

**Kinetic Modelling Of Thermal Cracking of Vacuum Residue  
on Eureka Process**

by

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13262

Dissertation submitted in partial fulfilment of  
the requirements for the  
Bachelor of Engineering (Hons)  
(Chemical Engineering)

JANUARY 2014

Universiti Teknologi PETRONAS  
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# CERTIFICATION OF APPROVAL

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Approved by,

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(Dr. P. Balasubramanian)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK.

January 2014

## 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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MUHAMMAD SYUKRI BIN MOHD SHAH

## ABSTRACT

In oil refineries, cracking process is an important process for upgrading the raw crude oil into higher quality product that can be used by the consumer. The refining process start from crude distillation unit (CDU), then vacuum distillation unit (VDU) for further product yield. The effluent of VDU is called vacuum residue which can later be upgraded by hydrocracking. In this case thermal cracking is favored than catalytic cracking due to impurities. The work presents the development of a binary reaction kinetic model for Eureka process, a type of thermal cracking chosen for further studies in its kinetics due to potential enhancement to yield more useful product recovery. The process is proven to have more advantage and environmental friendly than other conventional thermal cracking process. Despite of its advantages, there is limited research on the kinetics models of the process that render further enhancement to the current industrial application which is believed to be improved. Thus, the project proposed a binary reactions kinetic model using discrete lumping method by identifying its parameters and estimated the constant values. Discrete lumping method is chosen with basis of true boiling point for each lump to ease the calculation and development of kinetic model. There are five discrete lumps assumed which are feedstock Vacuum Residue (VR), demister oil (DMO), cracked heavy oil (CHO), cracked light oil (CLO) and off gas. In this project, three types of Kuwaiti vacuum residue were used as feed stock for analysis which are Ratawi Burgan (RB), Eocene (EC), and Lower-Fars (LF). By utilising MATLAB software, the kinetic model is established and the parameters are estimated to be compared with the current data existed to ensure its validity.

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background of Study**

Cracking is a crucial process in refinery to produce a good quality and quantity of refined petroleum products that can be useful for further industrial consumption. Due to the increasing availability of heavy crude oil, this lead to an increase to the production of atmospheric and vacuum residue. This residue can be upgraded into different type of other useful petroleum products such as lighter hydrocarbon gas by thermal cracking. Instead of using hydrocracking which use catalytic reaction, heavy crude oil residue shows a negative effect to catalyst due to the impurities in the substance to poison the catalyst and render its effectiveness thus thermal cracking is more favorable. This project covers the kinetic modelling of thermal cracking of vacuum residues on eureka process that consist of two parts, which are kinetic modelling development and parameters identification.

There are many kinds of mathematical model that had been developed to identify the rate of kinetics for hydrocracking process of refining petroleum with conventional method. In this project, the focus is on the vacuum residue thermal cracking process of Eureka process. In the industry, Eureka process is claimed as environmentally friendly thermal cracking process proven to produce valuable cracked oil and aromatic petroleum pitch from heavy residual materials. The pitch itself is in liquid state which enables the refiners to keep the refinery plant cleaner and can be further used as feedstock for gasification process or power generation.

## 1.2 Problem Statement

There are several models that had been developed that has different kind of approach to present the kinetic modelling of thermal cracking of petroleum residue but not specifically for eureka process.

The kinetic modelling of a certain process depends on a few parameters and assumptions that enable researcher to develop a model that can explain the reaction kinetics for the process. Among popular method described in the literature is by lumping together a few type of products from the residue itself or a single lump of binary reaction.

A new kinetics model of thermal cracking on Eureka process is to be developed and the important constant parameters need to be identified. The pre exponential constant,  $A$  and activation energy,  $E_k$  will be estimated in order to produce reliable results to represent the thermal cracking in Eureka process at any condition in industry.

## 1.3 Objectives

- a. To develop a binary reaction kinetic model for thermal cracking of vacuum residue in Eureka process and validate with F. AlHumaidan, Haitham M.S. Lababidi, and Hassan Al-Rabiah (2013) works on Kuwaiti residues through Eureka Process.
- b. To estimate the kinetics constant included in the kinetic model by nonlinear parameter estimation.

## 1.4 Scope of Study

By using the available data from previous research on thermal cracking kinetics in Eureka process, a new kinetic modelling is to be developed accordingly and the important parameters will be identified. The thermal cracking kinetic modelling reaction usually distinguished by two common type of reaction which is monomolecular reaction and binary reaction.

In this project, the kinetic model developed using the binary reaction kinetic based on True Boiling Point (TBP) as basis using the data acquired from literature. The method of developing the kinetic model adopted the lumping method which enable us to develop a reliable model that represent the process with ease rather than indulge into much complexity by considering the reactions in the process in lumps.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Thermal cracking of vacuum residue**

According to AlHumaidan F., Lababidi H.M.S., and Al-Rabiah H. (2013), thermal cracking processes is more attractive for processing vacuum residues as compared to catalytic processes because the vacuum residue itself have high content of metals and asphaltene which will poison the catalyst thus affecting production yield. This is supported by Jasvinder S., Surendra K. and Madhukar O.G. (2012) that the presence of large amount of heavy molecules as well as high metals contents of residual feedstocks render this unsuitable for processes via catalytic routes thus thermal cracking is preferred for upgradation of crude oil residue. There are many thermal cracking processes that commonly used in the industry such as Delayed Coking, Fluid Coking, Flexi-coking, Visbreaking and Eureka.

#### **2.2 Eureka Process**

In contrast to other thermal cracking method, Eureka process designed to prevent oil from over cracking by continuously stripping the product resulting in high liquid yield and a low gas yield. The residual product is in the form pitch flowing out of reactor at reaction temperature which can later be utilized as fuel that contain higher heat of combustion than coal. Other advantage of Eureka process is the pitch is solidified in closed system reducing noise and dust which proven environmentally friendly (Ohba T et al., 2008). According to Hideki N., (2007), the products yield of

Eureka process in mass percentage are cracked gas 4%, cracked light oil (CLO) 20%, cracked heavy oil (CHO) 44%, and pitch 32%. The pitch is acquired in formed of liquid slurry that can be converted into high strength coke, boiler fuel and gasification feed.

### **2.3 Kinetic Modelling in Eureka Process**

To maximize the desired yield, predicting the product distribution in conversion process is essential to maximize the desired product yield. The prediction is normally achieved by utilizing a reliable kinetic model that can accurately anticipate the product yield at different operating conditions. The main problem occurred as to determine the exact chemical reaction involved in the conversion processes are very difficult. A simplified approach for modelling namely discrete lumping is normally adopted to overcome the model complexity (F. AlHumaidan et al., 2013).

Jia N. et al (2009) claimed that for an explicitly correct representation of hydrocarbon cracking, a large number of chemical species would be considered. Such a system would be impractical, as it would increase the calculation burden. Therefore, pseudo-components must be designed to simplify the whole calculation procedure.

The main advantage of the lumping technique are its easy computational implementation and small amount of data required for parameter estimation. The more lump, the better description, but increasing the number of lumps also increase the number of parameters to be estimated (Elizalde I., Rodríguez M.A and Ancheyta G., 2009).

Takatsuka T. et al. (1988) explained for design and control of residual thermal cracking process, there are a few key independent variables: reaction temperature, reaction pressure, residence time, residence time distribution, and feedstock. The variables must be investigated thoroughly as possible so the model can simulate any process in commercial use.

For accurate results, the kinetic model should take account all the elementary reactions which the different component in the feedstock undergo but it would be practically not possible to consider all the reactions in the reactor at molecular level. Hence, hydrocarbon mixture is lumped into fractions on the basis like carbon number and true boiling point (TBP). This will allow the kinetics of reactions determined in average at macro level of reactions. (Balasubramanian P. and Pushpavanam S., 2008).

