9.262 | 0.910 | | 360 | 363 | -3.0 | | 0.028 | | 0.033 | | -0.004 | | |
| 59 | 0.884 | 7.114 | 0.991 | | 356 | 366 | -9.3 | | 0.042 | | 0.043 | | -0.001 | | |
| 60 | 0.899 | 6.459 | 0.825 | | 343 | 349 | -5.9 | | 0.049 | | 0.064 | | -0.015 | | |
| 61 | 0.841 | 7.451 | 0.859 | | 352 | 366 | -14.8 | | 0.040 | | 0.049 | | -0.010 | | |
| 62 | 0.847 | 8.673 | 0.813 | | 355 | 362 | -6.6 | | 0.031 | | 0.043 | | -0.011 | | |
| 63 | 0.830 | 10.966 | 0.846 | | 366 | 371 | -5.5 | | 0.022 | | 0.028 | | -0.007 | | |
| 64 | 0.838 | 9.282 | 1.018 | | 362 | 361 | 0.6 | | 0.028 | | 0.028 | | 0.001 | | |
| 65 | 0.720 | 7.324 | 0.998 | | 361 | 361 | -0.1 | | 0.041 | | 0.041 | | 0.000 | | |

ภาคผนวก ค (ต่อ)

| Data number | Cf | New Right hand side value | Diff left/right | Predicted WABT using Cf | | Actual WABT | | Difference between Predict WABT-Actual WABT | | Predict Sp using Cf | | Actual Sp | | Difference between Predict Sp - Actual Sp | |
|-------------|-------|---------------------------|-----------------|-------------------------|-----|-------------|------|---|-------|---------------------|--------|-----------|--|---|--|
| | | | | DegC | | DegC | | DegC | | % wt | | % wt | | % wt | |
| 66 | 0.806 | 6.897 | 0.982 | | 357 | 358 | -0.6 | | 0.045 | 0.046 | -0.001 | | | | |
| 67 | 0.799 | 7.085 | 1.074 | | 356 | 354 | 2.2 | | 0.043 | 0.039 | 0.004 | | | | |
| 68 | 0.763 | 8.319 | 1.029 | | 365 | 364 | 0.9 | | 0.034 | 0.033 | 0.001 | | | | |
| 69 | 0.734 | 7.506 | 1.129 | | 365 | 361 | 3.9 | | 0.040 | 0.033 | 0.007 | | | | |
| 70 | 0.847 | 6.691 | 0.937 | | 350 | 352 | -2.0 | | 0.047 | 0.052 | -0.005 | | | | |
| 71 | 0.724 | 8.742 | 1.050 | | 367 | 365 | 1.6 | | 0.032 | 0.029 | 0.002 | | | | |
| 72 | 0.855 | 6.424 | 0.896 | | 347 | 351 | -3.4 | | 0.050 | 0.059 | -0.008 | | | | |
| 73 | 0.804 | 8.742 | 1.059 | | 363 | 361 | 1.8 | | 0.032 | 0.029 | 0.003 | | | | |
| 74 | 0.761 | 7.252 | 1.049 | | 357 | 356 | 1.5 | | 0.042 | 0.039 | 0.003 | | | | |
| 75 | 0.889 | 7.677 | 1.166 | | 369 | 364 | 5.0 | | 0.039 | 0.031 | 0.008 | | | | |
| 76 | 0.732 | 7.511 | 1.038 | | 359 | 358 | 1.2 | | 0.040 | 0.038 | 0.002 | | | | |
| 77 | 0.684 | 8.593 | 1.025 | | 369 | 368 | 0.8 | | 0.034 | 0.032 | 0.001 | | | | |
| 78 | 0.659 | 7.076 | 1.027 | | 362 | 361 | 0.9 | | 0.045 | 0.044 | 0.001 | | | | |
| 79 | 0.673 | 8.753 | 1.053 | | 371 | 369 | 1.7 | | 0.033 | 0.030 | 0.003 | | | | |
| 80 | 0.708 | 7.993 | 0.939 | | 362 | 364 | -2.0 | | 0.038 | 0.042 | -0.004 | | | | |
| 81 | 0.670 | 8.053 | 0.993 | | 365 | 365 | -0.2 | | 0.037 | 0.038 | 0.000 | | | | |
| 82 | 0.672 | 8.699 | 0.983 | | 369 | 370 | -0.6 | | 0.033 | 0.034 | -0.001 | | | | |
| 83 | 0.664 | 7.805 | 0.976 | | 366 | 366 | -0.8 | | 0.039 | 0.041 | -0.001 | | | | |
| 84 | 0.703 | 8.669 | 0.907 | | 366 | 369 | -3.2 | | 0.033 | 0.039 | -0.006 | | | | |
| 85 | 0.665 | 9.587 | 1.051 | | 373 | 371 | 1.6 | | 0.028 | 0.026 | 0.002 | | | | |
| 86 | 0.632 | 8.870 | 1.075 | | 374 | 372 | 2.4 | | 0.032 | 0.029 | 0.004 | | | | |
| 87 | 0.632 | 7.187 | 0.999 | | 363 | 363 | 0.0 | | 0.046 | 0.046 | 0.000 | | | | |
| 88 | 0.578 | 10.199 | 1.069 | | 378 | 376 | 2.2 | | 0.026 | 0.024 | 0.003 | | | | |
| 89 | 0.562 | 8.818 | 1.079 | | 375 | 372 | 2.5 | | 0.034 | 0.030 | 0.004 | | | | |
| 90 | 0.651 | 9.696 | 0.941 | | 371 | 373 | -2.0 | | 0.029 | 0.032 | -0.003 | | | | |
| 91 | 0.622 | 6.459 | 0.979 | | 359 | 360 | -0.7 | | 0.055 | 0.057 | -0.002 | | | | |
| 92 | 0.466 | 9.648 | 1.179 | | 388 | 382 | 5.7 | | 0.029 | 0.022 | 0.007 | | | | |
| 93 | 0.453 | 9.696 | 1.046 | | 386 | 384 | 1.5 | | 0.029 | 0.027 | 0.002 | | | | |
| 94 | 0.458 | 8.949 | 1.200 | | 388 | 382 | 6.3 | | 0.033 | 0.024 | 0.009 | | | | |
| 95 | 0.474 | 10.028 | 1.180 | | 389 | 384 | 5.7 | | 0.048 | 0.021 | 0.007 | | | | |
| 96 | 0.501 | 7.051 | 0.964 | | 369 | 371 | -1.2 | | 0.031 | 0.051 | -0.003 | | | | |
| 97 | 0.408 | 9.434 | 1.204 | | 394 | 387 | 6.5 | | 0.031 | 0.022 | 0.008 | | | | |
| 98 | 0.395 | 8.547 | 1.120 | | 390 | 386 | 3.9 | | 0.036 | 0.030 | 0.006 | | | | |
| 99 | 0.395 | 8.187 | 1.105 | | 388 | 385 | 3.5 | | 0.039 | 0.033 | 0.006 | | | | |
| 100 | 0.421 | 7.356 | 1.082 | | 382 | 380 | 2.7 | | 0.046 | 0.041 | 0.005 | | | | |
| 101 | 0.365 | 7.418 | 1.273 | | 392 | 384 | 8.4 | | 0.045 | 0.031 | 0.015 | | | | |

