Lumping Analysis in Modeling of Binary Cracking Kinetics in Hydrocracking Reactions

by

Md Hairman Md Esa

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

SEPTEMBER 2012

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
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Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

_____

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MD HAIRMAN BIN MD ESA

ABSTRACT

Hydrocracking is a conversion process of heavy oil fractions such as naphtha and middle distillates into lighter products in a relative high pressure and temperature condition. Hydrocracking process has benefits petroleum industries in producing high quality products such as diesel, jet fuels and gasoline. In order to predict the product yields at different operating conditions, it is necessary to have the modelling of hydrocracking kinetics. In this project, the modelling of binary cracking kinetics was verified by using discrete lumping approach, which involve carbon number and true boiling point of hydrocarbon as model compound.

Four hydrocracker models representing four different stoichiometric kernels were verified at two different temperatures, 663K and 723K to find the exact lumping system for each model. Lumping analysis for each hydrocracker model was carried out based on Wei and Kou criteria where the system that disobey the criteria was classified as not exactly lumpable.

Analysis on the results indicated that carbon number basis produced three exact lumping systems for model 1 and model 2 of hydrocracker at temperature 663K and 723K. Another analysis on true boiling point indicated that no exact lumping systems produced as both model 3 and model 4 of the hydrocracker models violated the criteria stated by Wei and Kuo.

ACKNOWLEDGEMENTS

First and foremost I would like to express my utmost gratitude and appreciation to Allah for His love and blessing, I managed to complete this project within the allocated time period.

I would like to express my very great appreciation to my supervisor, Dr. P. Balasubramanian for his great supervision in helping me from the first day until the end of the project. Without his encouragement and guidance, I would not be able to gain such a great knowledge and experiences.

To all my friends, thank you for your kindness and moral support. Thank you for the friendship and memories. I would like to thank Universiti Teknologi PETRONAS for providing me all the important information and guidelines in completing this thesis. Not to be forgotten to everyone who has contributed directly or indirectly during the completion of this thesis.

Last but not least, my special appreciation goes to my beloved parents and family for their endless love, prayers, encouragement and supports. Thank you for supporting me mentally and physically in completing this thesis.

Thank You.

Md Hairman Md Esa

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Petroleum products are the most important element in generating energy nowadays. In order to get this valuable product, there are many process involved from the drilling of petroleum until the final stage of refining process before it can be used. One of the important processes in the refining of petroleum products is hydrocracking.

Hydrocracking is a process of conversion of heavy oil fractions such as naphtha and middle distillates into lighter products in a relative high pressure and temperature condition. This process usually operated at temperature 350^{o}C to 850^{o}C in a various high pressure range, usually 40 bar to 150bar. Hydrogen supply and special catalyst is the major requirement for this process to occur. The presence of hydrogen in the process is purposed to break paraffin chains, open naphthene rings as well as dealkylation of aromatic and naphthene rings. This high temperature process also helps in converting sulphur and nitrogen compounds to hydrogen sulphide and ammonia and this process use a special catalyst such as zeolite (Robinson & Dolbear, 2006). According to Basak et al. (2004), excess hydrogen supply is also important in order to inhibit coke formation and secondary cracking.

Over the past decades, hydrocracking process has benefits petroleum industries in producing high quality products such as diesel, jet fuels and gasoline. Petroleum refining industries has drawn their attention to hydrocracking process due to limited oil resources and small portion of crude oil as heavy bottom distillate. Hydrocracking process is more preferred by the refiners because of its advantage in environmental aspect (Sadghi et al. 2010). As claimed by Basak et al. (2004), hydrocracked fuels are clean and environmental friendly because hydrocracking process reduce molecular weight significantly, produce no hetero-atoms and unsaturated compound in the products.

Thus, modelling complex hydrocracking kinetics is important in petroleum refining industries because it allow refiners to predict the product yields at different operating conditions which affect the process optimization, unit design as well as catalyst selection for the particular hydrocracking process (Haitham & Alhumaidan, 2011). The main reason of having kinetic modelling for hydrocracking unit is to ensure that all the chemistry of the different reactions are taking place accurately in the reactor (Basak et al. 2004).

Since decades ago, there are many kinetic modeling with a different approach has been developed for the usage of hydrocracking process. In this thesis, modelling of binary cracking kinetics using lumping technique will be analyzed by using discreet lumping approach. A few hydrocracker model will be verified by using few parameters.

1.2 Objectives

In order to determine the kinetic modelling of the binary cracking kinetics of the hydrocracking reactions, this project is carried out with the objective of:

i. To verify the lumping analysis of binary cracking kinetics using Wei and Kuo criteria for the carbon number and true boiling point based hydrocracker models.

Therefore, to achieve the objective of the project, four hydrocracker models will be used in the analysis under two parameters. The two parameters are carbon number and true boiling point where each parameter has two hydrocracker models.

CHAPTER 2

LITERATURE REVIEW

2.1 Lumping Analysis

According to Robinson & Dolbear (2006), in order to formulate reaction kinetic for conversion units, lumping analysis is used due to the complexity of heavy petroleum fractions. By using simple modeling, empirical correlations is applied to adjust for product objectives and feed properties by assuming first-order kinetics and treat the feed as a single entity. This modeling has been used for the design of commercial units petroleum refinery since early 1960s.

Modelling hydrocracking of heavy oil is difficult because it require detailed characterization of feed and products which is more complex to perform due to huge amount of heavy hydrocarbon in the composition (Elizalde et al. 2009). In hydrocracking, various kinetic models has been developed such as lumping technique, continuous mixture, structured oriented lumping and single event models. In this thesis, lumping technique approach has been selected.

According to Haitham & Alhumaidan (2011), there are two approach in the lumped empirical models which are discreet lumping approach and continuous lumping approach. Discreet lumping is a simplified approach where the complex hydrocracking chemistry and kinetics are viewed as a set of model compounds or pseudo-components. Alternatively, the chemically similar species of the complex mixture are combined or lumped together and treated as pseudo-components. The selection of pseudo-components can be based on product slate, true boiling point, carbon number or molecular weight.

Previously, hydrocarbons are lumped according to their carbon number and true boiling point values as well as the types of hydrocarbons, such as in PONA analysis where hydrocarbons is separated into four classes; paraffins, olefins, naphthenes and aromatics

(Balasubramanian & Gupta, 2011). Balasubramanian & Gupta (2011) also claimed that kinetic equations for lumped reaction system are derived based on the macroscopic reactions between the lumps, not by the individual species. Hence, the kinetic information will vary upon the changing in the feedstock characteristics as well as catalyst. By lumping the hydrocarbons according to their similar characters and properties, the kinetic information can be retrieved.

The effectiveness of discreet lumping model is depending on the easiness of application and incorporation into reactor models by considering the limited number of reactions and rate parameters involved. Simplicity is the key advantage of discreet lumping approach. During the application, increasing number of lumps affected the simplicity of the approach as it increases the number of kinetic parameters numerously (Haitham & Alhumaidan, 2011).

Despite the advantages of having kinetic data in hydrocracking reactions, lumping of hydrocarbons also have another disadvantages. As the process is conducted, lumping will cause some important information to be lost. For example, some important data might be lost during the characterization of products (Wei & Kuo, 1969). Furthermore, Elizalde et al.(2009) claimed that in order to determine each lump properties, it is required to conduct mass and energy balances as the properties such as density, molecular weight, distillation curve and viscosity are changing continuously in the reactor.

2.2 Wei and Kuo Criteria

In the analysis of exact lumpable system by Wei & Kuo (1969), all exact lumping kinetic can be grouped into three categories which are proper lumping, semiproper lumping and improper lumping. In the proper lumping, chemical species of the systems is divided into several classes that may be considered independent entities for kinetic purposes. For semiproper and improper lumping, each chemical species is not necessarily assigned to a unique class. In semiproper lumping, the corresponding lumped system follows a monomolecular reaction scheme. However, the lumped system resulting from an improper lumping will not follow a monomolecular reaction scheme.

In exact lumping (Balasubramanian & Gupta, 2011), the n species reaction system described by equation

$$S_i \xrightarrow{k_{j,i}} S_j \tag{1}$$

Where i varies from 1 to $n-1$, j varies from 2 to n, and $k_{j,i}$represent the kinetic constant for the formation for product j from reactant i. It is lumped into the $\hat{n}$ species by the use of lumping matrix M where the element in the matrix M is 1 and 0. The vector form of kinetic equation for the first order irreversible reaction system is

$$\dot{z} = R_k z \tag{2}$$

where R_k is the coefficient of the kinetic equation, z is the vector mole fraction for the reacting species.

Due to the loss of information during lumping of hydrocarbon, the selection of matrix M is necessary for proper lumping as this matrix divides all species into few classes where each column must be a unit vector.

$$M = \begin{bmatrix} 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{3}$$

The stoichiometry of the relumped reaction system can be represented by

$$\hat{S}_i \xrightarrow{\hat{k}_{j,i}} \hat{S}_j \tag{4}$$

The vector form of kinetic equation for the relumped system is given by

$$\dot{\hat{z}} = \hat{R}_k \hat{z} \tag{5}$$

Therefore, the necessary and sufficient conditions for proper lumping according to Wei & Kuo (1969) are:

i) The necessary condition for first order irreversible reaction system to be exactly lumpable is

$$[M]_{\hat{n}\times n}\,[R_k]_{n\times n} = [\hat{R}_k]_{\hat{n}\times\hat{n}}\,[M]_{\hat{n}\times n} \tag{6}$$

ii) In kinetic equation, V_i will be the eigenvector of the matrix R_k corresponding to eigenvalue λ_i and MV_i vectors must vanish for the system to be exactly lumpable.

2.3 Kinetic Modeling

2.3.1 Carbon Number

In binary cracking reaction, Balasubramanian & Pushpavanam (2008) assumed that heavier molecules with the property of y breaks into two smaller molecules which have property given by x and $y - x$ in each reaction. This is similar with C-C bond cleavage at β-position in hydrocracking. The general stoichiometry of the reaction can be expressed as

$$c(y) \xrightarrow{k(x,y,T)} c(x) + c(y-x) \tag{7}$$

In the equation, $k(x, y, T)$ represent the rate coefficient at which the property y gives rise to products with property x and $y - x$.

Since most of the hydrocracking kinetic model developed based on the first order kinetics, therefore the reactions assumed to be in the first order, irreversible and isothermal. The rate coefficient of the cracking reactions follows the Arrhenius equation:

$$k(x, y, T) = A(x, y)exp\left(-\frac{E(x,y)}{RT}\right) \tag{8}$$

Where $A(x, y)$ is the pre-exponential factor (h^{-1}), $E(x, y)$ is the activation energy (kJ mol^{-1}) for cracking of the property y into x and $y - x, R$ is the gas law constant (kJ $kmol^{-1}$ K^{-1}), and T is the reaction temperature (K). The values of pre-exponential factors and activation energy are show in Table 1 for hydrocracking of VGO (vacuum gas oil) using discrete lumped kinetic model.

Table 1: Estimated Exponential factors and activation energy for hydrocracker model 1 and model 2

Kinetic constants	Model 1 ($m = 0$)		Model 2 ($m = 1$)	
	$A\ (h^{-1})$	$E\ (kJ/mol)$	$A\ (h^{-1})$	$E\ (kJ/mol)$
$k_{1,2}$	8.7×10^{11}	188.0	1.0×10^{12}	188.0
$k_{1,3}$	1.6×10^{12}	170.3	1.8×10^{12}	170.3
$k_{1,4}$	9.5×10^{11}	167.7	9.5×10^{11}	167.7
$k_{2,4}$	7.9×10^{11}	166.5	7.9×10^{11}	166.5
$k_{1,5}$	7.0×10^{11}	157.8	7.0×10^{11}	157.8
$k_{2,5}$	3.7×10^{11}	156.3	3.5×10^{11}	156.3

Source: Adapted from "Model discrimination in hydrocracking of vacuum gas oil using discrete lumped kinetics", by Balasubramanian, P., & Pushpavanam, S. (2008), Fuel, Vol. 87(July 2008), pg 1660-1672.

There are five groups or lump in this analysis which are gases, gasoline, kerosene, gas oil and residue. In the analysis using carbon number basis, the two model of governing mass balance equations are

i. Random scission kernel (Model 1)

$$\frac{dw_r}{dt} = 2\sum_{j=r+1}^{n} A_{r,j}\ exp\left(-\frac{E_{r,j}}{RT}\right)\left(\frac{r}{j\,(j-1)}\right)w_j - \sum_{j=1}^{r-1} A_{j,r}\ exp\left(-\frac{E_{j,r}}{RT}\right)\left(\frac{1}{r-1}\right)w_r \quad (9)$$

ii. Symmetric kernel (Model 2)

$$\frac{dw_r}{dt} = 2\sum_{j=r+1}^{n} A_{r,j}\ exp\left(-\frac{E_{r,j}}{RT}\right)\left(\frac{6r^2(j-r)}{j^2(j^2-1)}\right)w_j - \sum_{j=1}^{r-1} A_{j,r}\ exp\left(-\frac{E_{j,r}}{RT}\right)\left(\frac{6j\,(r-j)}{r(r^2-1)}\right)w_r \quad (10)$$

where r varies from 1 to 5.

2.3.2 True Boiling Point

In this part, high boiling point petroleum fractions crack into two products in the lower boiling point range. The lump is fixed independently where the boiling point of the first product is not determined by the second product. The products may lie in the same boiling point of fraction lump.

For calculation, x is assumed to be the true boiling point of hydrocarbon and treated as continuous variable. The isomerization reactions are neglected and the general stoichiometry of the cracking reaction can be expressed as

$$c(y) \xrightarrow{k(x,y,T)} c(x) + c(x_1) \tag{11}$$

where $x < y$, $x_1 < y$ and $x_1 \neq y - x$.

The reactions is assumed to be the first order reaction, irreversible and isothermal and the rate coefficient of the cracking reactions follows Arrhenius equation:

$$k(x, x_1, y, T) = A(x, x_1, y) exp\left(-\frac{E(x,x_1,y)}{RT}\right) \tag{12}$$

The hydrocracker models involved in this part are:

i. Random scission kernel (Model 3)

$$\frac{dw_r}{dt} = 2\sum_{j=r+1}^{n}\sum_{i=1}^{j-1} A_{r,i,j}\ exp\left(-\frac{E_{r,i,j}}{RT}\right)\left(\frac{r}{i + r(j-1)^2}\right) w_j - \sum_{i=1}^{r-1}\sum_{j=1}^{r-1} A_{i,j,r}\ exp\left(-\frac{E_{i,j,r}}{RT}\right)\left(\frac{1}{(r-1)^2}\right) w_r \tag{13}$$

ii. Symmetric kernel (Model 4)

$$\frac{dw_r}{dt} = 2\sum_{j=r+1}^{n}\sum_{i=1}^{j-1} A_{r,i,j}\ exp\left(-\frac{E_{r,i,j}}{RT}\right)\left(\frac{4r(j-r)(j-i)}{(i+r)j^2(j-1)^2}\right) w_j - \sum_{i=1}^{r-1}\sum_{j=1}^{r-1} A_{i,j,r}\ exp\left(-\frac{E_{i,j,r}}{RT}\right)\left(\frac{4(r-i)(r-j)}{r^2(r-1)^2}\right) w_r \tag{14}$$

Table 2: Estimated Exponential factors and activation energy for hydrocracker model 3 and model 4

Kinetic constants	Model 3 ($m = 0$)		Model 4 ($m = 1$)	
	$A\ (h^{-1})$	$E\ (kJ/mol)$	$A\ (h^{-1})$	$E\ (kJ/mol)$
$k_{1,1,2}$	1.3×10^{12}	210.8	1.2×10^{12}	197.4
$k_{1,2,3}$	1.1×10^{11}	150.9	9.2×10^{11}	106.9
$k_{2,2,3}$	1.1×10^{11}	150.9	9.2×10^{11}	106.9
$k_{1,1,3}$	1.1×10^{11}	187.2	9.2×10^{11}	181.9
$k_{1,3,4}$	9.8×10^{10}	168.5	1.1×10^{11}	148.9
$k_{2,3,4}$	9.8×10^{10}	168.5	1.1×10^{11}	148.9
$k_{3,3,4}$	9.8×10^{10}	168.5	1.1×10^{11}	148.9
$k_{1,2,4}$	9.8×10^{10}	147.8	1.1×10^{11}	168.1
$k_{2,2,4}$	9.8×10^{10}	147.8	1.1×10^{11}	168.1
$k_{1,1,4}$	9.8×10^{10}	152.8	1.1×10^{11}	162.3
$k_{1,4,5}$	1.1×10^{8}	106.9	1.2×10^{9}	115.9
$k_{2,4,5}$	1.1×10^{8}	106.9	1.2×10^{9}	115.9
$k_{3,4,5}$	1.1×10^{8}	106.9	1.2×10^{9}	115.9
$k_{4,4,5}$	1.1×10^{8}	106.9	1.2×10^{9}	115.9
$k_{1,3,5}$	1.1×10^{8}	107.0	1.2×10^{9}	120.9
$k_{2,3,5}$	1.1×10^{8}	107.0	1.2×10^{9}	120.9
$k_{3,3,5}$	1.1×10^{8}	107.0	1.2×10^{9}	120.9
$k_{1,2,5}$	1.1×10^{8}	143.5	1.2×10^{9}	131.1
$k_{2,2,5}$	1.1×10^{8}	143.5	1.2×10^{9}	131.1
$k_{1,1,5}$	1.1×10^{8}	130.9	1.2×10^{9}	152.9

Source: Adapted from "Model discrimination in hydrocracking of vacuum gas oil using discrete lumped kinetics", by Balasubramanian, P., & Pushpavanam, S. (2008), Fuel, Vol. 87(July 2008), pg 1660-1672.

CHAPTER 3

METHODOLOGY

3.1 General Method

This research will be carried out based on its objectives. The first part of this research will be focusing on achieving the first objective, an analysis according to carbon number basis while the second part will be followed next. The proposed project timeline is provided in the appendix of this report.

The steps involved in the lumping analysis are described below:

(i) Write a kinetic constant matrix K for the reaction system.

(ii) Calculate the coefficients of matrix R_k

(iii) Determine the eigenpairs (λ_i, V_j) of a matrix R_k

(iv) Calculate vector MV_i corresponding to each eigenvector V_i

(v) Check the criterion (ii) for proper lumping

(vi) If criteria (ii) is satisfied, then calculate $\hat{V}_i$ by placing non vanishing MV_i column-wise

(vii) Determine $\hat{\Lambda}$ by making diagonal matrix of the eigenvalues of V_i for non vanishing MV_i vectors

(viii) Calculate the matrix $\hat{R}_k$ from the following expression

$$\hat{R}_k = \hat{V}\,\hat{\Lambda}\,\hat{V}^{-1} \tag{15}$$

For an analysis to be exactly lumpable, all of the calculations must have the entire calculation step described above. However, the analysis may fall under approximately lumpable if the calculations stop at step (v), where the result does not satisfy the criterion (ii) of proper lumping which is MV_i vectors must vanish when V_i will be the eigenvector of the matrix R_k corresponding to eigenvalue λ_i.

3.2 Project Activity

3.2.1 Stoichiometry of Calculation

By using carbon number of 5(C_5) as example, the general stoichiometry of the calculations is defined as below:

$$C_r \xrightarrow{k_{j,r}} C_j + C_{r-j} \tag{16}$$

where r varies from 2 to n, and j from 1 to $r-1$.

Reactions involved,

$$C_5 \xrightarrow{k_{1,5}} C_1 + C_4 \qquad C_4 \xrightarrow{k_{1,4}} C_1 + C_3$$

$$C_5 \xrightarrow{k_{2,5}} C_2 + C_3 \qquad C_4 \xrightarrow{k_{2,4}} C_2 + C_2$$

$$C_5 \xrightarrow{k_{3,5}} C_3 + C_2 \qquad C_4 \xrightarrow{k_{3,4}} C_3 + C_1$$

$$C_5 \xrightarrow{k_{4,5}} C_4 + C_1$$

$$C_3 \xrightarrow{k_{1,3}} C_1 + C_2 \qquad C_2 \xrightarrow{k_{1,2}} C_1 + C_1$$

$$C_3 \xrightarrow{k_{2,3}} C_2 + C_1$$

Where,

$$k_{2,5} = k_{3,5}$$

$$k_{1,4} = k_{3,4}$$

$$k_{1,3} = k_{2,3}$$

$$k_{1,5} = k_{4,5}$$

The molar concentration distribution can be defined using the ordinary differential equation below:

$$\frac{dc_r}{dt} = 2\sum_{j=r+1}^{n} k_{r,j}\Omega(r,j)c_j - \sum_{j=1}^{r-1} k_{j,r}\Omega(j,r)c_r \tag{17}$$

Then, the mass balance equation is rewritten using equation:

$$w_r\rho = M_r C_r \tag{18}$$

The rewritten equation is defined as

$$\frac{dw_r}{dt} = 2\sum_{j=r+1}^{n} \delta(r,j)k_{r,j}\Omega(r,j)w_j - \sum_{j=1}^{r-1} k_{j,r}\Omega(j,r)w_r \tag{19}$$

where r varies from 1 to n. ρ is the mass density of mixture, M_r is the molecular weight of hydrocarbon in lump of r, n is the number of lumps and

$$\delta(r,j) = \frac{M_r}{M_j} = \frac{r}{j} \tag{20}$$

The stoichiometric kernel in the carbon number basis must satisfy the normalization and symmetric conditions:

$$\sum_{j=1}^{r-1} \Omega(j,r) = 1 \tag{21}$$

$$\Omega(j,r) = \Omega(r,j) \tag{22}$$

Where r varies from 2 to n. Random scission stoichiometric kernel ($m = 0$) can be expressed as

$$\Omega(j,r) = \frac{1}{r-1} \tag{23}$$

The stoichiometric kernel when $m = 1$ is

$$\Omega(j,r) = \frac{6j(r-j)}{r(r^2-1)} \tag{24}$$

j varies from 1 to $r-1$ and r varies from 2 to n for both two kernels.

Next, constant matrix K and coefficients of matrix R_k for the monomolecular first order irreversible reaction system is derived by using the stoichiometry.

From equation 15,

$$\frac{dw_1}{dt} = 2\left[\delta(1,5)k_{1,5}\Omega(1,5)\right]w_5 + 2\left[\delta(1,4)k_{1,4}\Omega(1,4)\right]w_4$$

$$+2\left[\delta(1,3)k_{1,3}\Omega(1,3)\right]w_3 + 2\left[\delta(1,2)k_{1,2}\Omega(1,2)\right]w_2$$

$$\frac{dw_2}{dt} = 2\left[\delta(2,5)k_{2,5}\Omega(2,5)\right]w_5 + 2\left[\delta(2,4)k_{2,4}\Omega(2,4)\right]w_4$$

$$+2\left[\delta(2,3)k_{2,3}\Omega(2,3)\right]w_3 - \left[k_{1,2}\Omega(1,2)\right]w_2$$

$$\frac{dw_3}{dt} = 2\left[\delta(3,5)k_{3,5}\Omega(3,5)\right]w_5 + 2\left[\delta(3,4)k_{3,4}\Omega(3,4)\right]w_4$$

$$-\left[k_{1,3}\Omega(1,3) + k_{2,3}\Omega(2,3)\right]w_3$$

$$\frac{dw_4}{dt} = 2\left[\delta(4,5)k_{4,5}\Omega(4,5)\right]w_5 - \left[k_{1,4}\Omega(1,4) + k_{2,4}\Omega(2,4) + k_{3,4}\Omega(3,4)\right]w_4$$

$$\frac{dw_5}{dt} = -\left[k_{1,5}\Omega(1,5) + k_{2,5}\Omega(2,5) + k_{3,5}\Omega(3,5) + k_{4,5}\Omega(4,5)\right]w_5$$

The matrix form for mass balance equation,

$$\begin{bmatrix} dw_1 \\ dw_2 \\ dw_3 \\ dw_4 \\ dw_5 \end{bmatrix} = \begin{bmatrix} 0 & 2\left[\delta(1,2)k_{1,2}\Omega(1,2)\right] & 2\left[\delta(1,3)k_{1,3}\Omega(1,3)\right] & 2\left[\delta(1,4)k_{1,4}\Omega(1,4)\right] & 2\left[\delta(1,5)k_{1,5}\Omega(1,5)\right] \\ 0 & -\left[k_{1,2}\Omega(1,2)\right] & 2\left[\delta(2,3)k_{2,3}\Omega(2,3)\right] & 2\left[\delta(2,4)k_{2,4}\Omega(2,4)\right] & 2\left[\delta(2,5)k_{2,5}\Omega(2,5)\right] \\ 0 & 0 & -\begin{bmatrix} k_{1,3}\Omega(1,3) \\ +\, k_{2,3}\Omega(2,3) \end{bmatrix} & 2\left[\delta(3,4)k_{3,4}\Omega(3,4)\right] & 2\left[\delta(3,5)k_{3,5}\Omega(3,5)\right] \\ 0 & 0 & 0 & -\begin{bmatrix} k_{1,4}\Omega(1,4) + \ k_{2,4}\Omega(2,4) \\ +\, k_{3,4}\Omega(3,4) \end{bmatrix} & 2\left[\delta(4,5)k_{4,5}\Omega(4,5)\right] \\ 0 & 0 & 0 & 0 & -\begin{bmatrix} k_{1,5}\Omega(1,5) + \ k_{2,5}\Omega(2,5) \\ +\, k_{3,5}\Omega(3,5) + \ k_{4,5}\Omega(4,5) \end{bmatrix} \end{bmatrix} \begin{bmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \end{bmatrix}$$

Mass balance equation for symmetric kernel,

$$\begin{bmatrix} dw_1 \\ dw_2 \\ dw_3 \\ dw_4 \\ dw_5 \end{bmatrix} = \begin{bmatrix} 0 & [k_{1,2}] & 2\left[\frac{1}{6}k_{1,3}\right] & 2[0.75k_{1,4}] & 2[0.04k_{1,5}] \\ 0 & -[k_{1,2}] & 2\left[\frac{1}{3}k_{1,3}\right] & 2[0.2k_{2,4}] & 2[0.12k_{2,5}] \\ 0 & 0 & -[k_{1,3}] & 2[0.25k_{3,4}] & 2[0.18k_{2,5}] \\ 0 & 0 & 0 & -\begin{bmatrix}0.3k_{1,4} + 0.4k_{2,4} \\ +\ 0.3k_{1,4}\end{bmatrix} & 2[0.16k_{1,5}] \\ 0 & 0 & 0 & 0 & -\begin{bmatrix}0.4k_{1,5} \\ +\ 0.6k_{2,5}\end{bmatrix} \end{bmatrix} \begin{bmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \end{bmatrix}$$

Mass Balance for Random scission kernel,

$$\begin{bmatrix} dw_1 \\ dw_2 \\ dw_3 \\ dw_4 \\ dw_5 \end{bmatrix} = \begin{bmatrix} 0 & [k_{1,2}] & 2\left[\frac{1}{6}k_{1,3}\right] & 2\left[\frac{1}{12}k_{1,4}\right] & 2[0.05k_{1,5}] \\ 0 & -[k_{1,2}] & 2\left[\frac{1}{3}k_{2,3}\right] & 2\left[\frac{1}{6}k_{2,4}\right] & 2[0.1k_{2,5}] \\ 0 & 0 & -[k_{2,3}] & 2[0.25k_{3,4}] & 2[0.15k_{2,5}] \\ 0 & 0 & 0 & -\begin{bmatrix}0.3k_{1,4} + 0.3k_{2,4} \\ +\ 0.3k_{1,4}\end{bmatrix} & 2[0.2k_{1,5}] \\ 0 & 0 & 0 & 0 & -\begin{bmatrix}0.5k_{1,5} \\ +\ 0.5k_{2,5}\end{bmatrix} \end{bmatrix} \begin{bmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \end{bmatrix}$$

The rate coefficients values for the reactions involved can be determined using the Arrhenius equations. When all the required values calculated, the analysis can be continued by using the general procedures. The results obtained will be analyzed and tabulated and recalculations may be conducted if the results is not satisfied the main research objectives.

All of the projects activities were carried out based on the scheduled timeline which have been scheduled at the beginning of the research. The Gantt chart of the project are provided at the appendix section. At certain time within the project period, a small target or milestone is expected to be achieved. This is to ensure the project is managed successfully. Below are the target and key milestones of the project;

Table 3: Project target and key milestones

No	Details	Target Milestone (Week)
1	Completion of literature review	4
2	Preparation of draft of methodology	5
3	Complete the simulation for carbon number	11
4	Completion of results analysis & discussion	14
5	Complete the simulation for true boiling point	18
6	Completion of results analysis & discussion	21
7	Submission of final report & technical report	27

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Carbon Number

4.1.1 Stoichiometric of calculations for five lump

$$C_r \xrightarrow{k_{j,r}} C_j + C_{r-j}$$

where r varies from 2 to n, and j from 1 to $r-1$. Reactions involved;

$$C_5 \xrightarrow{k_{1,5}} C_1 + C_4 \qquad C_4 \xrightarrow{k_{1,4}} C_1 + C_3$$

$$C_5 \xrightarrow{k_{2,5}} C_2 + C_3 \qquad C_4 \xrightarrow{k_{2,4}} C_2 + C_2$$

$$C_5 \xrightarrow{k_{3,5}} C_3 + C_2 \qquad C_4 \xrightarrow{k_{3,4}} C_3 + C_1$$

$$C_5 \xrightarrow{k_{4,5}} C_4 + C_1$$

$$C_3 \xrightarrow{k_{1,3}} C_1 + C_2 \qquad C_2 \xrightarrow{k_{1,2}} C_1 + C_1$$

$$C_3 \xrightarrow{k_{2,3}} C_2 + C_1$$

Where,

$$k_{2,5} = k_{3,5}, \qquad k_{1,4} = k_{3,4}$$

$$k_{1,3} = k_{2,3}, \qquad k_{1,5} = k_{4,5}$$

General form of K matrix

$$K = \begin{bmatrix} 0 & k_{1,2} & k_{1,3} & \cdots & k_{1,n} \\ 0 & 0 & k_{2,n} & \cdots & k_{2,n} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & k_{n-1,n} \\ 0 & 0 & 0 & \cdots & 0 \end{bmatrix}$$

K matrix for the lumping system,

$$K = \begin{bmatrix} 0 & k_{1,2} & k_{1,3} & k_{1,4} & k_{1,5} \\ 0 & 0 & k_{2,3} & k_{2,4} & k_{2,5} \\ 0 & 0 & 0 & k_{3,4} & k_{3,5} \\ 0 & 0 & 0 & 0 & k_{4,5} \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

4.1.2 Random Scission Stoichiometric Kernel (Model 1)

R_k matrix,

$$R_k = \begin{bmatrix} 0 & [k_{1,2}] & 2\left[\frac{1}{6}k_{1,3}\right] & 2\left[\frac{1}{12}k_{1,4}\right] & 2[0.05k_{1,5}] \\ 0 & -[k_{1,2}] & 2\left[\frac{1}{3}k_{2,3}\right] & 2\left[\frac{1}{6}k_{2,4}\right] & 2[0.1k_{2,5}] \\ 0 & 0 & -[k_{2,3}] & 2[0.25k_{3,4}] & 2[0.15k_{2,5}] \\ 0 & 0 & 0 & -\begin{bmatrix}0.3k_{1,4} + 0.3k_{2,4} \\ +\,0.3k_{1,4}\end{bmatrix} & 2[0.2k_{1,5}] \\ 0 & 0 & 0 & 0 & -\begin{bmatrix}0.5k_{1,5} \\ +\,0.5k_{2,5}\end{bmatrix} \end{bmatrix}$$

<u>Temperature: 663K</u>

Kinetic constant matrix, $K = \begin{bmatrix} 0 & 0.0015 & 0.0688 & 0.0582 & 0.2584 \\ 0 & 0 & 0.0688 & 0.0602 & 0.1696 \\ 0 & 0 & 0 & 0.0582 & 0.1696 \\ 0 & 0 & 0 & 0 & 0.2584 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$

Coefficient of kinetic constant matrix,

$$R_K = \begin{bmatrix} 0 & -0.0015 & -0.0229 & -0.0097 & -0.0258 \\ 0 & 0.0015 & -0.0459 & -0.0201 & -0.0339 \\ 0 & 0 & 0.0688 & -0.0291 & -0.0509 \\ 0 & 0 & 0 & 0.0589 & -0.1034 \\ 0 & 0 & 0 & 0 & 0.2140 \end{bmatrix}$$

Eigenpairs of matrix R_K,

$$D = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0.0015 & 0 & 0 & 0 \\ 0 & 0 & 0.0688 & 0 & 0 \\ 0 & 0 & 0 & 0.0589 & 0 \\ 0 & 0 & 0 & 0 & 0.2140 \end{bmatrix}$$

$$V = \begin{bmatrix} 1.0000 & -0.7071 & -0.2541 & -0.2883 & -0.0547 \\ 0 & 0.7071 & -0.5449 & -0.6287 & -0.0408 \\ 0 & 0 & 0.7991 & 0.6834 & -0.1772 \\ 0 & 0 & 0 & 0.2336 & -0.5443 \\ 0 & 0 & 0 & 0 & 0.8171 \end{bmatrix}$$

Case 1: Lump of 5 to 4 group

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \begin{bmatrix} 0 & -0.0688 & -0.0299 & -0.0599 \\ 0 & 0.0688 & -0.0290 & -0.0508 \\ 0 & 0 & 0.0589 & -0.1033 \\ 0 & 0 & 0 & 0.2140 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 0.0688 & 0.0897 & 0.3594 \\ 0 & 0 & 0.0897 & 0.1524 \\ 0 & 0 & 0 & 0.3594 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

Case 2: Lump of 5 to 3 group

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \begin{bmatrix} 0 & -0.0589 & -0.1107 \\ 0 & 0.0589 & -0.1033 \\ 0 & 0 & 0.2140 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 0.0589 & 0.3321 \\ 0 & 0 & 0.3321 \\ 0 & 0 & 0 \end{bmatrix}$$

Case 3: Lump of 5 to 2 group

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \begin{bmatrix} 0 & -0.2140 \\ 0 & 0.2140 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 0.2140 \\ 0 & 0 \end{bmatrix}$$

Temperature: 723K

Kinetic constant matrix, $K = \begin{bmatrix} 0 & 0.0261 & 0.8936 & 0.7269 & 2.7803 \\ 0 & 0 & 0.8936 & 0.7380 & 1.7842 \\ 0 & 0 & 0 & 0.7269 & 1.7842 \\ 0 & 0 & 0 & 0 & 2.7803 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$

Coefficient of kinetic constant matrix,

$$R_K = \begin{bmatrix} 0 & -0.0261 & -0.2979 & -0.1211 & -0.2780 \\ 0 & 0.0261 & -0.5957 & -0.2460 & -0.3568 \\ 0 & 0 & 0.8936 & -0.3634 & -0.5353 \\ 0 & 0 & 0 & 0.7306 & -1.1121 \\ 0 & 0 & 0 & 0 & 2.2823 \end{bmatrix}$$

Eigenpairs of matrix R_K,

$$D = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0.0261 & 0 & 0 & 0 \\ 0 & 0 & 0.8936 & 0 & 0 \\ 0 & 0 & 0 & 0.7306 & 0 \\ 0 & 0 & 0 & 0 & 2.2823 \end{bmatrix}$$

$$V = \begin{bmatrix} 1.000 & -0.7071 & -0.2501 & -0.2878 & -0.0462 \\ 0 & 0.7071 & -0.5481 & -0.6463 & -0.0222 \\ 0 & 0 & 0.7982 & 0.6449 & -0.1586 \\ 0 & 0 & 0 & 0.2892 & -0.5744 \\ 0 & 0 & 0 & 0 & 0.8014 \end{bmatrix}$$

Case 1: Lump of 5 to 4 group

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \begin{bmatrix} 0 & -0.8936 & -0.3673 & -0.6349 \\ 0 & 0.8936 & -0.3633 & -0.5352 \\ 0 & 0 & 0.7306 & -1.1122 \\ 0 & 0 & 0 & 2.2823 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 0.8936 & 1.1019 & 3.8094 \\ 0 & 0 & 1.1019 & 1.6056 \\ 0 & 0 & 0 & 3.8094 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

Case 2: Lump of 5 to 3 group

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \begin{bmatrix} 0 & -0.7306 & -1.1701 \\ 0 & 0.7306 & -1.1122 \\ 0 & 0 & 2.2823 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 0.7306 & 3.5103 \\ 0 & 0 & 3.5103 \\ 0 & 0 & 0 \end{bmatrix}$$

Case 3: Lump of 5 to 2 group

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Eigenvectors of relumped matrix,

$$MV = \begin{bmatrix} 1 & 0 & 0 & 0 & -0.8014 \\ 0 & 0 & 0 & 0 & 0.8014 \end{bmatrix}$$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \begin{bmatrix} 0 & -2.2823 \\ 0 & 2.2823 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 2.2823 \\ 0 & 0 \end{bmatrix}$$

4.1.3 Symmetric Stoichiometric Kernel (Model 2)

R_k matrix,

$$R_k = \begin{bmatrix} 0 & [k_{1,2}] & 2\left[\frac{1}{6}k_{1,3}\right] & 2[0.75k_{1,4}] & 2[0.04k_{1,5}] \\ 0 & -[k_{1,2}] & 2\left[\frac{1}{3}k_{1,3}\right] & 2[0.2k_{2,4}] & 2[0.12k_{2,5}] \\ 0 & 0 & -[k_{1,3}] & 2[0.25k_{3,4}] & 2[0.18k_{2,5}] \\ 0 & 0 & 0 & -\begin{bmatrix} 0.3k_{1,4} + 0.4k_{2,4} \\ +\ 0.3k_{1,4} \end{bmatrix} & 2[0.16k_{1,5}] \\ 0 & 0 & 0 & 0 & -\begin{bmatrix} 0.4k_{1,5} \\ +\ 0.6k_{2,5} \end{bmatrix} \end{bmatrix}$$

Temperature: 663K

Kinetic constant matrix, $K = \begin{bmatrix} 0 & 0.0015 & 0.0688 & 0.0582 & 0.2584 \\ 0 & 0 & 0.0688 & 0.0602 & 0.1696 \\ 0 & 0 & 0 & 0.0582 & 0.1696 \\ 0 & 0 & 0 & 0 & 0.2584 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$

Coefficient of kinetic equation matrix,

$$R_K = \begin{bmatrix} 0 & -0.0015 & -0.0229 & -0.0087 & -0.0207 \\ 0 & 0.0015 & -0.0459 & -0.0241 & -0.0407 \\ 0 & 0 & 0.0688 & -0.0262 & -0.0611 \\ 0 & 0 & 0 & 0.0590 & -0.0827 \\ 0 & 0 & 0 & 0 & 0.2051 \end{bmatrix}$$

Eigenpairs of matrix R_K,

$$D = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0.0015 & 0 & 0 & 0 \\ 0 & 0 & 0.0688 & 0 & 0 \\ 0 & 0 & 0 & 0.0590 & 0 \\ 0 & 0 & 0 & 0 & 0.2051 \end{bmatrix}$$

$$V = \begin{bmatrix} 1.000 & -0.7071 & -0.2541 & -0.2808 & -0.0320 \\ 0 & 0.7071 & -0.5449 & -0.6400 & -0.0472 \\ 0 & 0 & 0.7991 & 0.6697 & -0.2827 \\ 0 & 0 & 0 & 0.2511 & -0.4715 \\ 0 & 0 & 0 & 0 & 0.8334 \end{bmatrix}$$

Case 1: Lump of 5 to 4 group

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Eigenvectors of relumped matrix,

$$MV = \begin{bmatrix} 1.0000 & 0 & -0.7991 & -0.9208 & -0.0791 \\ 0 & 0 & 0.7991 & 0.6697 & -0.2827 \\ 0 & 0 & 0 & 0.2511 & -0.4715 \\ 0 & 0 & 0 & 0 & 0.8334 \end{bmatrix}$$

Eigenpairs of relumped system,

$$\hat{\Lambda} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0.0688 & 0 & 0 \\ 0 & 0 & 0.0590 & 0 \\ 0 & 0 & 0 & 0.2051 \end{bmatrix}$$

$$\hat{V} = \begin{bmatrix} 1.0000 & -0.7991 & -0.9208 & -0.0791 \\ 0 & 0.7991 & 0.6697 & -0.2827 \\ 0 & 0 & 0.2511 & -0.4715 \\ 0 & 0 & 0 & 0.8334 \end{bmatrix}$$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \hat{V}\,\hat{\Lambda}\,\hat{V}^{-1}$$

$$\hat{R}_k = \begin{bmatrix} 0 & -0.0688 & -0.0329 & -0.0614 \\ 0 & 0.0688 & -0.0261 & -0.0610 \\ 0 & 0 & 0.0590 & -0.0827 \\ 0 & 0 & 0 & 0.2051 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 0.0688 & 0.0987 & 0.4093 \\ 0 & 0 & 0.0987 & 0.1525 \\ 0 & 0 & 0 & 0.4093 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

<u>Case 2: Lump of 5 to 3 group</u>

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Eigenvectors of relumped matrix,

$$MV = \begin{bmatrix} 1.0000 & 0 & 0 & -0.2511 & -0.3618 \\ 0 & 0 & 0 & 0.2511 & -0.4715 \\ 0 & 0 & 0 & 0 & 0.8334 \end{bmatrix}$$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \begin{bmatrix} 0 & -0.0590 & -0.1224 \\ 0 & 0.0590 & -0.0827 \\ 0 & 0 & 0.2051 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 0.0590 & 0.3672 \\ 0 & 0 & 0.3672 \\ 0 & 0 & 0 \end{bmatrix}$$

Case 3: Lump of 5 to 2 group

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \begin{bmatrix} 0 & -0.2051 \\ 0 & 0.2051 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 0.2051 \\ 0 & 0 \end{bmatrix}$$

Temperature: 723K

Kinetic constant matrix, $K = \begin{bmatrix} 0 & 0.0261 & 0.8936 & 0.7269 & 2.7803 \\ 0 & 0 & 0.8936 & 0.7380 & 1.7842 \\ 0 & 0 & 0 & 0.7269 & 1.7842 \\ 0 & 0 & 0 & 0 & 2.7803 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$

Coefficient of kinetic equation matrix,

$$R_K = \begin{bmatrix} 0 & -0.0261 & -0.2979 & -0.1090 & -0.2224 \\ 0 & 0.0261 & -0.5957 & -0.2952 & -0.4282 \\ 0 & 0 & 0.8936 & -0.3271 & -0.6423 \\ 0 & 0 & 0 & 0.7313 & -0.8897 \\ 0 & 0 & 0 & 0 & 2.1826 \end{bmatrix}$$

Eigenpairs of matrix R_K,

$$D = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0.0261 & 0 & 0 & 0 \\ 0 & 0 & 0.8936 & 0 & 0 \\ 0 & 0 & 0 & 0.7313 & 0 \\ 0 & 0 & 0 & 0 & 2.1826 \end{bmatrix}$$

$$V = \begin{bmatrix} 1.000 & -0.7071 & -0.2500 & -0.2878 & -0.0199 \\ 0 & 0.7071 & -0.5481 & -0.6590 & -0.0163 \\ 0 & 0 & 0.7982 & 0.6261 & -0.2804 \\ 0 & 0 & 0 & 0.3107 & -0.5015 \\ 0 & 0 & 0 & 0 & 0.8181 \end{bmatrix}$$

Case 1: Lump of 5 to 4 group

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \begin{bmatrix} 0 & -0.8936 & -0.4042 & -0.6507 \\ 0 & 0.8936 & -0.3271 & -0.6423 \\ 0 & 0 & 0.7313 & -0.8897 \\ 0 & 0 & 0 & 2.1826 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 0.8936 & 1.2126 & 4.3380 \\ 0 & 0 & 1.2126 & 1.6057 \\ 0 & 0 & 0 & 4.3380 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

Case 2: Lump of 5 to 3 group

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \begin{bmatrix} 0 & -0.7313 & -1.2929 \\ 0 & 0.7313 & -0.8897 \\ 0 & 0 & 2.1826 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 0.7313 & 3.8787 \\ 0 & 0 & 3.8787 \\ 0 & 0 & 0 \end{bmatrix}$$

Case 3: Lump of 5 to 2 group

Lumping matrix, $M = \begin{bmatrix} 1 & 1 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$

Relumped matrix $\hat{R}_k$,

$$\hat{R}_k = \begin{bmatrix} 0 & -2.1826 \\ 0 & 2.1826 \end{bmatrix}$$

Relumped k matrix, $\hat{k}$,

$$\hat{k} = \begin{bmatrix} 0 & 2.1826 \\ 0 & 0 \end{bmatrix}$$

4.1.4 Discussion

Based on the results obtained from the analysis, carbon number analysis produced three lumping matrix that positively analyzed to become exact lumping system for both symmetric and random scission kernel. In both kernels, all lumping matrix obeyed the criteria of exact lumping system by Wei and Kuo.

The first lumping matrix is a lump of five groups of heavy oil fraction into four groups. In the analysis, one of the column in the eigenvectors of relumped matrix vanished as it show zero values in all row of the matrix. This scenario has fulfilled the second criteria stated by Wei and Kuo and enables the continuation of the calculation. In order to continue the analysis, a new matrix is formed by removing the zero values column, merging the matrix into four by four dimension. Further calculation is proceeded to find the final values of $\hat{R}_k$ and $\hat{k}$ matrices for the relumped systems.

The second lumping matrix features the lump of five groups of heavy oil fraction into three groups of lighter oil fractions. All the scenario in the first lumping scheme is repeated but there is a small difference between the two lumping. Since the lump is narrowed from five to three groups of oil fractions, the vanishing column of the eigenvectors of relumped matrix increased with two columns.

Third lumping matrix features the lump of five groups into two groups of lighter oil fractions. In this calculation, the system is become smaller as there are three column of the eigenvectors of relumped matrix vanished. The final $\hat{R}_k$ and $\hat{k}$ matrices for the relumped systems also shrunk to two by two matrix dimension.

All the lumping matrices that contribute to exact lumping system are valid for all the temperature range in both symmetric and random scission kernel. Therefore, in carbon number analysis, there are six exact lumping systems at two different temperatures for each hydrocracker model.

Out of eleven possible lumping matrices that expected to contribute to exact lumping systems, only three matrices are valid. The remaining eight matrices are considered as not lumpable as the matrices do not contribute to exact lumping system. This happened due to the violation of the second criteria of Wei and Kuo stated earlier in the theory.

4.2 True Boiling Point

4.2.1 Stoichiometric of Calculations

Number of lumps = 5

$$C_r \xrightarrow{k_{i,j,r}} C_i + C_j$$

where r varies from 2 to n, and i and j from 1 to $r-1$. Reactions involved,

$$C_5 \xrightarrow{k_{1,4,5}} C_1 + C_4 \qquad C_4 \xrightarrow{k_{1,3,4}} C_1 + C_3$$

$$C_5 \xrightarrow{k_{2,3,5}} C_2 + C_3 \qquad C_4 \xrightarrow{k_{2,2,4}} C_2 + C_2$$

$$C_5 \xrightarrow{k_{3,2,5}} C_3 + C_2 \qquad C_4 \xrightarrow{k_{3,1,4}} C_3 + C_1$$

$$C_5 \xrightarrow{k_{4,1,5}} C_4 + C_1$$

$$C_3 \xrightarrow{k_{1,2,3}} C_1 + C_2 \qquad\qquad C_2 \xrightarrow{k_{1,2,2}} C_1 + C_1$$

$$C_3 \xrightarrow{k_{2,1,3}} C_2 + C_1$$

Where,

$$k_{2,3,5} = k_{3,2,5}$$

$$k_{1,3,4} = k_{3,1,4}$$

$$k_{1,2,3} = k_{2,1,3}$$

$$k_{1,4,5} = k_{4,1,5}$$

Model equations,

iii. Random scission kernel (Model 3)

$$\frac{dw_r}{dt} = 2\sum_{j=r+1}^{n}\sum_{i=1}^{j-1} A_{r,i,j}\ exp\left(-\frac{E_{r,i,j}}{RT}\right)\left(\frac{r}{i+r(j-1)^2}\right)w_j - \sum_{i=1}^{r-1}\sum_{j=1}^{r-1} A_{i,j,r}\ exp\left(-\frac{E_{i,j,r}}{RT}\right)\left(\frac{1}{(r-1)^2}\right)w_r$$

Symmetric kernel (Model 4)

$$\frac{dw_r}{dt} = 2\sum_{j=r+1}^{n}\sum_{i=1}^{j-1} A_{r,i,j}\ exp\left(-\frac{E_{r,i,j}}{RT}\right)\left(\frac{4r(j-r)(j-i)}{(i+r)j^2(j-1)^2}\right)w_j - \sum_{i=1}^{r-1}\sum_{j=1}^{r-1} A_{i,j,r}\ exp\left(-\frac{E_{i,j,r}}{RT}\right)\left(\frac{4(r-i)(r-j)}{r^2(r-1)^2}\right)w_r$$

where r varies from 1 to 5.

4.2.2 Random Scission Kernel (Model 3)

Temperature: 663K

R_k matrix,

$$R_k = \begin{bmatrix} 0 & -0.0013 & -0.2903 & -0.1814 & -0.5540 \\ 0 & 0.0003 & -0.2903 & -0.1814 & -0.5540 \\ 0 & 0 & 0.1462 & -0.1814 & -0.5540 \\ 0 & 0 & 0 & 0.1175 & -0.5540 \\ 0 & 0 & 0 & 0 & 0.5102 \end{bmatrix}$$

Lumping matrix, M,

$$M = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Eigenpairs of matrix R_K,

$$D = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0.0003 & 0 & 0 & 0 \\ 0 & 0 & 0.1462 & 0 & 0 \\ 0 & 0 & 0 & 0.1175 & 0 \\ 0 & 0 & 0 & 0 & 0.5102 \end{bmatrix}$$

$$V = \begin{bmatrix} 1.000 & -0.9701 & -0.6620 & -0.6786 & -0.0614 \\ 0 & 0.2425 & -0.6697 & -0.6885 & -0.0616 \\ 0 & 0 & 0.3365 & 0.2527 & -0.4264 \\ 0 & 0 & 0 & 0.0401 & -0.7345 \\ 0 & 0 & 0 & 0 & 0.5207 \end{bmatrix}$$

Eigenvectors of relumped matrix,

$$MV = \begin{bmatrix} 1.0000 & -0.7276 & -1.3317 & -1.3671 & -0.1231 \\ 0 & 0 & 0.3365 & 0.2527 & -0.4264 \\ 0 & 0 & 0 & 0.0401 & -0.7345 \\ 0 & 0 & 0 & 0 & 0.5207 \end{bmatrix}$$

Temperature: 723K

R_k matrix,

$$R_k = \begin{bmatrix} 0 & -0.0263 & -3.2727 & -1.7071 & -3.1719 \\ 0 & 0.0066 & -3.2727 & -1.7071 & -3.1719 \\ 0 & 0 & 1.6529 & -1.7071 & -3.1719 \\ 0 & 0 & 0 & 1.1162 & -3.1719 \\ 0 & 0 & 0 & 0 & 2.9872 \end{bmatrix}$$

Lumping matrix, M,

$$M = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Eigenpairs of matrix R_K,

$$D = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0.0066 & 0 & 0 & 0 \\ 0 & 0 & 1.6529 & 0 & 0 \\ 0 & 0 & 0 & 1.1162 & 0 \\ 0 & 0 & 0 & 0 & 2.9872 \end{bmatrix}$$

$$V = \begin{bmatrix} 1.000 & -0.9701 & -0.6588 & -0.6803 & 0.0674 \\ 0 & 0.2425 & -0.6721 & -0.7009 & 0.0681 \\ 0 & 0 & 0.3381 & 0.2042 & -0.1048 \\ 0 & 0 & 0 & 0.0642 & -0.8526 \\ 0 & 0 & 0 & 0 & 0.5029 \end{bmatrix}$$

Eigenvectors of relumped matrix,

$$MV = \begin{bmatrix} 1.0000 & -0.7276 & -1.3309 & -1.3813 & 0.1355 \\ 0 & 0 & 0.3381 & 0.2042 & -0.1048 \\ 0 & 0 & 0 & 0.0642 & -0.8526 \\ 0 & 0 & 0 & 0 & 0.5029 \end{bmatrix}$$

4.2.3 Exponential Kernel (Model 4)

Temperature: 663K

R_k matrix,

$$R_k = \begin{bmatrix} 0 & -0.0013 & -0.2581 & -0.1361 & -0.3546 \\ 0 & 0.0003 & -0.1290 & -0.0907 & -0.2659 \\ 0 & 0 & 0.1094 & -0.0454 & -0.1773 \\ 0 & 0 & 0 & 0.0696 & -0.0886 \\ 0 & 0 & 0 & 0 & 0.3107 \end{bmatrix}$$

Lumping matrix, M,

$$M = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Eigenpairs of matrix R_K,

$$D = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0.0003 & 0 & 0 & 0 \\ 0 & 0 & 0.1094 & 0 & 0 \\ 0 & 0 & 0 & 0.0696 & 0 \\ 0 & 0 & 0 & 0 & 0.3017 \end{bmatrix}$$

$$V = \begin{bmatrix} 1.000 & -0.9701 & -0.8343 & -0.8523 & -0.2001 \\ 0 & 0.2425 & -0.4210 & -0.4785 & -0.2844 \\ 0 & 0 & 0.3560 & 0.1589 & -0.5754 \\ 0 & 0 & 0 & 0.1395 & -0.2642 \\ 0 & 0 & 0 & 0 & 0.6915 \end{bmatrix}$$

Eigenvectors of relumped matrix,

$$MV = \begin{bmatrix} 1.0000 & -0.7276 & -1.2553 & -1.3307 & -0.4845 \\ 0 & 0 & 0.3560 & 0.1589 & -0.5754 \\ 0 & 0 & 0 & 0.1395 & -0.2642 \\ 0 & 0 & 0 & 0 & 0.6915 \end{bmatrix}$$

<u>Temperature: 723K</u>

R_k matrix,

$$R_k = \begin{bmatrix} 0 & -0.0263 & -2.9091 & -1.2803 & -2.0300 \\ 0 & 0.0066 & -1.4545 & -0.8536 & -1.5225 \\ 0 & 0 & 1.2416 & -0.4268 & -1.0150 \\ 0 & 0 & 0 & 0.6735 & -0.5075 \\ 0 & 0 & 0 & 0 & 1.8064 \end{bmatrix}$$

Lumping matrix, M,

$$M = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Eigenpairs of matrix R_K,

$$D = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0.0066 & 0 & 0 & 0 \\ 0 & 0 & 1.2416 & 0 & 0 \\ 0 & 0 & 0 & 0.6735 & 0 \\ 0 & 0 & 0 & 0 & 1.8064 \end{bmatrix}$$

$$V = \begin{bmatrix} 1.000 & -0.9701 & -0.8321 & -0.8457 & 0.6275 \\ 0 & 0.2425 & -0.4228 & -0.4905 & 0.2229 \\ 0 & 0 & 0.3590 & 0.1263 & -0.5964 \\ 0 & 0 & 0 & 0.1681 & -0.1832 \\ 0 & 0 & 0 & 0 & 0.4090 \end{bmatrix}$$

Eigenvectors of relumped matrix,

$$MV = \begin{bmatrix} 1.0000 & -0.7276 & -1.2549 & -1.3362 & 0.8504 \\ 0 & 0 & 0.3590 & 0.1263 & -0.5964 \\ 0 & 0 & 0 & 0.1681 & -0.1832 \\ 0 & 0 & 0 & 0 & 0.4090 \end{bmatrix}$$

4.2.4 Discussion

Based on the results obtained from the analysis, true boiling point analysis produced no lumping matrix that positively analyzed to become exact lumping system for both symmetric and random scission kernel. In both kernels, all lumping matrix violate the second criteria of exact lumping system by Wei and Kuo, which stated that MV_i vectors must vanish for the system to be exactly lumpable.

By taking the first lumping matrix is a lump of five groups of heavy oil fraction into four groups as example, none of the vectors in the eigenvectors of relumped matrix vanished where no vector show zero values in any single column of the matrix. Therefore, the matrix cannot be merged into four by four dimension, which later will be used to calculate the final values of $\hat{R}_k$ and $\hat{k}$ matrices for the relumped systems.

Analysis on different temperature also showed that no lumping matrix that positively analyzed to become exact lumping system for both model 3 and model 4 of the hydrocracker model. Therefore, in true boiling point analysis, there is no exact lumping system produced by using model 3 and model 4 as the hydrocracker models.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In conclusion, carbon number analysis indicated that three lumping matrix is exactly lumpable to form an exact lumping systems. This showed that hydrocracker model 1 and model 2 is contributed to exact lumping system and can be used in the hydrocracking process. However, true boiling point analysis indicated no exact lumping systems due to the violation of the second criteria of Wei and Kuo criteria. Therefore, hydrocracker model 3 and model 4 does not contribute to exact lumping systems.

5.2 Recommendations

Further analysis in this project can be done in the future research. This research can be improved by using another parameter to verify the kinetic models of binary cracking kinetics. There are many parameters or selection pseudo-component that can be used for further analysis for this project. One of the parameters that suitable for further analysis is molecular weight.

Since there are a lot of kinetics models for hydrocracking, it is recommended for further analysis to use another hydrocracker model that is suitable for the current type of the reactions. An analysis by using other hydrocracker model at different temperature degree will give a set of new result which might contribute to the betterment of the future.

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APPENDIX

1. Project Gantt Chart

No	Details/Week	1	2	4	6	8	10	12	14	16	18	20	22	24	26	28
1	Research title confirmation															
2	Literature review															
3	Draft of methodology															
4	Simulation of carbon number															
5	Analysis of results & discussion															
6	Simulation of true boiling point															
7	Analysis of results & discussion															
8	Compilation of results															
9	Documentation of report															
10	Documentation of technical report															
11	Submission of draft report															
12	Submission of final report & technical report															