AlHumaidan F. et al. (2013) had developed kinetic model that describes the thermal cracking reactions in Eureka process by using the discrete lumping approach assuming five discrete lump. The first lump represent total amount of crackable oil residue, while other four lump represent the cracked products that being stripped throughout the process produced at different temperature.

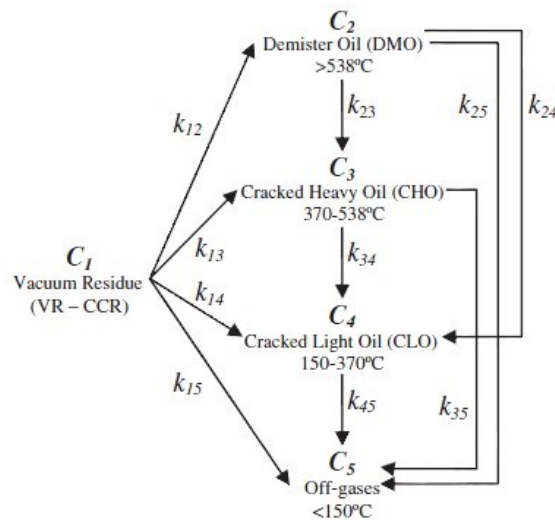


Figure 1: Five discrete lumping model by  
F. AlHumaidan et al., (2013)

According to AlHumaidan F., Lababidi H.M.S., and Al-Rabiah H. (2013), the result of from their kinetic model shown that the cracked oil and off-gases yields increase with residence time and temperature while the pitch yield decrease. This is also supported by Del Bianco A. et.al (1993) that found that the activation energy for cracked oil production are greater than the activation energy of gas formation which suggest higher tendency for cracked oil production as the temperature increases.

AlHumaidan F., Lababidi H.M.S., and Al-Rabiah H. (2013) had use the Kuwaiti vacuum residue in Eureka process in order to develop the kinetics modelling for the process. In this work, the data originated from the Kuwaiti vacuum residue also.

Takatsuka T. et al., (1988) claimed that very few practical models of residue thermal cracking have been published and most of them are rarely used in general. It is believe that very limited work reported about the Eureka process as it is unique as compared to other thermal cracking processes thus limiting the studies reported in this literature review.

## CHAPTER 3

### METHODOLOGY

#### 3.1 Methodology

This part explains on the methodology of the project. The methodology is described in the flow chart as below:

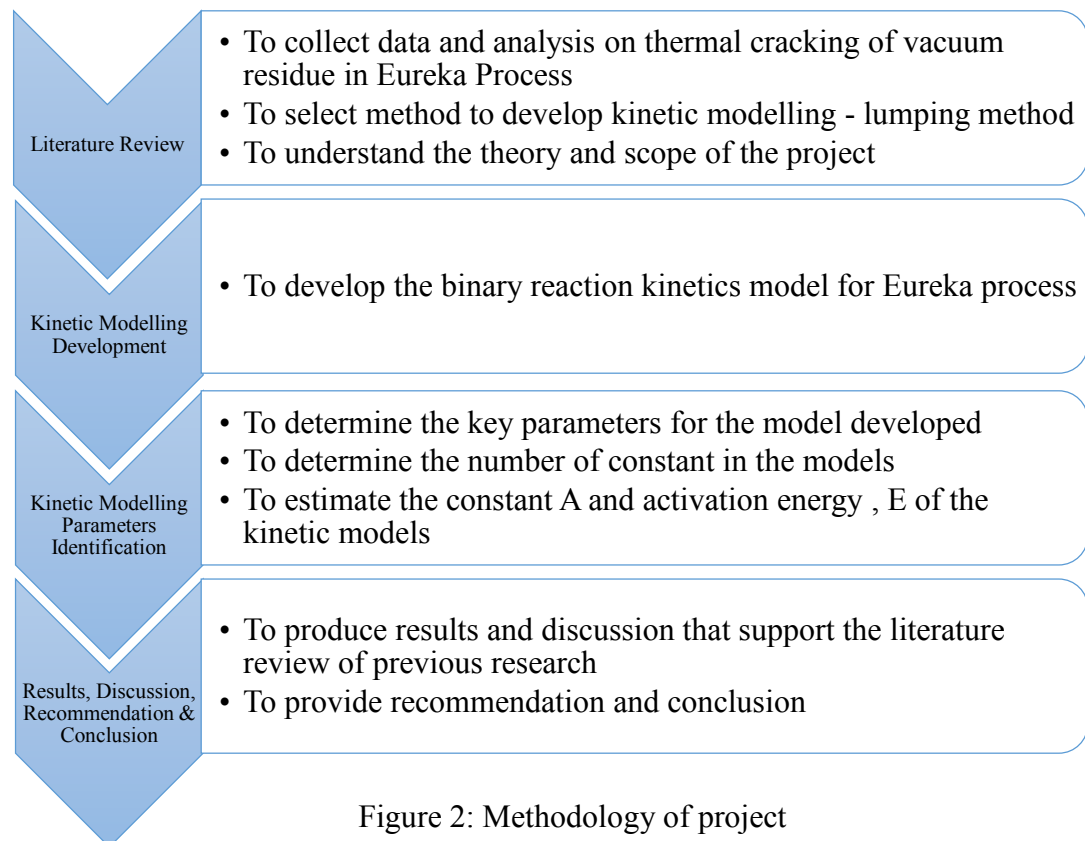


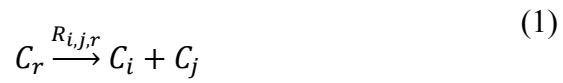
Figure 2: Methodology of project

The model is developed using MATLAB software that is available for analyzing high mathematical calculation. From the manual derivation set of equations of kinetic modelling, the model was further developed with the MATLAB. The results obtain are compared with the experimental data acquired in the literature review to ensure its validity.



### 3.2 Kinetic Modelling Development

#### 3.2.1 General Full Stoichiometry of Hydrocracking Reaction



$C_r$  : Molar Concentration of Component

$N_L$  : Number of Lumps

$r = 1$  to  $N_L$

$i, j = 1$  to  $r$

$R_{i,j}$  = Kinetic rate

$r \rightarrow i + j$

Assumption: The reaction are all first order irreversible reaction

In this project, the discrete lumps are defined according to its True Boiling Point (TBP) and 5 lumps are identified.

Table 1: Thermal Cracking of Residue (Lumps based on True Boiling Point)

Lump	Name	True Boiling Point
C <sub>5</sub>	VR-CCR (Feed Stock) – 3 types RB-VR, EC-VR, LF-VR	-
C <sub>4</sub>	Demister Oil (DMO)	T > 538 °C
C <sub>3</sub>	Crack Heavy Oil (CHO)	370 - 538 °C
C <sub>2</sub>	Cracked Lighter Oil (CLO)	150 – 370 °C
C <sub>1</sub>	Off Gas	T < 150 °C

There are two ways to classify lumps based on boiling point which are:

- a. Full Stoichiometry
- b. Reduced Stoichiometry

Number of Lump Combined: 5

Based on the Eq. 1, the kinetic constant of full stoichiometry is based on Eq. 2:

$$N_k = \frac{(2M + 1)(2M + 2)}{2} \text{ when } N_L \text{ is odd and } N_L = 2M + 1 \quad (2)$$

Thus,  $N_L=5$ ,  $2M=4$ , replace the value into Eq.2, and the number of kinetic constants,  $N_k$  are 15. Using the Arrhenius equation the activation energy of each reaction is calculated by assuming each lump has their own pre-exponential factor,  $A$ . Hence, the total parameters identified to develop the kinetic model is 20 parameters including five pre-exponential factor from each lumps.