ภาคผนวก ง

แสดงโปรแกรมการคำนวณหาอุณหภูมิของเครื่องปฏิกรณ์โดยใช้แบบจำลองทางคณิตศาสตร์ที่หา
ได้

| Prediction of Hydro-desulfurization Reactor Temperature and Sulphur in Product | | | | |
|--|----------------|--------------------------------|-----------|-------------------------------|
| | | 1) Predict Reactor Temperature | | 2) Predict Sulphur in Product |
| Part I Input Data | Symbol | Unit | | |
| Date | | | 15-12-03 | 15-12-03 |
| Sulphur in feed | Sf | % wt. | 0.366 | 0.366 |
| Sulphur in product (Target) | Sp | % wt. | 0.030 | 0.030 |
| Feed Boiling Range | | | | |
| | ASTM 10% | degc | 203.4 | 203.4 |
| | ASTM 30% | degc | 224.8 | 224.8 |
| | ASTM 50% | degc | 245.2 | 245.2 |
| | ASTM 70% | degc | 264.7 | 264.7 |
| | ASTM 90% | degc | 285.9 | 285.9 |
| Feed rate | | t/d | 8,636 | 8,636 |
| Reactor Pressure | | bar | 52.5 | 52.5 |
| Reactor Temperature | WABT | degc | | 349.5 |
| Part II Calculation Result | | | | |
| Predict Reactor Temperature | WABT | degc | 352.5 | |
| Predict sulphur in product | Sp | | | 0.034 |
| Part III Calculation Part | | | | |
| WHSV | WHSV | ton/m3 hr | 3.01 | 3.01 |
| Reactor Temp | WABT | K | | 622.50 |
| Over all reaction order | n | | 1.5 | 1.5 |
| Molar average boiling point | T _B | K | 512 | 512 |
| Log of boiling range factor | log M | | 0.54 | 0.54 |
| Boiling range factor | M | | 3.430 | 3.430 |
| Feed factor | F | | 1 | 1 |
| Hydrogen partial pressure ^(.5) | P | bar | 7.25 | 7.25 |
| Reaction rate constant | Ko | ton/m ³ hr | 500000000 | 500000000 |
| Activation Energy | Ea | kcal/kmol | 25000 | 25000 |
| Gas constant | R | kmol/kcal K | 1.987 | 1.987 |
| Left hand side value | | | 8.284 | |
| Reaction rate | k | ton/m3 hr | | 0.834 |
| Right hand side value | | | | 6.877 |
| Correction Factor | Cf | | 1.092 | 1.092 |
| Calculated WABT | WABT | K | 625.5 | |
| (1/(Sp ⁿ⁻¹)) | | | | 5.41 |
| Sp | | | | 0.034 |

Note: formular in this sheet

$$1/(n-1) (1/(Sp^{n-1}) - 1/(Sf^{n-1})) = F * M * P * Cf / WHSV * ko \exp (-Ea/RT)$$

$$Cf = -0.9343525 * Sf - 0.3276005 * M - 0.0009067 * date + 36.984932$$

ประวัติผู้เขียนวิทยานิพนธ์

นางสาวนิตยา บุญฤทธิ์ จบการศึกษาปริญญาตรีเมื่อปี พ.ศ.2538 จากภาควิชาเคมีอุตสาหกรรม คณะวิทยาศาสตร์ประยุกต์ สถาบันเทคโนโลยีพระจอมเกล้าพระนครเหนือ

หลังจากจบการศึกษาแล้วได้ทำงานในตำแหน่งวิศวกรกระบวนการผลิตที่บริษัท วนชัยเคมีคอลจำกัด จากนั้นในปี พ.ศ. 2540 ได้เข้าทำงานในตำแหน่งวิศวกรกระบวนการผลิตที่บริษัท โรงกลั่นน้ำมันระยอง จำกัด ซึ่งปัจจุบันได้ทำการกลั่นน้ำมันร่วมกับบริษัทสตาร์ไฟนิงจำกัด และเปลี่ยนชื่อเป็นบริษัทอัลลายแอนซ์ไฟนิงจำกัด

ตั้งแต่ปี พ.ศ. 2543 ได้เริ่มทำการศึกษาในระดับปริญญาโท ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย