

THERMAL STABILITY ANALYSIS OF HYDROPROCESSING UNIT

A Thesis

by

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ABSTRACT

Thermal stability is one of the most critical safety issues in the hydroprocessing units. Runaway reactions in the units can lead to catastrophic consequences as the reactors are being operated at high temperature and pressure, and the reactor effluent is a highly explosive mixture which contains hydrogen and hydrocarbons. For example, a fire and explosion due to a runaway reaction in a hydrocracking unit caused one death and forty-six injuries in 1997, in California. While the temperature runaway is the topic which has been studied extensively, most of the studies worked on simple reactions and little focused on the complex reactions such as hydroprocessing reactions. Also, in the studies on the hydroprocessing reactions, a lumping kinetic model was used which is less accurate and requires experiments for each application. In this research, the thermal stability of a naphtha hydrotreater will be analyzed by using a commercial process simulator ProMax where a novel mechanistic kinetic model, Single Event Kinetics has been integrated. Also, a simplified model will be established by using the data provided by ProMax for further analysis. The continuity and energy equations and parametric sensitivity equations will be solved by Matlab based on the methodology presented by Morbidelli and Varma.

DEDICATION

To my parents

ACKNOWLEDGEMENTS

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Contributors

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All the work conducted for the thesis was completed by the author independently.

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NOMENCLATURE

a_j	Reaction order for component i with respect to the component
b_k	Reaction order for component i with respect to hydrogen
A_i	Frequency factor for component i , n -th reaction order $(\text{mol}/\text{m}^3)^{1-n}/\text{s}$
C_i	Molar concentration for component i (mol/m^3 s)
C_p	Mean specific heat capacity ($\text{J}/(\text{K mol})$)
d_t	Diameter of the reactor (m)
E_a	Activation energy (kJ/kmol)
E_i	Activation energy for component i (kJ/kmol)
E°	Intrinsic activation barrier (kJ/kmol)
F	Molar flow rate (mol/m^3 s)
F_i	Molar flow rate for component i (mol/m^3 s)
h	Planck constant (kJ s)
H	Enthalpy (kJ/kmol)
\bar{H}_i	Molar enthalpy of component i (kJ/kmol)
H_j	Enthalpy of component j (kJ/kmol)
ΔH_i	Heat of reaction for component i (kJ/kmol)
ΔH_r	Difference between the heats of formation of reactant and product (kJ/kmol)
k_B	Boltzmann constant (kJ/K)

$k_{T,\sigma}$	Reaction rate coefficient of thiophen at σ site (kmol/kg _{cat} s)
$k_{B,\tau}$	Reaction rate coefficient of butene at τ site (kmol/kg _{cat} s)
$K_{T,\sigma}$	Adsorption equilibrium constant for thiophene on σ site (Pa ⁻¹)
$K_{H_2,\sigma}$	Adsorption equilibrium constant for hydrogen on σ site (Pa ⁻¹)
$K_{B,\tau}$	Adsorption equilibrium constant for butene on τ site (Pa ⁻¹)
$K_{H_2,\tau}$	Adsorption equilibrium constant for hydrogen on τ site (Pa ⁻¹)
L	Reactor length (m)
n_e	Number of single events
p_T	Partial pressure for thiophene (Pa)
p_{H_2}	Partial pressure for hydrogen (Pa)
Pe	Peclet number
$r_{T,\sigma}$	Rate of reaction of thiophene at σ site (kmol/kg _{cat} s)
$r_{B,\tau}$	Rate of reaction of butene τ site (kmol/kg _{cat} s)
R	Gas constant (kJ/kmol K)
R_i	Overall reaction rate for component i (mol/kg s)
t	Time (s)
T	Temperature (K)
T_{wall}	Wall temperature (K)
u	Superficial velocity (m/s)
U	Overall heat transfer coefficient (J/(m ² s K))
z	Fractional length

Greek Letters

α	Transfer coefficient
ρ	Mean fluid density (kg/m ³)
ρ_b	Bulk density (kg/m ³)

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CHAPTER I

INTRODUCTION

1.1 Hydroprocessing unit

The hydroprocessing unit is the term which denotes hydrotreating units and hydrocracking units. Although primary functions of the hydrotreating units and hydrocracking units are different, they share many common features. For example, the typical configuration of the reactor section in both units are as shown in Figure 1.

In the hydroprocessing unit, the hydrogen and hydrocarbon feeds are combined and fed to the reactor. The hydrocarbon feed usually consists of cracked feed and straight run feed to enhance the operational flexibility. The combined feed is heated through the process heater to the reaction temperature. The reactor effluent is separated in the downstream section, and the products are sent out of the unit. The hydrogen is fed with the excessive amount, and unreacted hydrogen is recycled through the recycle gas compressor. The hydrogen sulfide generated through the hydroprocessing is captured by the amine and sent to the sulfur recovery unit. The make-up hydrogen is added to the combined feed to compensate the amount of consumed hydrogen.

The purpose of the hydrotreating unit is to remove contaminants such as sulfur and nitrogen in the oil fractions using hydrogen. Comparing to other technologies such as Merox, the

hydrotreating is capable of handling feeds in which the contaminants are deeply entangled in complex structures of hydrocarbon. With the increasing interests and requirements on the environment such as enactment of Euro-V, the importance of the units has also been increasing.