### 3.2.2 Mathematical Presentation of Binary Reaction Kinetic for Full Stoichiometry Model

As per mentioned before the reaction kinetics of the model is based on first order irreversible reactions thus the molar concentration of hydrocarbon  $c_r$  in the lump  $r$  is governed by the following ordinary differential Eq. 3:

$$\frac{dC_r}{dr} = 2 \sum_{j=r}^{N_L} \sum_{i=1}^j \Omega(r, i, j) k_{r,i,j} C_j - \sum_{i=1}^r \sum_{j=1}^r \Omega(i, j, r) k_{i,j,r} C_r \quad (3)$$

The Kuwaiti vacuum residue data obtained is provided in the form of weight fraction of discrete lumps [6]. In order to relate with the data, the reaction kinetics need to substitute Eq. 4 becoming Eq. 5.

$$\omega_r = \left(\frac{M_r}{P_o}\right) C_r \quad (4)$$

$$\frac{d\omega_r}{dr} = 2 \sum_{j=r}^{N_L} \sum_{i=1}^j \delta_{r,i,j} \Omega(r, i, j) k_{r,i,j} N_j - \sum_{i=1}^r \sum_{j=1}^r \Omega(i, j, r) k_{i,j,r} \omega_r \quad (5)$$

$$\delta_{r,i,j} = \frac{M_r}{M_j} = \frac{r}{i + r}$$

$$k_{r,i,j} = k_{i,j,r}$$

After that, the weight fraction of each lumps is determine by analytical solution using Laplace Transform expressed by Eq. 6.

$$\omega_r = \sum_{m=r}^{N_L} D_{r,m} \exp[(\alpha_m - \beta_m)t] \quad (6)$$

When  $r \rightarrow N_L$

$$\alpha_m = 2 \sum_{j=1}^m \alpha_{m,j,m} \Omega(m, j, m) k_{i,j,m}$$

$$\beta_m = \sum_{i=1}^m \sum_{j=1}^m \Omega(i, j, m) k_{i,j,m}$$

$$D_{r,r} = \omega_{r,0} - \sum_{j=r+1}^{N_L} D_{r,j}$$

$$D_{r,m} = 2 \sum_{j=r+1}^m \sum_{i=1}^j \delta_{r,i,j} \Omega(r, i, j) k_{r,i,j} D_{j,m} / ((B_r - B_m) + (\alpha_m - \alpha_r))$$

$$D \rightarrow (N_L, N_L)$$

$$D_{1,1}$$

The parameter estimation is represented in the Eq. 7 with the objective function considered to minimize the residual sum of squares error (RSSE) between experimental data of Kuwaiti vacuum residue and the model calculated value.

### 3.2.3 Parameter Estimation

After the model data is verified with the experimental data, the kinetics parameters consist of pre exponential factor of each lumps and the activation energy can be estimated. . By using MATLAB software, the kinetic parameters for full stoichiometry model are estimated at three reaction temperature which are 673K, 688K, and 703K applying the Levenberg-Marquardt method using Dynamic Global and Local Combined Particle Swarm Optimization (DGLCPSO). The objective function considered in the parameter optimization is to minimize the residual sum of squares error (RSSE) between the experimental data and the model calculated values which is practiced before in the literature review. The mathematical expression is represented as:

$$f(k) = \sum_{i=1}^N \sum_{j=1}^{N_L} (w_{exp}(i, j) - w_{model}(i, j))^2$$

According to V. Kumar and P. Balasubramanian (2009), heuristic optimization methods such as genetic algorithm (GA), simulated annealing (SA) and particle swarm optimization (PSO) are based on empirical evolutionary rules that frequently mimic successful optimization strategies found in nature but it they does not determine the exact optimum solution because of the randomness and it gives a good approximation of the searched optimum solution. Thus, a combination of heuristic and gradient based optimization methods need to be use.

In this work, the method used is DGLCPSO which does the global search in the parameter space and determines the required global minimum. The latter algorithm (Levenberg-Marquardt) takes the global minimum determined from the heuristic method as initial guesses and does the necessary local search around the global minimum and determines the required optimal parameter values.

### 3.2.4 Full Stoichiometry Model

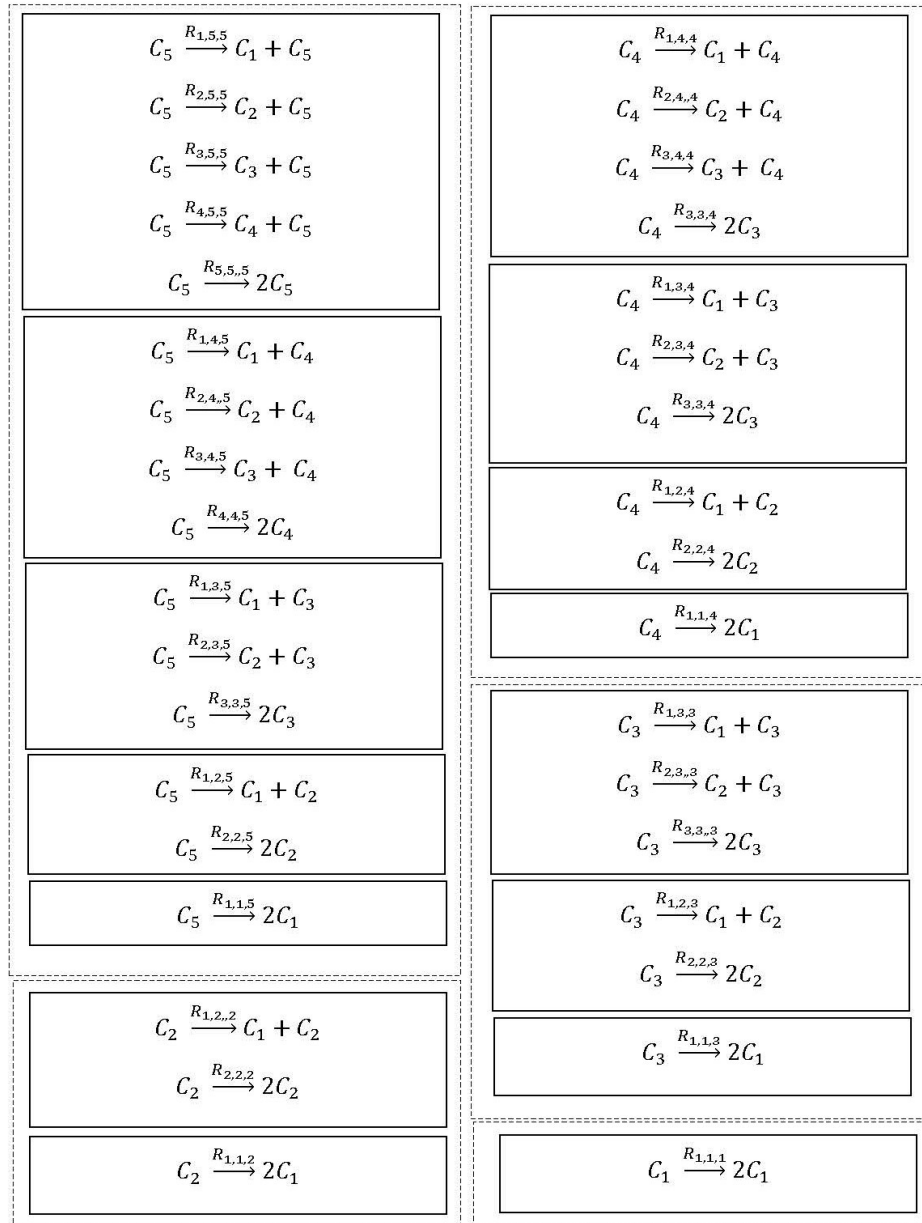


Figure 3: Full Stoichiometric Model

Full Stoichiometry Kinetic Constants Values

A = 5 (One family use same A value)

E= 15 (One group use same activation energy value)

Total parameters: 20

### 3.3 GANTT CHART AND KEY MILESTONES

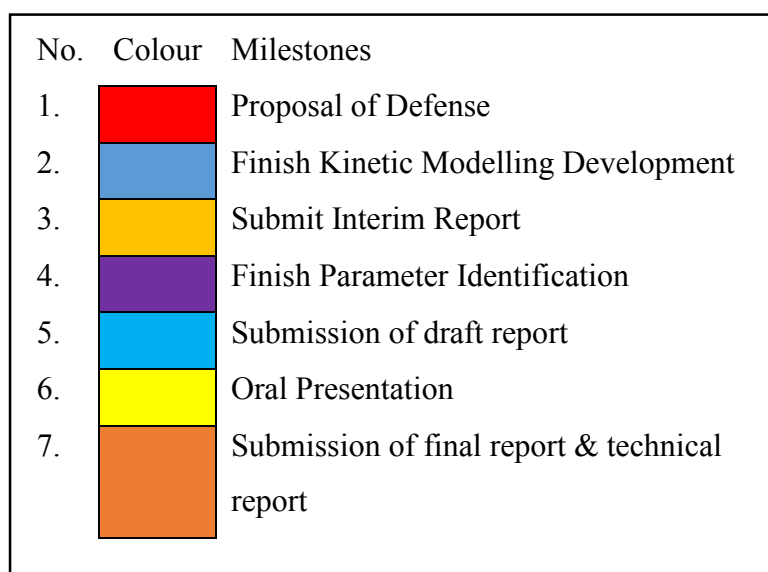
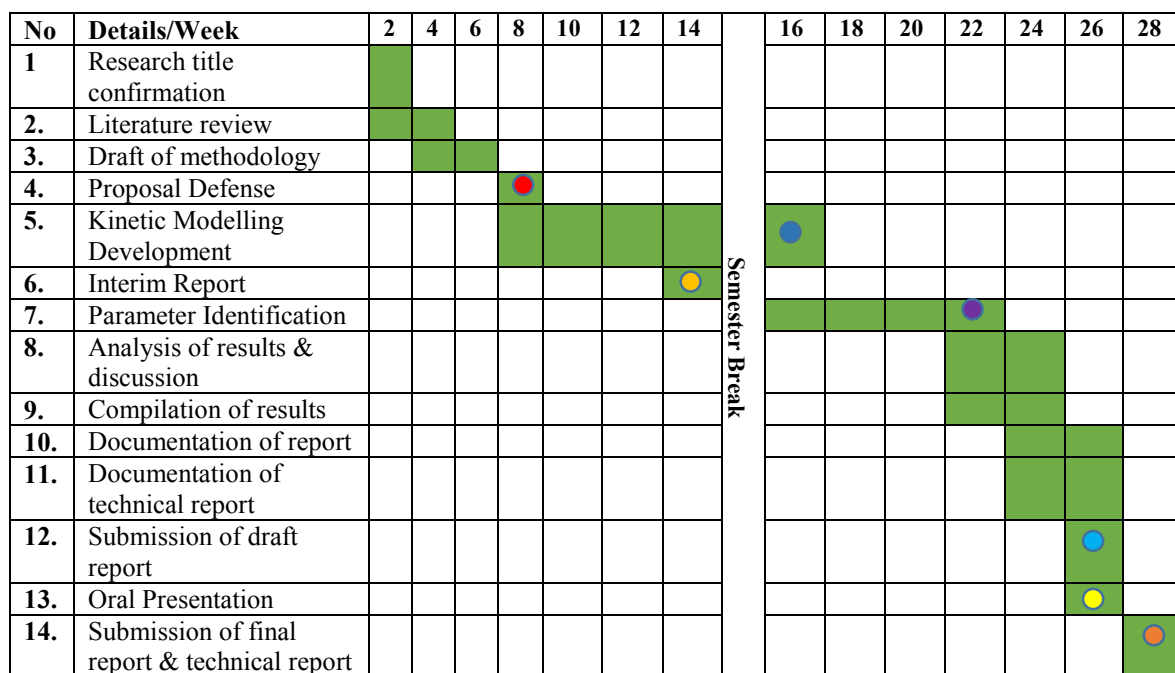


Figure 4: Project Gantt chart and key milestones

## CHAPTER 4

### RESULTS AND DISCUSSION

Using the MATLAB software, a series of programme had been executed to calculate the lump composition at the specified temperature and residence time based on the developed binary reaction kinetic model of Eureka Process. The results produced from the programme are compared with the current experimental data obtained from the literature review.

The data in Table 2 shows the Dynamic Global and Local Combined Particle Swarm Optimization (DGLCPSO) parameters were used in the MATLAB programmed.

Table 2 DGLCPSO parameters

Parameter	Value
Number of iterations	400
Number of particles	60
<i>a</i>	1
<i>b</i>	1
<i>c</i>	2
<i>w<sub>min</sub></i>	0.35
<i>w<sub>max</sub></i>	0.9

The results are tabulated as in Table 3 and the parity diagrams has been developed to show the differences between the experimental data and the model results. The model had been developed using the proposed thermal cracking model based on true boiling points (TBP), represented by the equations that involved in the analytical solution in the previous chapter.

The kinetics parameters estimated are also recorded in Table 3. The pre exponential value 'A', of each lumps according to Fig. 1 share the same value. Three Kuwaiti vacuum residue feedstock were used to compare the validity of kinetic model.