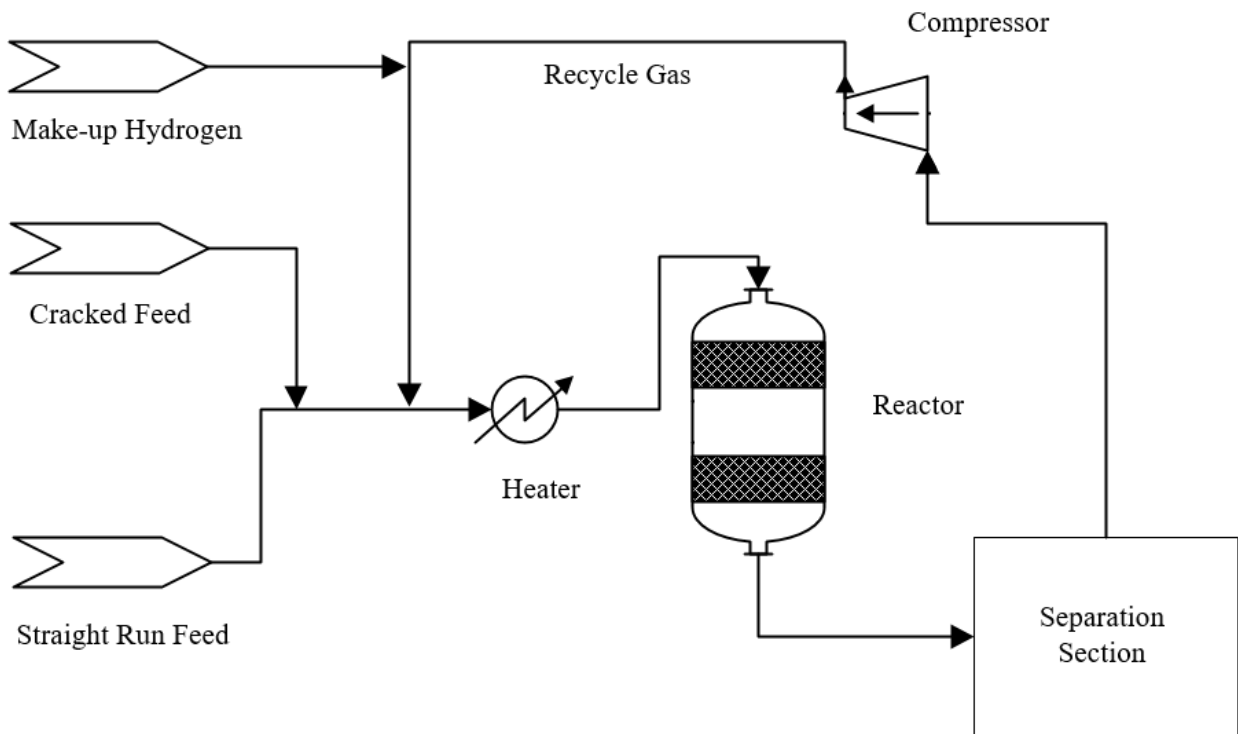


Figure 1. Typical configuration of the reaction section in the hydroprocessing unit

Hydrocracking is adopted in a refinery to upgrade the value of heavy oil by transforming it to lighter ones. In the hydrocracking reactors, hydrotreating reactions also occur although it is not the main purpose of the unit. Typically, hydrocracking units have larger and more complex fractionation section to separate cracked hydrocarbons. The capital and operating costs are also higher due to more severe operating conditions and higher complexity of the process.

1.2 Motivation

Before pursuing the master's program at the Texas A&M University, the author worked for more than seven years as a process engineer on the operation and design of three hydroprocessing units: Vacuum Residue Hydrocracker, Diesel Hydrotreater, and Vacuum Gas Oil Hydrocracker.

Until recently, the author had retained the notion that hydroprocessing reactions were too complicated to grasp so that only empirical and approximate analyses were available in practice. Often, the analyses had to rely on the assumptions which were plausible but not proved and the errors by limited understating of the heart of the process propagated throughout the units and throughout the phases of the projects.

The author saw the possibility of more rigorous analyses when he learned various approaches to handle complex reactions in Chemical Kinetics and Reaction Design class (CHEN 624) during the spring semester in 2017. Through the literature review, he found that the

hydroprocessing reactions had been studied intensively at the Texas A&M university by the research group of Froment and he had developed methodologies for the analysis of the complex reactions.

The high complexity of the hydroprocessing reactions is due to the innumerable element steps and components involved in the reactions. Also, the numbers increase exponentially as the feed gets heavier. For instance, the cracking of C-20 normal paraffin yields thousands of olefins while C-40 normal paraffin yields over one and a half million olefins. (Froment, 2011)

Due to the complexity, the hydroprocessing reactions were mostly analyzed with the lump sum models. In the models, it is assumed that all the components in the reaction are lumped into a few classes. The lumped models have two problems. Firstly, they are less accurate. Secondly, the kinetic parameter should be estimated experimentally for each application which hinders the practical usage.

Froment established a novel kinetic model which is known as Single Event Kinetics for complex reactions such as hydroprocessing reactions based on first principles other than the lumping assumption. The model has been recently integrated into ProMax, a commercial process simulator which has been used for the analysis in this study.

While the rigorous kinetic model can be connected to solving the problems in various topics more effectively, in this research, it will be used for the thermal stability analysis of the hydroprocessing units which is one of the most critical safety issues in the hydroprocessing units.

1.3 Research objectives

The runaway behavior in hydroprocessing units can lead to catastrophic consequences as the reactors are mostly being operated at high temperature and pressure, and the reactor effluents are the highly explosive mixture which contains hydrogen and hydrocarbons. For example, a fire and explosion due to the runaway in a hydrocracking unit caused one death and forty-six injuries in 1997, in California. However, according to the author's experience, the preventive measures for the runaway behavior are only relying on empirical guidelines.

With these backgrounds, the ultimate goal of this study is to make the rigorous analysis of thermal stability available in practice for persons working on hydroprocessing units. Under the goal, the followings will be accomplished. Firstly, the temperature profiles of a naphtha hydrotreater will be simulated by ProMax with varying the feed conditions. Secondly, the theoretical backgrounds of the simulation will be studied and presented. Thirdly, suggestions to Bryan and Research Engineering will be made for making their users able to do thermal stability analysis with ProMax. Lastly, a methodology to do the stability analysis will be presented using the Matlab with the data provided by the current version of ProMax. (4.0.17179)

1.4 Outline of the research in this thesis

For this research, two bodies of knowledge were prerequisite. The first one is the theoretical background of Single Event Kinetics and reaction model used in ProMax, and another one is of the theories for thermal stability analysis. Besides the literature review, the first part has been supported by Bryan and Research Engineering, the developer of the simulator.

The results of the simulation have been reviewed based on the theories regarding the thermal stability, and suggestions will be made which may be incorporated into later revision of ProMax. The sensitivity analysis has been done with a simplified model to show how the suggestions can be incorporated. It will also serve as an example for users when they need to do the analysis with the current version of ProMax.

Within the scope of this thesis, the research goes once-through with an example of a naphtha hydrotreater. The research will continue iteratively with other hydroprocessing units which are known that the hazards concerning the thermal instability are higher. The overall configuration will be similar with that used in this thesis. A reasonably simplified model will be established by the author as necessary.

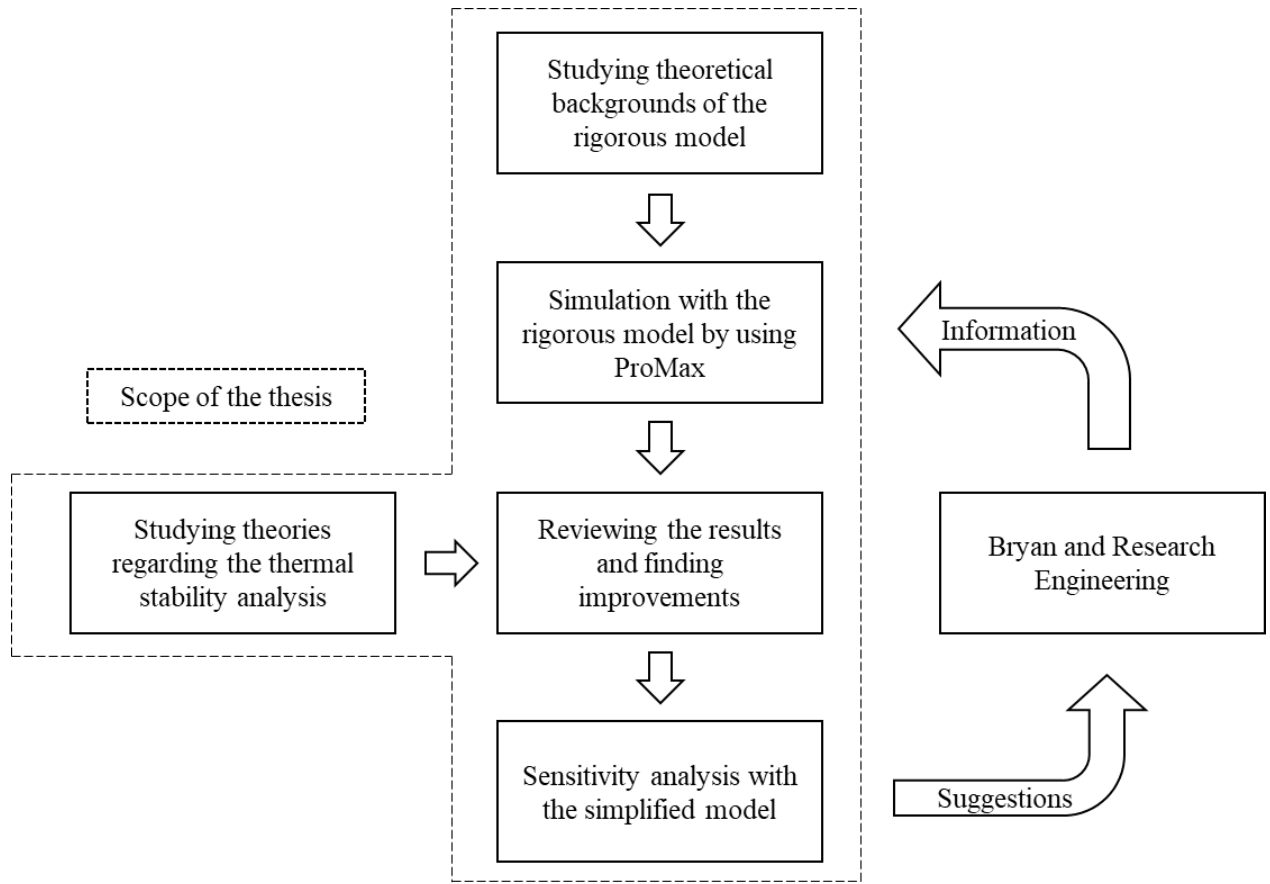


Figure 2. Outline of the research

CHAPTER II

LITERATURE REVIEW

2.1 Case history

EPA reported incident due to a runaway in a hydrocracking unit. (1998) Stage 2 Reactor 3 effluent pipe ruptured due to excessively high temperature caused by the runaway in 1997 in California. It led to the release of gas and oil mixture, and in turn fire and explosion. One operator at the base of the reactor was killed, and forty-six personnel were injured. The temperature limit to start emergency depressuring was specified in the operating procedures, but the limit was not considered trustworthy, and the emergency depressuring was not initiated. This case supports the necessity of the rigorous analysis of the temperature limit to maintain the thermal stability in hydroprocessing unit.

2.2 Single event kinetics

Froment and Baltanas developed Single Event Kinetics with which kinetics parameters for all the elementary steps can be derived. (Vynckier, 1999) Baltanas and Froment created the computer algorithm to generate reaction networks for the Single Event Kinetics. (1985) Ertas and Kumar applied the Single Event Kinetics for modeling of hydrocracking reactions in their theses (Ertas, 2005; Kumar, 2004) and a dissertation (Kumar, 2006) at Texas A&M University with having Froment as the chair of the committee.

2.3 Theories of runaway criteria

The research on thermal explosion was pioneered by Semenov. (1959) Semenov's theory was established assuming that the system was highly explosive and reactant consumption is negligible. It provides the concept of critical temperature and Semenov number, which function as the basis for other theories. Thomas and Bowes determined critical points where the second derivative and the third derivative equals zero in the time-temperature plot. (1961) Adler and Enig's method is similar to Thomas and Bowes' method, but it finds the critical points in the conversion-temperature plot. (1964) Van Welsenaere and Froment provided two criteria for finding the critical points. (1970) The first criterion uses so-called maxima curve which is a set of maximum temperatures with respect to varying wall temperatures. According to the first criterion, the critical point is located at the maximum of a pressure-temperature trajectory which intersects the maxima curve in its maximum. The second criterion sets the critical point where the pressure-temperature trajectory is tangent to loci of inflection points. This criterion is equivalent to the critical point in Thomas and Bowes' method. Morbidelli and Varma used a parametric sensitivity concept. They focused on that a small change in an operating parameter leads to a drastic change of system behavior in a runaway region. Accordingly, the sensitivity can be calculated by solving continuity and energy equations, and sensitivity equations with given operating conditions. (1988)

2.4 Thermal stability analysis of hydroprocessing unit

While the temperature runaway is the topic which has been extensively studied, most of the studies worked on simple reactions, and only two dealt with hydroprocessing reactions based on the literature search. Palma and coworkers studied the runaway reaction of a LCO hydrotreater using 15 lumped hydrocarbon chemical families and Morbidelli and Varma's method. (2010) Schweizer and coworkers used the same lumping method and applied the dynamic stability analysis. (2010) The limitation of the studies for the application in practice is that the lumping kinetic model cannot reflect the accurate components and reactions, and it requires experiments for each analysis.

CHAPTER III

METODOLOGY AND MODEL DEVELOPMENT

3.1 Heterogeneous model

In many applications, the reactor feed of hydroprocessing consist of two kinds. One of them is directly from crude distillation, and another one is from a conversion unit. The latter contains more amounts of components which generate large heats by exothermic reactions. Hence, it is recommended to limit the ratio of the cracked feed to the total feed under the certain value by empirical guidelines to prevent sudden and excessive temperature increase in the reactor. In general, the temperature increase becomes larger as the feed becomes heavier.

In this chapter, the effect on the temperature increase with respect to the feed ratio of a naphtha hydrotreater has been analyzed by using ProMax. Accordingly, the straight run feed is straight run naphtha, and the cracked feed is cracked naphtha. The reason why the naphtha hydrotreater was chosen is that the number of components and reactions are smallest among hydroprocessing unit so that the running time is minimized. However, ultimately the study aims to analyze the units treating heavier feed such as vacuum gas oil hydrocracking unit which is known to have huge temperature increase. Due to the analogy among the hydroprocessing units, the methodology used in this study will be used for the analyses.

It should be noted that the details of the methods applied in the simulator are proprietary as ProMax is commercial software. Theoretical backgrounds based on published literature are described in this chapter for the deeper understanding of the models, but they may not exactly match the methods actually used in the simulator.

The process conditions have been taken from a practical example in a training material. They show the typical characteristic of the unit although there must be variance from a case to a case. Operating conditions and reactor specifications are tabulated in Table 1 and 2, respectively. (Bryan Research & Engineering LLC, 2017)

Table 1. Operating conditions

Operating Conditions	Unit	Value
Total Feed Standard Liquid Volumetric Flowrate	Mbbl/d	19
Recycle Gas Standard Vapor Volumetric Flowrate	m ³ /s	2.68
Recycle Gas Hydrogen Molar Fraction	%	93.0
Temperature	K	550.0
Reactor Pressure	kPa	2826.85

Table 2. Reactor specifications

Reactor Specifications	Unit	Value
Shell Inner Diameter	meter	1.5
Bed Length	meter	21
Catalyst Mass	kg	24500
Catalyst Particle Diameter	mm	4
Catalyst Particle Density	kg/m ³	1100
Catalyst Particle Void Fraction	%	30
Catalyst Particle Packing Fraction	%	60
Acid Site Density	mol/kg	1
Metal (II) Site Density	mol/kg	1

In the example, the straight run naphtha, cracked naphtha, and recycled gas are combined as the reactor feed. The combined feed contains 305 components. The components include hydrogen, paraffins, olefins, aromatics, thiols, sulfides and thiophenes up to C₁₀. The sulfur content mostly comes from the cracked naphtha where the sulfur mass fraction is 1.75%. The sulfur mass fraction in the straight run naphtha is 500 ppm. As only the contaminant in the feed

is sulfur, the hydrotreating reactions consist of hydrodesulfurization and hydrogenation of alkene in the feed.

Hydrodesulfurization includes hydrogenolysis reactions and hydrogenations. For example, the hydrodesulfurization of thiophene undergoes hydrogenolysis which removes sulfur and generates alkene chains, then hydrogenation which saturates the alkenes. The reactions occur at different sites which are called σ site and τ site, respectively. Then the reaction rates of the desulfurization of thiophene are expressed by Hougen-Watson rate equations as follows.

(Vanrysselberghe, 2002)

For the σ site:

$$r_{T,\sigma} = \frac{k_{T,\sigma} K_{T,\sigma} K_{H_2,\sigma} p_T p_{H_2}}{(1 + K_{H_2,\sigma} p_{H_2} + K_{T,\sigma} p_T + K_{S,\sigma} p_{H_2S} / p_{H_2})^2} \quad (1)$$

For the τ site:

$$r_{B,\tau} = \frac{k_{B,\tau} K_{B,\tau} K_{H_2,\tau} p_B p_{H_2}}{(1 + K_{H_2,\tau} p_{H_2} + K_{B,\tau} p_B + K_{A,\tau} p_A)^2} \quad (2)$$

Baltanas and Froment developed the computer algorithm which generates the large reaction network by using Boolean matrices. (1985) Together with the Single Event Kinetics, the reaction network generation algorithm enabled the rigorous modeling of the hydroprocessing reactions which takes into account all the elementary reactions and has been integrated into ProMax. In this example, 1180 elementary reaction steps are generated in total as follows.

Table 3. Elementary reaction steps

Elementary reaction steps	Number
Alkane Adsorption	90
Alkene Protonation	165
Alkene Hydrogenation (Eley-Rideal)	165
Alkane Dehydrogenation (Eley-Rideal)	165
Diene Protonation (equilibrium allyl intermediate)	165
Cycloalkane Protonation (equilibrium allyl intermediate)	46
Aromatics Protonation	12
Aromatic Adsorption	12
Hydrogen Sulfide Adsorption	1
Sulfide Desulfurization	96
Sulfide Formation	96
Thiol Adsorption	14
Thiol Desulfurization	44
Thiol Formation	44
Thiophene Adsorption	5
Thiophene Desulfurization	30
Thiophene Formation	30
Total	1180

The kinetic parameters are determined by single event kinetics. According to the transition theory, the rate coefficient is expressed as follows.

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S'^{o\ddagger}}{R}\right) \exp\left(\frac{\Delta H'^{o\ddagger}}{RT}\right) \quad (3)$$

The standard entropy is the summation of the intrinsic entropy and the entropy change due to the change in symmetry. The latter is expressed with the global symmetry numbers of the reactant and the transition state as follows.

$$\Delta S'_{\text{sym}}{}^{o\ddagger} = R \ln\left(\frac{\sigma_{\text{gl}}^r}{\sigma_{\text{gl}}^{\ddagger}}\right) \quad (4)$$

By replacing the standard entropy with the two terms, the rate coefficient is expressed as

$$k = \left(\frac{\sigma_{\text{gl}}^r}{\sigma_{\text{gl}}^{\ddagger}}\right) \frac{k_B T}{h} \exp\left(\frac{\Delta \hat{S}'^{o\ddagger}}{R}\right) \exp\left(\frac{\Delta H'^{o\ddagger}}{RT}\right) \quad (5)$$

The equation is divided into three parts. The first part, the ratio of global symmetry numbers is equivalent to the number of single events. It is determined by a quantum chemical package such as GAUSSIAN.

$$n_e = \left(\frac{\sigma_{gl}^r}{\sigma_{gl}^\ddagger} \right) \quad (6)$$

The second part is defined as the single event frequency factor as follows. It only contains the intrinsic entropy so that each elementary step has a unique value regardless of the molecular structure of reactants and intermediates. The single event frequency factor is basically determined by experiments.

$$\tilde{A} = \frac{k_B T}{h} \exp\left(\frac{\Delta \hat{S}'^{\ddagger}}{R}\right) \quad (7)$$

In the third part, the activation energy is expressed by Evans-Polanyi relationship with the intrinsic activation barrier, transfer coefficient, and heats of formation as follows. The heat of formation for a single event can be calculated by a quantum chemical package.

For exothermic reactions:

$$E_a = E^0 - \alpha \Delta H_r \quad (8)$$

For endothermic reactions:

$$E_a = E^0 - (1 - \alpha) \Delta H_r \quad (9)$$

The parameters for the rate coefficient provided by ProMax are as follows.

Table 4. Reaction parameters

Reaction Parameters	Unit	Value
Surface Ion Stabilization Energy (acid strength)	kJ/mol	756.85
Alkene Hydrogenation (Eley-Rideal) Log Frequency Factor	kg/(s*mol)	8.36
Alkene Hydrogenation (Eley-Rideal) Activation Energy	kJ/mol	91.15
Alkane Adsorption on Metal (II) Standard Entropy	J/(K*mol)	-88.16
Alkane Adsorption on Metal (II) Standard Enthalpy	kJ/mol	-6.21
Aromatic Adsorption on Metal (II) Standard Entropy	J/(K*mol)	-95.62
Aromatic Adsorption on Metal (II) Standard Enthalpy	kJ/mol	-3.22
Hydrogen Adsorption on Metal (II) Standard Entropy	J/(K*mol)	-11.40
Hydrogen Adsorption on Metal (II) Standard Enthalpy	kJ/mol	-2.31
Sulfide Desulfurization Log Frequency Factor	kg/(s*mol)	2.60
Sulfide Desulfurization Activation Energy	kJ/mol	70.01
Hydrogen Sulfide Adsorption on Metal (II) Standard Entropy	J/(K*mol)	-170.17
Hydrogen Sulfide Adsorption on Metal (II) Standard Enthalpy	kJ/mol	-88.63
Thiol Desulfurization Log Frequency Factor	kg/(s*mol)	14.91
Thiol Desulfurization Activation Energy	kJ/mol	81.39
Thiol Adsorption on Metal (II) Standard Entropy	J/(K*mol)	-32.00
Thiol Adsorption on Metal (II) Standard Enthalpy	kJ/mol	-2.11

Table 4. Continued.

Thiophene Desulfurization Log Frequency Factor	kg ² /(s*mol ²)	10.39
Thiophene Desulfurization Activation Energy	kJ/mol	105.90
Thiophene Adsorption on Metal (II) Standard Entropy	J/(K*mol)	-30.10
Thiophene Adsorption on Metal (II) Standard Enthalpy	kJ/mol	-4.60

The reaction parameters are incorporated into the reaction models with the following equations. As the example is assumed a steady state, the concentration change with respect to time is removed, and the molar flow rate along the flowline will be determined only the reaction rates. In the energy equation, the temperature along the flowline will be the function of pressure drop, the heat of reaction and the heat due to the change in molar fraction.

Continuity equations:

$$\frac{\partial F_i}{\partial z} = \rho_b R_i + \frac{\partial C_i}{\partial t} \quad (10)$$

Energy equation:

$$F \frac{\partial H}{\partial T} \frac{\partial T}{\partial z} + F \frac{\partial H}{\partial P} \frac{\partial P}{\partial z} + \sum_i (\bar{H}_i + \sum_j x_j \frac{\partial H_j}{\partial x_j}) \frac{\partial F_i}{\partial z} = 0 \quad (11)$$

With varying the cracked naphtha flow rate from 1 to 19 Mbbbl/d, following results have been obtained.

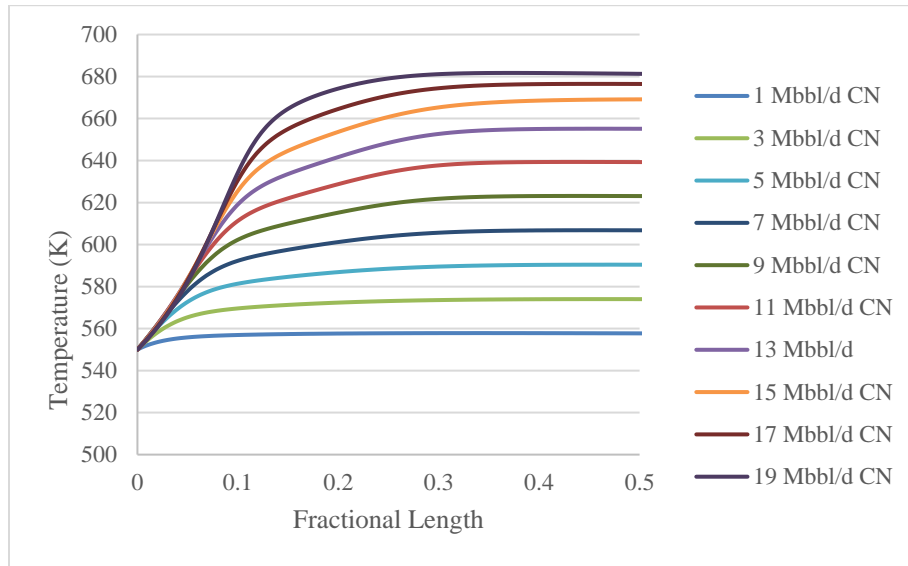


Figure 3. Temperature profiles with respect to varying cracked naphtha flow rate

Based on figure 3, there is no sudden temperature increase led by the increment of the ratio of cracked naphtha. That is, seemingly runaway is not likely for the reactor with given conditions although there can be other detrimental effects such as the damages on the catalyst and the vessel due to the high temperature.

One thing to be noted is that the heat loss to the ambient is not considered in the model as the current version of ProMax provides with two options for the simulation with single event

kinetics: either isothermal and adiabatic. As indicated in the Semenov theory, the interplay between heat generation and heat loss is the main factor determining the runaway behavior. (1959) Also, it was shown that the runaway behavior depended on the wall temperature in previous work for thermal stability analysis of LCO hydrotreater. (Palma, 2010) Hence, it is suggested to add the heat loss term to the energy equation for more accurate results in terms of thermal stability.

In the analysis of LCO hydrotreater, it was also shown that the runaway behavior was related to the degree of axial dispersion. Although it is expected that the effect of axial dispersion is negligible in the reactor as the feed is only the gas phase, adding the function of choosing the degree of axial dispersion will make more extensive analysis available, in particular for the reactor which includes the liquid phase.

Another concern is that the observation is only the approximation. According to Thomas and Bowes, the critical point for the runaway is placed where two inflection points first appear. (1961) It seems that the temperature profiles with 19 Mbbl/d cracked naphtha have two inflection points so that it may be concluded that the critical flow rate of cracked naphtha is placed somewhere below 19 Mbbl/d. However, the rough estimation contradicts the objective of this research.

For the mathematical analysis, it is required to work on the continuity and energy equation integrated into the ProMax which are not accessible. Hence, in the following chapter,

the mathematical analysis will be done with a simplified model. The methodology will be informed to Bryan Research Engineering as suggestions to add the function for the thermal stability analysis.

3.2 Pseudo-homogeneous model

For the further analysis, the heterogeneous model has been simplified as a pseudo-homogeneous model. The reason for simplification is that the rigorous model requires integration of single event kinetics and thermodynamic method which cannot be accomplished by the author alone within the time limit. Also, it does not create any value to repeat the same work which has already been done.

For the simplified model, below assumptions have been made with considering that the main purpose of the model is to see the trend and to show the methodology with which the rigorous model can be updated rather than to obtain accurate values.

- 1) One-dimensional homogeneous model
- 2) Only two reactions: alkene hydrogenation and thiophene desulfurization
- 3) Alkenes and thiophenes are grouped as single components respectively.
- 4) Irreversible reactions
- 5) Constant pressure through the reactor

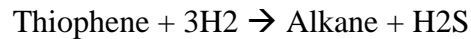
For establishing continuity and energy equations with the first assumption, the rate parameters have been set using the Arrhenius plot to make the reaction rates consistent with those determined by single event kinetics in ProMax. The second and third assumption is based on the observations that the heat of reaction from two reactions accounts for the most of the temperature increase. The fourth assumption may cause a significant impact on the result as it reduces the non-linear characteristic. Later, the model will be developed excluding this assumption. The fifth assumption is not expected to lower the accuracy significantly as the pressure drop through the reactor is not high.

The reaction formulas and equations are as follows.

Alkene hydrogenation:



Thiophene desulfurization:



Continuity equations:

$$\frac{d^2 C_i}{dz^2} = \text{Pe} \left(\frac{dC_i}{dz} + \frac{L}{u} A_i \exp \left(\frac{-E_i}{RT} \right) C_i^{a_j} H_2^{b_k} \right) \quad (12)$$

Energy equation:

$$\frac{dT}{dz} = \sum \frac{L}{u} \frac{-\Delta H}{\rho C_p} A_i \exp\left(\frac{-E_i}{RT}\right) C_i^{a_j} H_2^{b_k} - \frac{4UL}{ud_t \rho C_p} (T - T_{wall}) \quad (13)$$

The log frequency factors and activation energy has been determined by the Arrhenius plot as follows. The heats of reactions for each reaction has been set with the values presented in the literature for the hydrotreating reactions modeling. (Tarhan, 1983)

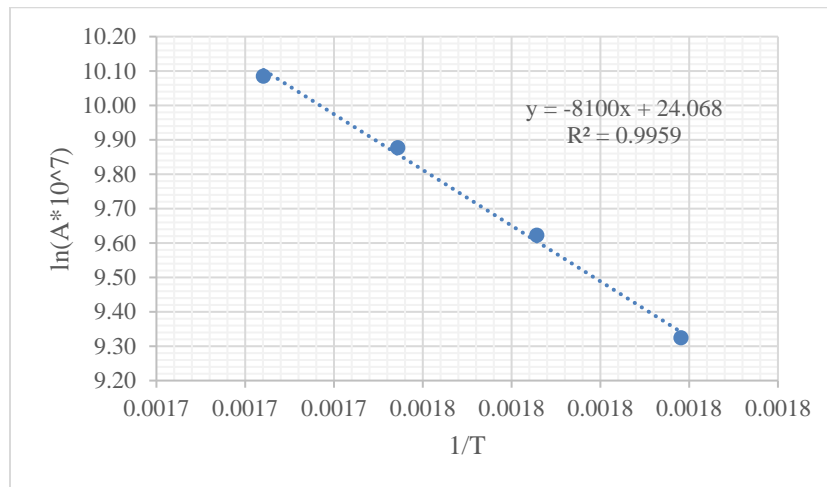


Figure 4. Arrhenius plot for alkene hydrogenation

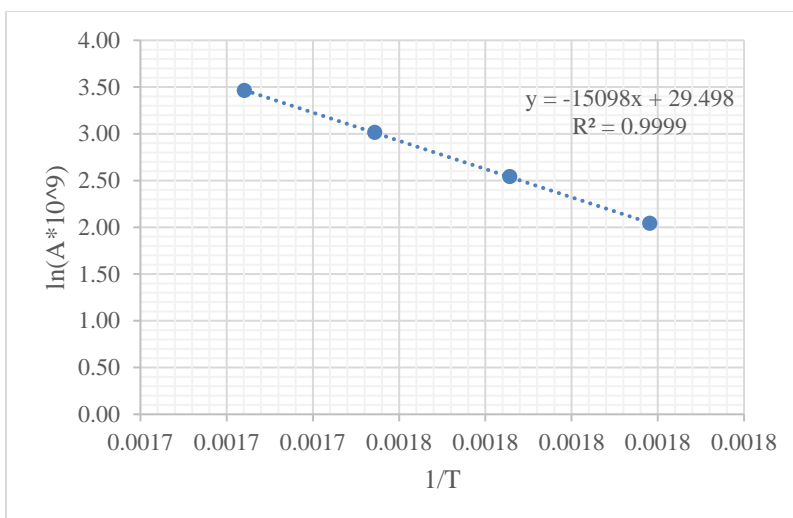


Figure 5. Arrhenius plot for thiophene desulfurization

Table 5. Reaction parameters for the simplified model

Reactions	Log Frequency Factor	Activation Energy (J*mol/K)	Heat of Reaction (J/mol)
Alkene Hydrogenation	2835.3	67343	-125520
Thiophene Desulfurization	6468.7	125525	-251000

In this example, the feed is only the gas phase so that axial dispersion is negligible so that the differential equations have been integrated by using the ode45 function in the Matlab. The

results are shown in figure 6. The temperature profiles are similar to those generated by ProMax regarding their shapes and maximum temperatures although the reactions reach the end faster as the result of simplification.

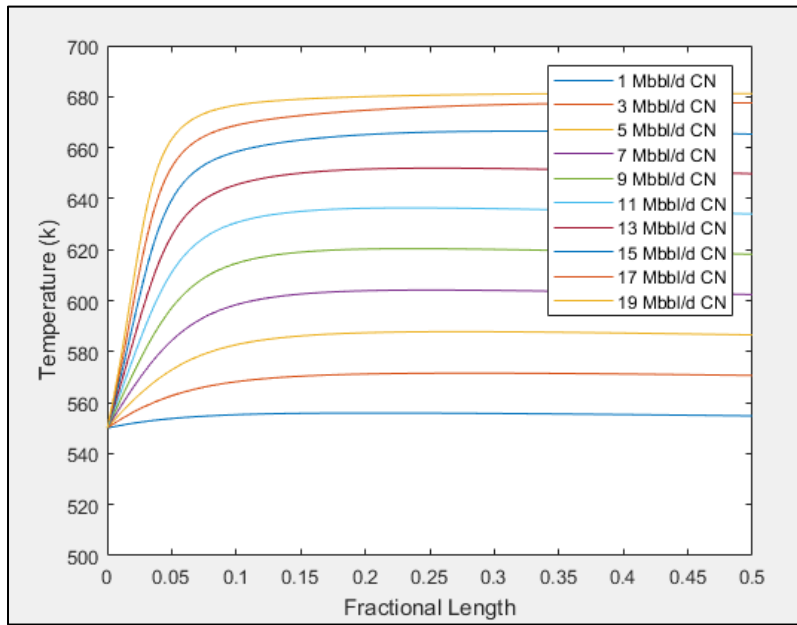


Figure 6. Temperature profiles generated by the simplified model

3.3 Sensitivity analysis

Morbidelli and Varma's method has been used for the sensitivity of the max temperature with respect to the cracked naphtha ratio for following reasons. Firstly, while the other methods reviewed in section 2.3 has been developed mainly for the first-order reaction, the Morbidelli and Varma's method can be readily applied regardless of the reaction orders. Secondly, the Morbidelli and Varma's method show not only the critical point but also the intensity of the runaway.

The differential equations for the sensitivity of output variables with respect to input parameter are defined as follows.

$$\frac{d\mathbf{s}(\mathbf{y}; \text{CN})}{dz} = \mathbf{J}(z) * \mathbf{s}(\mathbf{y}; \text{CN}) + \frac{\partial \mathbf{f}(z)}{\partial \text{CN}} \quad (14)$$

$\mathbf{f}(z)$ indicates the continuity and energy equations and CN is the feed flow rate of the cracked naphtha. Since the number of differential equations is three in this case, the vector $\mathbf{s}(\mathbf{y}; \text{CN})$ and $\frac{\partial \mathbf{f}(z)}{\partial \text{CN}}$ are set as follows.

$$\frac{d\mathbf{s}(\mathbf{y}; \text{CN})}{dz} = \begin{bmatrix} s(C_1; \text{CN}) \\ s(C_2; \text{CN}) \\ s(T; \text{CN}) \end{bmatrix}, \quad \frac{\partial \mathbf{f}(\mathbf{z})}{\partial \text{CN}} = \begin{bmatrix} \frac{\partial \mathbf{f}_1(\mathbf{z})}{\partial \text{CN}} \\ \frac{\partial \mathbf{f}_2(\mathbf{z})}{\partial \text{CN}} \\ \frac{\partial \mathbf{f}_3(\mathbf{z})}{\partial \text{CN}} \end{bmatrix} \quad (15)$$

Accordingly, the Jacobian $\mathbf{J}(\mathbf{z})$ is to be 3 x 3 matrix as follows.

$$\mathbf{J}(\mathbf{z}) = \begin{bmatrix} \frac{\partial \mathbf{f}_1(\mathbf{z})}{\partial C_1} & \frac{\partial \mathbf{f}_1(\mathbf{z})}{\partial C_2} & \frac{\partial \mathbf{f}_1(\mathbf{z})}{\partial T} \\ \frac{\partial \mathbf{f}_2(\mathbf{z})}{\partial C_1} & \frac{\partial \mathbf{f}_2(\mathbf{z})}{\partial C_2} & \frac{\partial \mathbf{f}_2(\mathbf{z})}{\partial T} \\ \frac{\partial \mathbf{f}_3(\mathbf{z})}{\partial C_1} & \frac{\partial \mathbf{f}_3(\mathbf{z})}{\partial C_2} & \frac{\partial \mathbf{f}_3(\mathbf{z})}{\partial T} \end{bmatrix} \quad (16)$$

The concentrations of alkenes and thiophenes in the straight run naphtha are negligible so they are proportional to the cracked naphtha flow rate. Hence, the initial conditions are defined as [1 1 0] for the equations 14.

By integrating the continuity and energy equations together with the sensitivity equations, the sensitivities of maximum temperature with respect to the cracked naphtha flow rate have been obtained as follows.

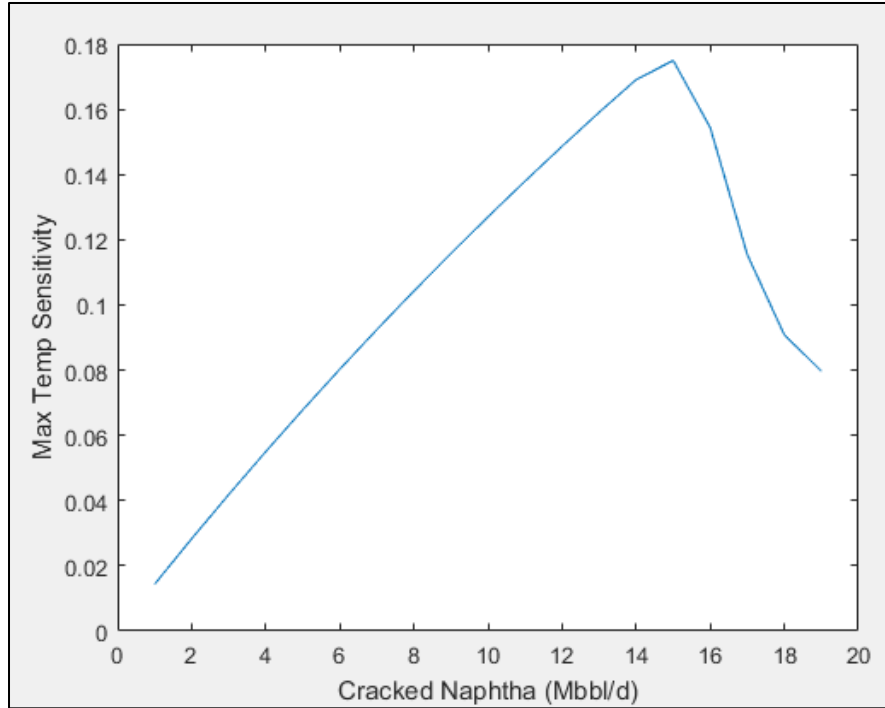


Figure 7. The sensitivity of maximum temperature with respect to the cracked naphtha flow rate when the heat loss is not considered

In figure 7, the sensitivity is at peak when the cracked naphtha is 15 Mbb/d, but the change is gradual compared to the sharp increases at the critical points presented in other studies. The scale of the sensitivity is also small. Therefore, the runaway due to the change of feed ratio is not likely in the naphtha hydrotreating unit with the given condition.

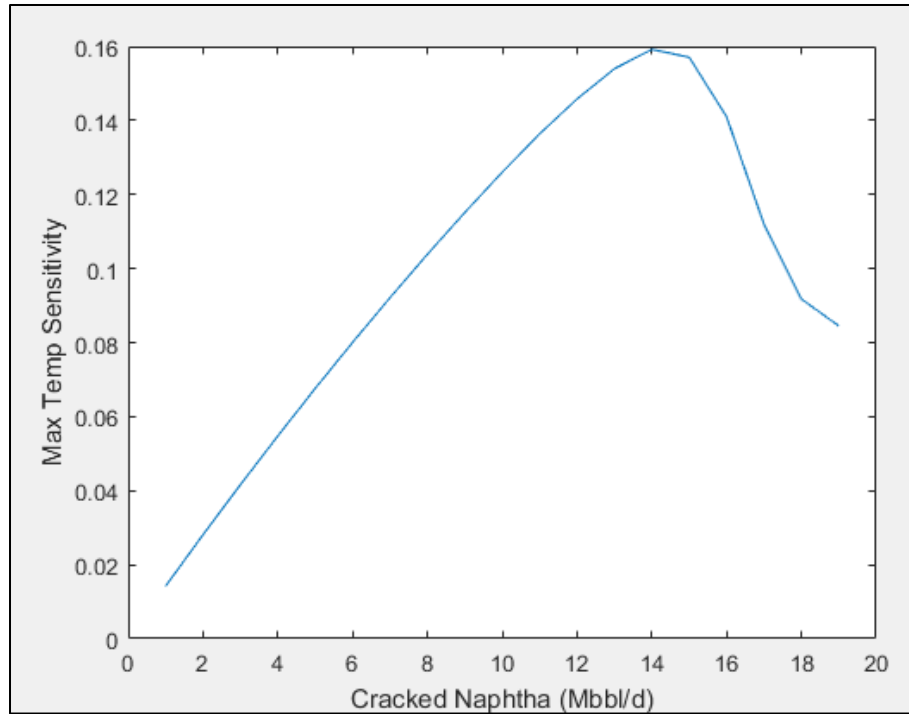


Figure 8. The sensitivity of maximum temperature with respect to the cracked naphtha flow rate when reactor wall temperature is 550 K and $U = 20\text{W/m}^2/\text{K}$

In figure 8, the peak has been moved from 15 Mbb/d to 14 Mbb/d as the heat loss is considered. This implies that the critical point for the runaway is affected by operating conditions, the heat loss to the ambient in this case.

CHAPTER IV

CONCLUSIONS

Temperature profiles for a naphtha hydrotreater with respect to varying the cracked feed ratio has been simulated with the ProMax. According to the results, maximum temperature gradually increases as the ratio of the cracked naphtha increases. Therefore, the runaway due to the feed change is not likely in the naphtha hydrotreater although there may be detrimental effects on the catalysis and the mechanical components because of the high temperature.

For making persons working on the hydroprocessing unit able to do thermal stability analysis in practice, it is suggested to incorporate the followings into the rigorous model.

- 1) Heat loss to the ambient
- 2) Degree of the axial dispersion
- 3) Parametric sensitivity analysis of maximum temperature with respect to an input parameter

A simplified model has been established to show how the parametric sensitivity analysis can be applied. The continuity, energy, and sensitivity equations have been solved by Matlab with the Morbidelli and Varma's method. The result shows the sensitivity is at its peak when the cracked naphtha feed flow rate is 15 Mbbbl/d. However, the peak is not sharp and also the value of sensitivity at the peak is low. It supports the result by the rigorous model that the runaway due to the feed change is not likely with more explicit and quantitative expression. The flow rate

corresponding to the peak of the sensitivity has been moved to 14 Mbbl/d as the heat loss is considered. This implies that the critical point varies as the operating condition changes and also the heat loss term should be taken into account in the model.

For future work, the sensitivity analysis present in section 3.3 may be done with the rigorous model in ProMax. Bryan and Research Engineering may work on the codes in the simulator to add the differential equations for the sensitivities. As the number of equations is very large, a differential method other than the conventional direct method such as Green's function method may need to be applied. It is suggested to include heat loss terms in the energy equation and axial dispersion in the continuity equations for more rigorous analysis

The sensitivity analysis with simplified equations for other hydroprocessing units such as a diesel hydrotreating unit and a vacuum gas oil hydrotreating unit will be done by the author. While the methodologies will be similar with that used in section 3.2 and 3.3, there must be some differences. Firstly, the diesel hydrotreating reactions will include liquid so that the physical conditions will be significantly different from the naphtha hydrotreater which is operating only in gas phase. In particular, the axial dispersion of the liquid may exert a significant impact on the runaway behavior. Secondly, the reaction mechanisms of vacuum gas oil hydrocracking reactions will be different and the representative reactions for simplification will differ from those in the hydrotreating units. Also, it is expected that the diesel hydrotreater and vacuum gas oil hydrocracker shows the runaway behavior. The expectation is supported by the previous work of Palma and coworkers and the incident in 1997 in California.

There will be some improvements in the simplified model. Firstly, the degree of axial dispersion will be taken into account. Accordingly, the `bpv4c` function other than the `ode45` will be used in the Matlab with Danckwert's boundary conditions. Secondly, the equilibrium constants for the reactions will be considered. Both of the changes will make the results better represent the non-linearity of the system so that more accurate analysis is expected.

The thermal stability analysis can improve the operation and design in various aspects such as operational guidelines in terms of the feed ratio handled in the example. Other applications include the determination of the set points for process control systems in the feed section and safety instrumented system to prevent the runaway in the reactor. Once the critical points for the targeted units are determined, the scope of analyses will be expended to the integration of other components.

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