Table 3 Estimated kinetic parameters for thermal cracking of vacuum residues

Kinetic constant (h <sup>-1</sup> )	RB-VR		LF-VR		EC-VR	
	<i>A</i> (h <sup>-1</sup> )	<i>E</i> (J mol <sup>-1</sup> )	<i>A</i> (h <sup>-1</sup> )	<i>E</i> (J mol <sup>-1</sup> )	<i>A</i> (h <sup>-1</sup> )	<i>E</i> (kJ mol <sup>-1</sup> )
<i>k</i> <sub>1,1,1</sub>	6.145×10 <sup>14</sup>	230.70	3.948×10 <sup>14</sup>	239.19	2.762×10 <sup>14</sup>	289.03
<i>k</i> <sub>1,1,2</sub>	9.093×10 <sup>12</sup>	178.98	5.008×10 <sup>12</sup>	172.24	5.081×10 <sup>12</sup>	229.85
<i>k</i> <sub>1,2,2</sub>	9.093×10 <sup>12</sup>	230.48	5.008×10 <sup>12</sup>	221.18	5.081×10 <sup>12</sup>	169.36
<i>k</i> <sub>2,2,2</sub>	9.093×10 <sup>12</sup>	230.48	5.008×10 <sup>12</sup>	221.18	5.081×10 <sup>12</sup>	169.36
<i>k</i> <sub>1,1,3</sub>	5.758×10 <sup>12</sup>	187.33	3.887×10 <sup>12</sup>	207.02	4.056×10 <sup>12</sup>	181.78
<i>k</i> <sub>1,2,3</sub>	5.758×10 <sup>12</sup>	207.47	3.887×10 <sup>12</sup>	210.41	4.056×10 <sup>12</sup>	193.56
<i>k</i> <sub>2,2,3</sub>	5.758×10 <sup>12</sup>	207.47	3.887×10 <sup>12</sup>	210.41	4.056×10 <sup>12</sup>	193.56
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<i>k</i> <sub>2,3,3</sub>	5.758×10 <sup>12</sup>	203.78	3.887×10 <sup>12</sup>	212.36	4.056×10 <sup>12</sup>	182.72
<i>k</i> <sub>3,3,3</sub>	5.758×10 <sup>12</sup>	203.78	3.887×10 <sup>12</sup>	212.36	4.056×10 <sup>12</sup>	182.72
<i>k</i> <sub>1,1,4</sub>	1.912×10 <sup>12</sup>	225.81	5.453×10 <sup>12</sup>	239.69	6.606×10 <sup>12</sup>	182.95
<i>k</i> <sub>1,2,4</sub>	1.912×10 <sup>12</sup>	247.50	5.453×10 <sup>12</sup>	230.71	6.606×10 <sup>12</sup>	220.64
<i>k</i> <sub>2,2,4</sub>	1.912×10 <sup>12</sup>	247.50	5.453×10 <sup>12</sup>	230.71	6.606×10 <sup>12</sup>	220.64
<i>k</i> <sub>1,3,4</sub>	1.912×10 <sup>12</sup>	225.81	5.453×10 <sup>12</sup>	236.69	6.606×10 <sup>12</sup>	207.65
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<i>k</i> <sub>2,4,4</sub>	1.912×10 <sup>12</sup>	245.29	5.453×10 <sup>12</sup>	229.25	6.606×10 <sup>12</sup>	190.09
<i>k</i> <sub>3,4,4</sub>	1.912×10 <sup>12</sup>	245.29	5.453×10 <sup>12</sup>	229.25	6.606×10 <sup>12</sup>	190.09
<i>k</i> <sub>4,4,4</sub>	1.912×10 <sup>12</sup>	245.29	5.453×10 <sup>12</sup>	229.25	6.606×10 <sup>12</sup>	190.09
<i>k</i> <sub>1,1,5</sub>	1.550×10 <sup>13</sup>	163.33	9.242×10 <sup>12</sup>	158.66	7.201×10 <sup>12</sup>	171.02
<i>k</i> <sub>1,2,5</sub>	1.550×10 <sup>13</sup>	159.50	9.242×10 <sup>12</sup>	156.68	7.201×10 <sup>12</sup>	154.82
<i>k</i> <sub>2,2,5</sub>	1.550×10 <sup>13</sup>	159.50	9.242×10 <sup>12</sup>	156.68	7.201×10 <sup>12</sup>	154.82
<i>k</i> <sub>1,3,5</sub>	1.550×10 <sup>13</sup>	165.39	9.242×10 <sup>12</sup>	162.90	7.201×10 <sup>12</sup>	161.57
<i>k</i> <sub>2,3,5</sub>	1.550×10 <sup>13</sup>	165.39	9.242×10 <sup>12</sup>	162.90	7.201×10 <sup>12</sup>	161.57
<i>k</i> <sub>3,3,5</sub>	1.550×10 <sup>13</sup>	165.39	9.242×10 <sup>12</sup>	162.90	7.201×10 <sup>12</sup>	161.57
<i>k</i> <sub>1,4,5</sub>	1.550×10 <sup>13</sup>	246.01	9.242×10 <sup>12</sup>	241.30	7.201×10 <sup>12</sup>	242.42
<i>k</i> <sub>2,4,5</sub>	1.550×10 <sup>13</sup>	246.01	9.242×10 <sup>12</sup>	241.30	7.201×10 <sup>12</sup>	242.42
<i>k</i> <sub>3,4,5</sub>	1.550×10 <sup>13</sup>	246.01	9.242×10 <sup>12</sup>	241.30	7.201×10 <sup>12</sup>	242.42
<i>k</i> <sub>4,4,5</sub>	1.550×10 <sup>13</sup>	246.01	9.242×10 <sup>12</sup>	241.30	7.201×10 <sup>12</sup>	242.42
<i>k</i> <sub>1,5,5</sub>	1.550×10 <sup>13</sup>	177.42	9.2423×10 <sup>12</sup>	170.83	7.201×10 <sup>12</sup>	173.72
<i>k</i> <sub>2,5,5</sub>	1.550×10 <sup>13</sup>	177.42	9.2423×10 <sup>12</sup>	170.83	7.201×10 <sup>12</sup>	173.72
<i>k</i> <sub>3,5,5</sub>	1.550×10 <sup>13</sup>	177.42	9.2423×10 <sup>12</sup>	170.83	7.201×10 <sup>12</sup>	173.72
<i>k</i> <sub>4,5,5</sub>	1.550×10 <sup>13</sup>	177.42	9.2423×10 <sup>12</sup>	170.83	7.201×10 <sup>12</sup>	173.72
<i>k</i> <sub>5,5,5</sub>	1.550×10 <sup>13</sup>	177.42	9.2423×10 <sup>12</sup>	170.83	7.201×10 <sup>12</sup>	173.72
RSSE	9.631×10 <sup>-7</sup>		6.649×10 <sup>-4</sup>		1.254×10 <sup>-3</sup>	
<i>F</i> -value	7.118×10 <sup>6</sup>		8569		5050.4	
Time (s)	266.0		269.1		280.1	



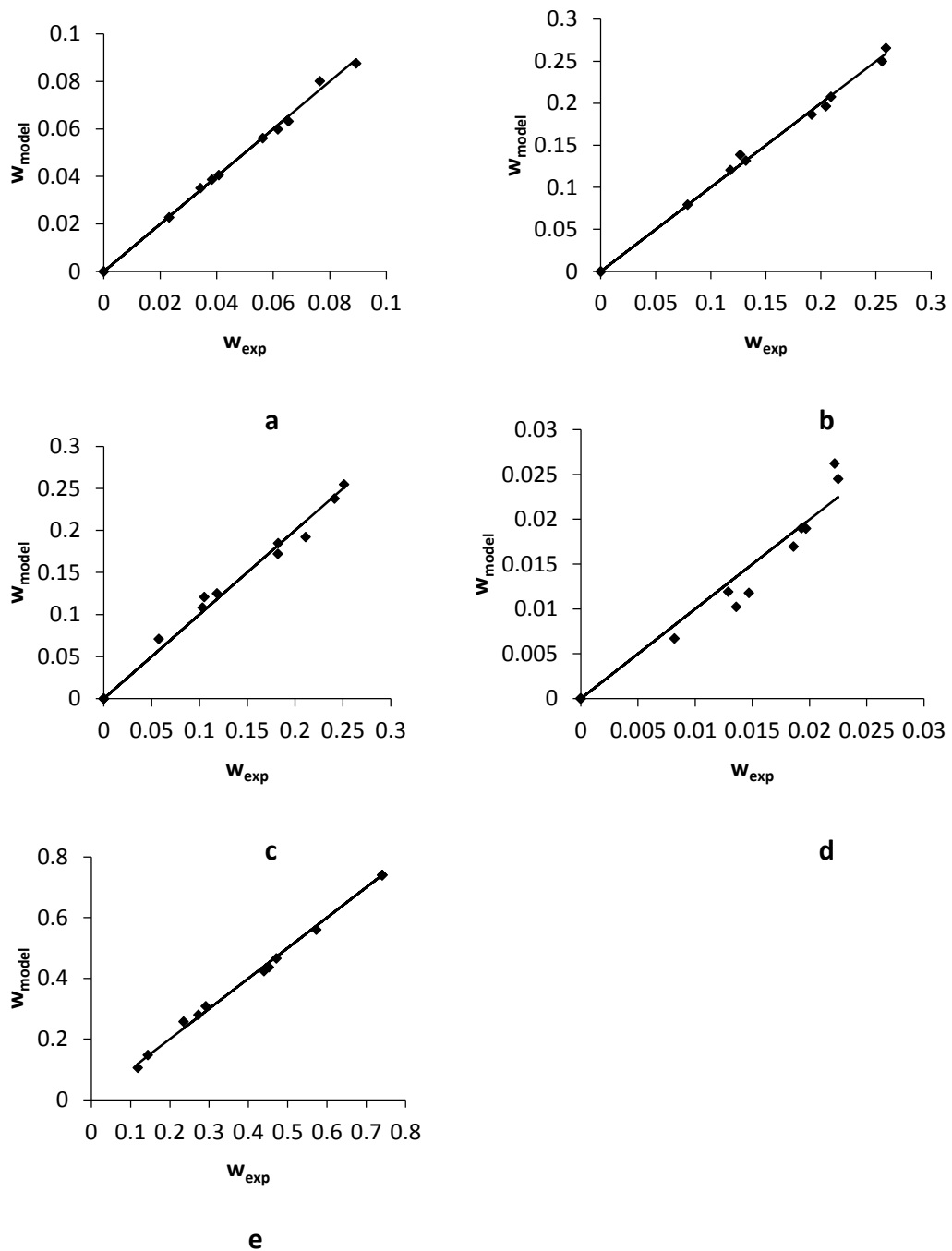


Figure 5. Parity diagram for thermal cracking of RB-VR. (a) off-gases, (b) cracked light oil, (c) cracked heavy oil, (d) demister oil, and (e) VR-CCR.

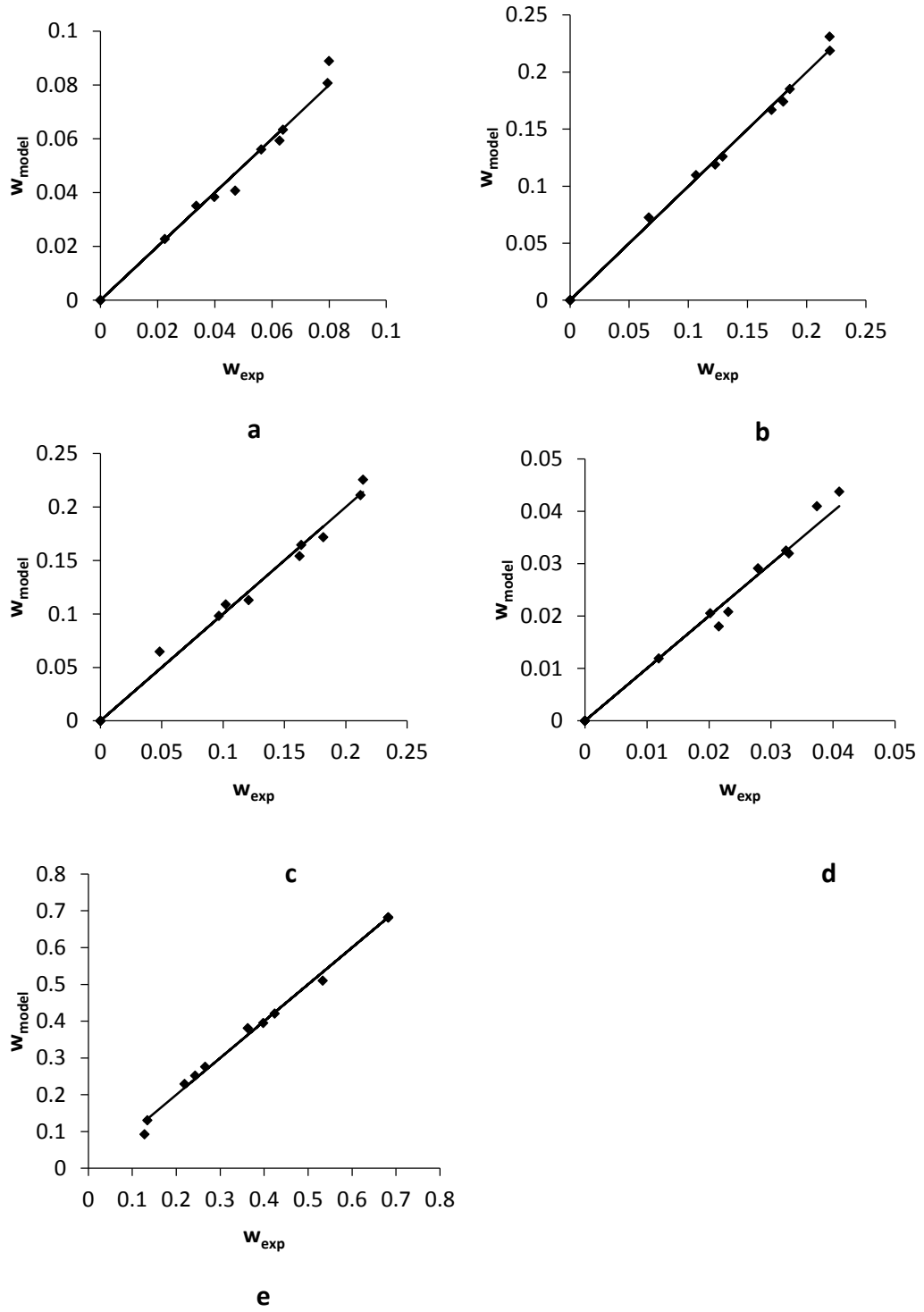


Figure 6. Parity diagram for thermal cracking of LF-VR. (a) off-gases, (b) cracked light oil, (c) cracked heavy oil, (d) demister oil, and (e) VR-CCR.

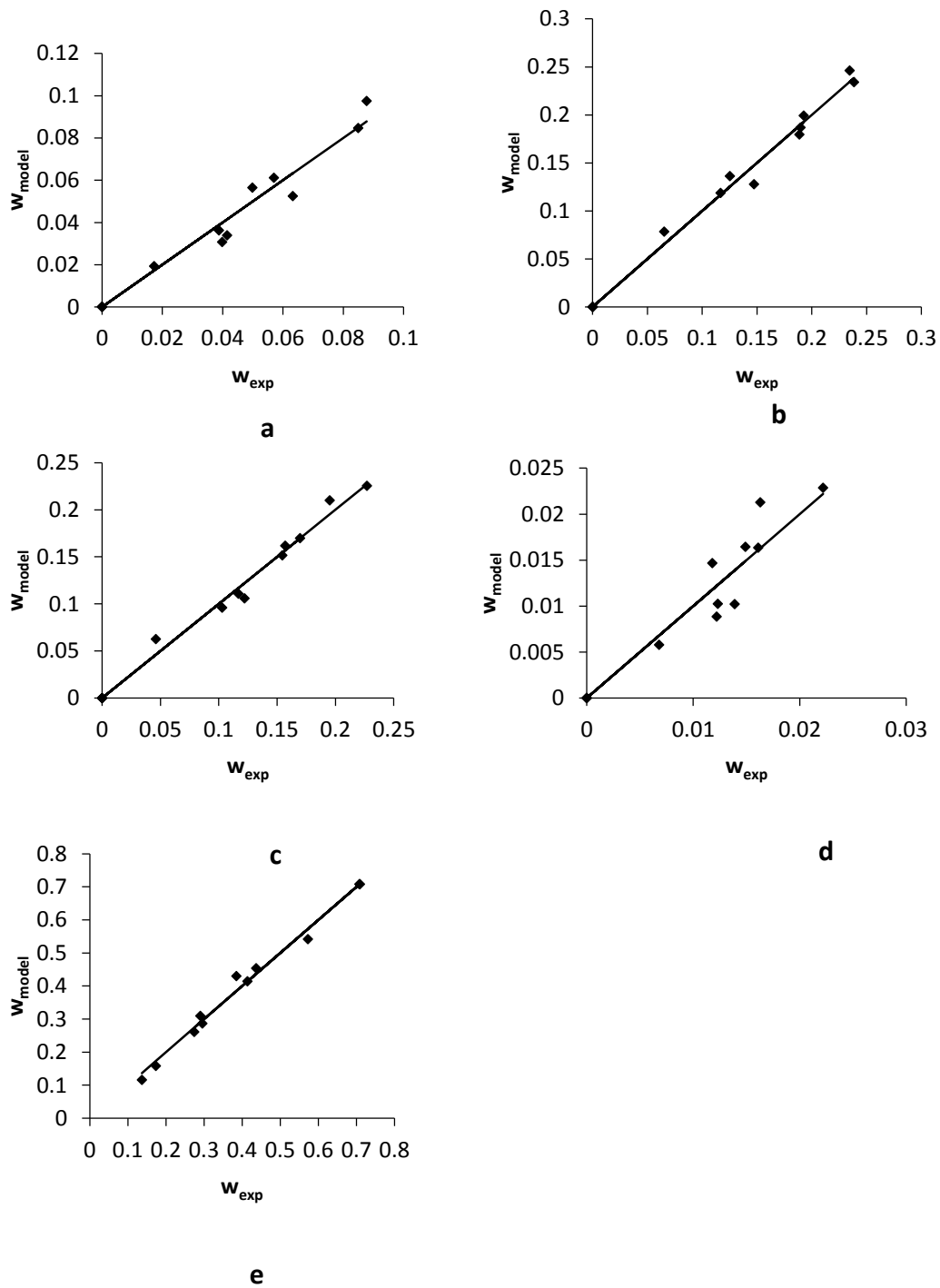


Figure 7. Parity diagram for thermal cracking of EC-VR. (a) off-gases, (b) cracked light oil, (c) cracked heavy oil, (d) demister oil, and (e) VR-CCR.

The kinetics parameters estimated are recorded in Table 2 and the parity diagram are shown to compare the model data  $w_{model}$  with experimental data  $w_{exp}$  from F. AlHumaidan et al. for each feedstock from the Kuwaiti Vacuum Residue which are Ratawi-Burgan (RB-VR), Lower-Fars (LF-VR) and Eocene (EC-VR). The parity diagram represent the whether the model is valid to be applied for Eureka Process.

From the parity diagram, all the lumps correspond each other quite the same with the experimental data but for demister oil (Lump 4,  $C_4$ ), the data show some discrepancy significantly for EC-VR feedstock compared to others. The most compatible data for  $C_4$  is LF-VR followed by RB-VR and the least one as mentioned previously, EC-VR. It is recognized that RB-VR is conventional crude oil with 27 API gravity, while EC-VR and LF-VR are heavy crude oil with API gravity of 18 and 16 respectively. Although LF-VR is heavier but the composition of asphaltene is higher in EC-VR from 15.82 wt% in LF-R compared to EC-VR with 15.98 wt% would contribute to higher carbon number in the lump hence higher hydrogen carbon (H/C) ratio. According to AlHumaidan F. et al. during the Saturate, Aromatic, Resin and Asphaltene (SARA) Analysis although the cracked oil has negligible amount of asphaltene but the SARA fraction might be affected the blending compatibility thus providing less accurate data.

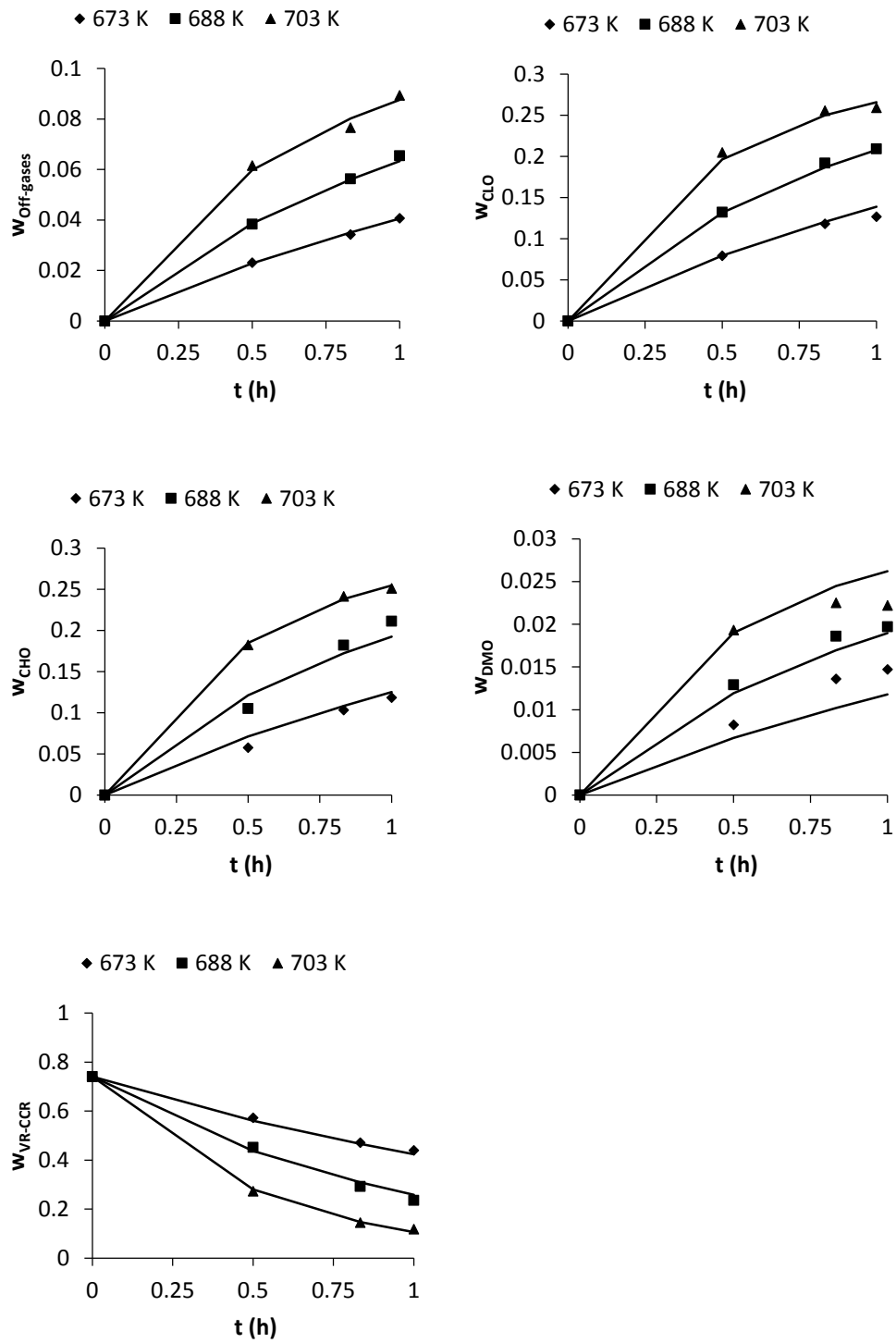


Figure 8. Weight fraction of lumps versus time plots for thermal cracking of RB-VR at different temperatures. Symbol: experimental data and solid line: model calculated data.

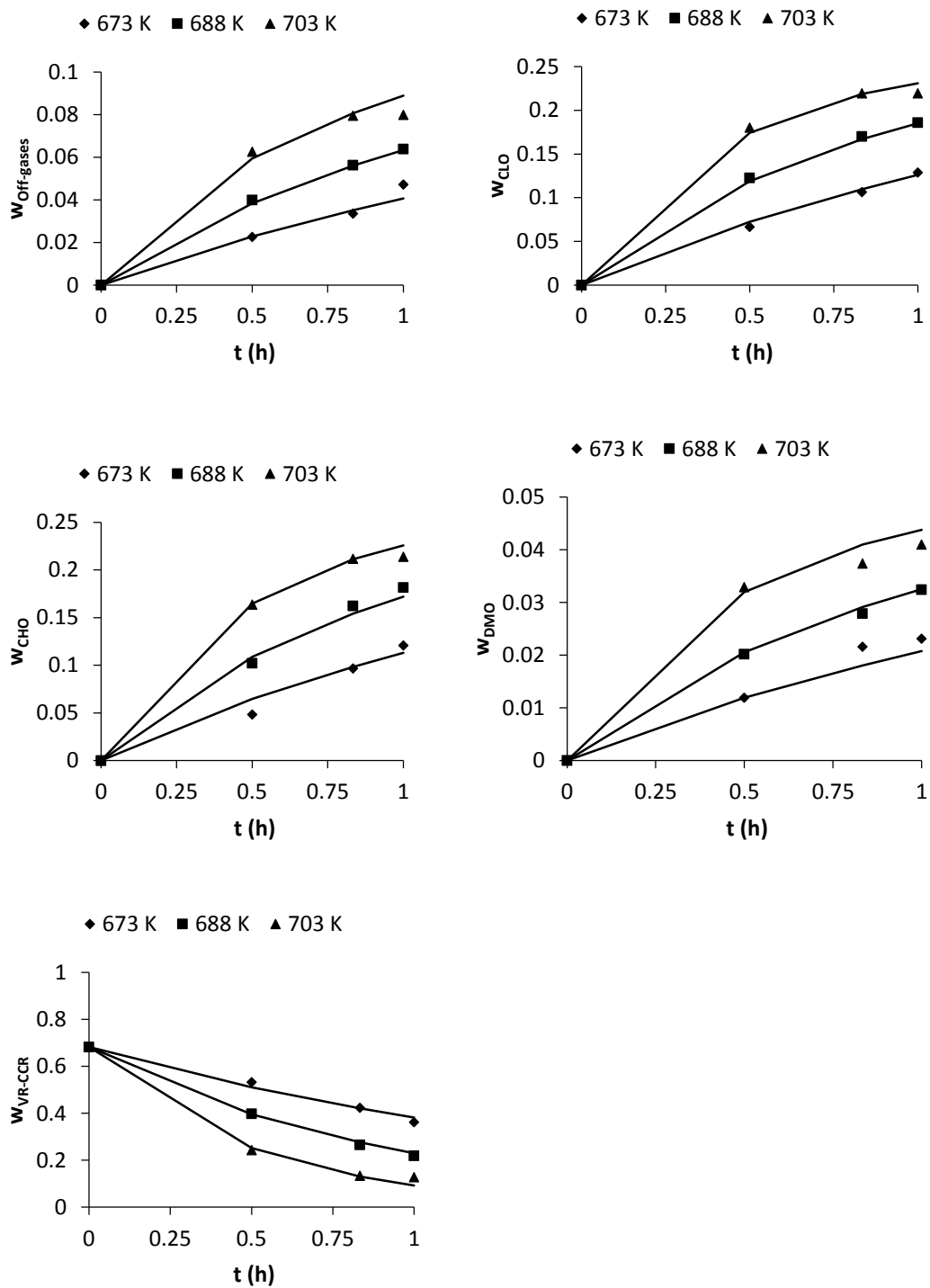


Figure 9. Weight fraction of lumps versus time plots for thermal cracking of LF-VR at different temperatures. Symbol: experimental data and solid line: model calculated data.

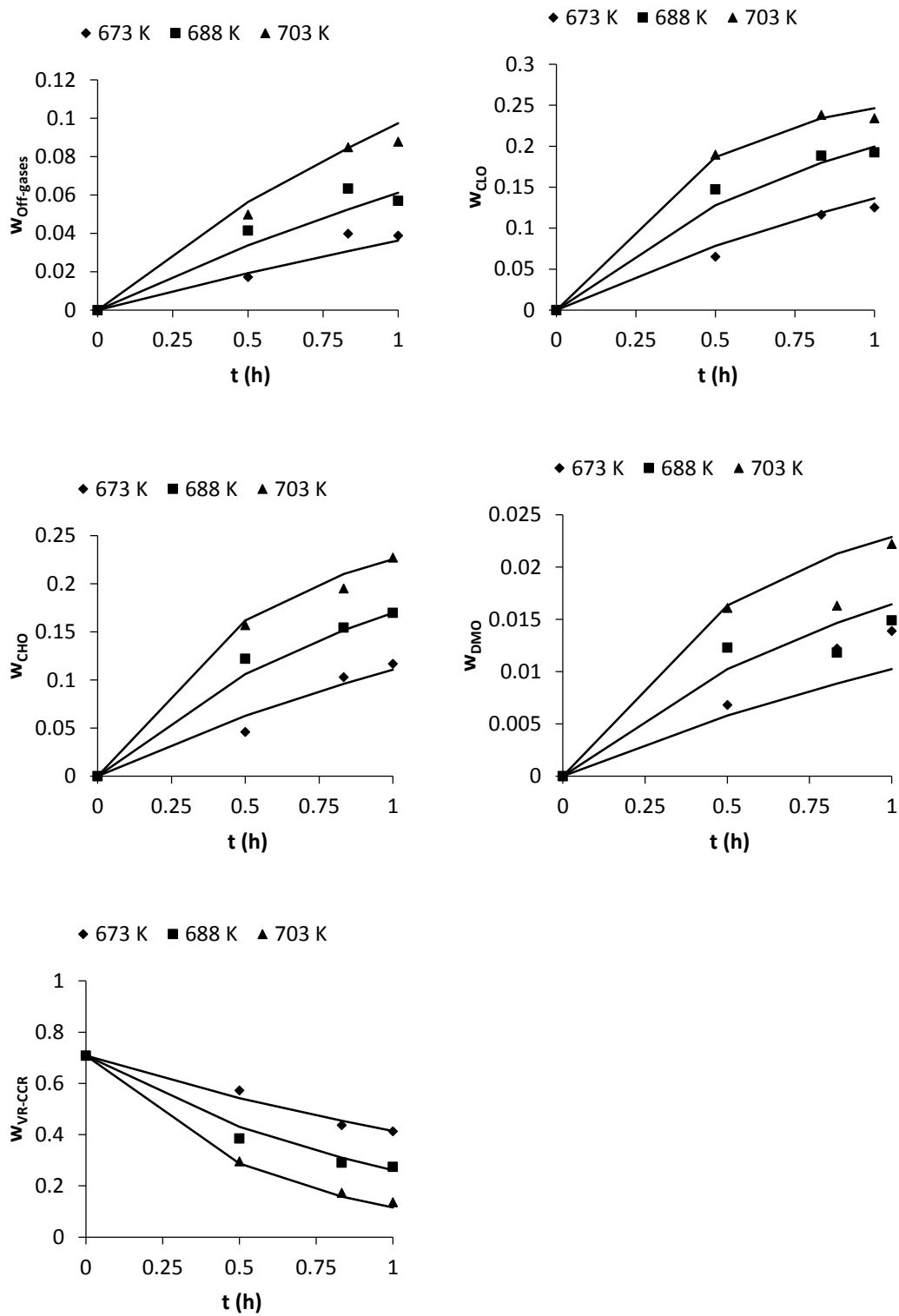


Figure 10. Weight fraction of lumps versus time plots for thermal cracking of EC-VR at different temperatures. Symbol: experimental data and solid line: model calculated data.

Based on the temperature versus weight fraction, the graph Fig. 8 to Fig. 10 generally shows that the cracked oil and off-gases yield is increasing as temperature and residence time increased. The result is expected and should follow the same rule as in literature claimed by F. AlHumaidan et al (2013). The novelty of Eureka Process itself which is stripping the products continuously hinder overcracking thus increase the cracked oil yield.

From Table 3, the activation energy of RB-VR, LF-VR and EC-VR are 177.42kJ/mol, 170.83kJ/mol, 173.72kJ/mol, respectively thus agree to the literature from F. AlHumaidan et.al (2013) that indicated the activation energy is in the range of 100-268kJ/mol or 24-64kcal/mol. Each feedstock has different reactivity due to its composition and attributed to the structural difference that occur between them. In addition, Fig. 4 shows the yield rate of the desired cracked oil, (b) cracked light oil and (c) cracked heavy oil are higher than the yield rate of (a) off-gases.

Based on overall observation, the parity diagram and graph plots are a good representation of the kinetic model performance for Eureka Process although there are some discrepancies occurred but it relate to accuracy of experimental data itself. As for the Residual Sum Square of Error (RSSE) of the model calculated is  $9.631 \times 10^{-7}$  for RB-VR,  $6.649 \times 10^{-4}$  for LF-VR, and  $1.254 \times 10^{-3}$  for EC-Vr indeed reflects that the kinetic model is reliable to demonstrate the Eureka Process reaction kinetics.



## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATION**

#### **5.1 Conclusion**

Thermal cracking of Eureka process is a very unique process which rarely being put attention before thus causing limited information to gather and analyze. Nevertheless, this project succeed to represent the Eureka Process accordingly with accurate prediction of kinetic parameters.

#### **5.2 Recommendation**

Further research on Eureka Process such as developing kinetic modelling of thermal cracking would absolutely being a helpful reference for its future research and operation optimization. To support this project validity, it is encourage for new set of data to be analyse and compared with the current model. This would strongly support the model to represent Eureka Process better for industrial needs.

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