Application of Flow Graph Theory Approach for the Solution of Discrete Lumped Kinetic Equation in Hydrocracking of Heavy Oils

by

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13398

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

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CERTIFICATION OF APPROVAL

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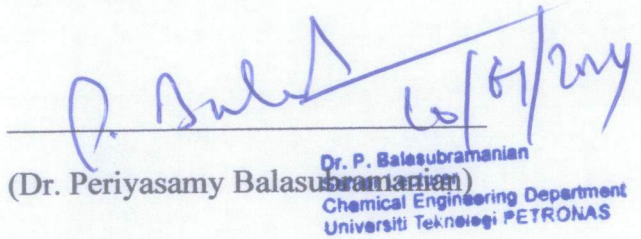
Approved by,



(Dr. Periyasamy Balasubramanian)

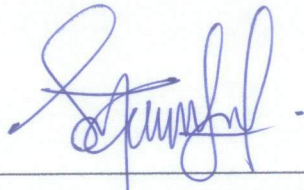
UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2013

CERTIFICATE 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.



(Syamsul Syahiran Bin Mohamad)

ABSTRACT

This report is the final manifestation of Final Year Project aimed to find the solution of discrete lumped kinetic equation in hydrocracking of heavy oils by using flow graph theory approach. This report details the practicability of applying flow graph theory approach in finding the exact solution for kinetic equations of complex reaction systems such as discrete lumped model in heavy oils hydrocracking. Flow graph theory approach is a method that can be used to determine exact solution if first order linear differential equations through using Cramer's method of determinants. The kinetic model developed for the heavy oil hydrocracking process was based on wide range of true boiling point of the hydrocarbon and the reaction which involves reactant lump is also considered. A general exact solution of the discrete lumped model for hydrocracking of heavy oils is derived using flow graph approach and the final result is consistent with the reported solution available in the literature through Laplace transforms.

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful. Praise to Him the Almighty that in His will and given strength, the final year project (FYP) is successfully completed within the allocated eight months period. Upon completing the project undertaking, the author owes a great thanks to a great many people for their help and support during the period.

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CHAPTER 1 INTRODUCTIONS

1.1 Background Study

Heavy oils are petroleum oils that are highly viscous and have specific gravity which is higher than that of light petroleum oils. They are categorized as dense nonaqueous phase liquids and has low solubility as well as viscosity and density lower than that of water. In petroleum industries, heavy oils play a major role in the economics of the business as it can be break down into more commercially valuable products such as gasoline, kerosene, jet fuel and diesel oil. Moreover, heavy oil fields are often more relatively shallow hence may contribute to lower production costs. However, the offset are that the extraction and recovery of heavy oils are much more difficult and more costly. This is due to the nature of the oil that has high density and thus requiring special techniques and technology. Not to mention the refining of heavy oils also incur increased costs due to desulfurization and demetallization needed. Despite the costs and technical disadvantage, heavy oil resources in the world are more than twice those of conventional light oils, making its production a very interesting topic indeed in petroleum industries.

Hydrocracking is catalytic chemical process which involves the breakdown of high molecular compound in heavy oils to much lighter compound products that are economically more valuable. It is usually carried out in high hydrogen atmosphere and involves desulfurization and often demetallizaation of the heavy oils. Hydrocracking technology was first developed from as early as 1915 and the first literature to have complete review on this technology may possibly be as early as 1975 by *Choudhary and Saraf (1975)* which discussed on types of hydrocracking, catalysts, effects of feed and more. Hydrocracking technology literatures are not as publicly available as one expect would be despite its wide industries. This is because companies took a great effort in ensuring their trade secrets and safeguard their patents very well. Designing of a hydrocracker reactor and its process route requires extensive experimental data and industrial experience. One such way the designing may also be done is through kinetic modeling.

1.2 Problem Statement

Kinetic modeling of heavy oils hydrocracking is a very complex and arduous process due to the huge number of hydrocarbons involved. From the detailed knowledge of each respective reaction, it may give a mechanistic description of the overall hydrocracking process. The actual application of this method to real feeds is difficult due to several analytical complexity and limitations in computations. This is because as more compounds are included in the model, the more kinetic parameters that need to be estimated. Hence, one such way to simplify the problem is through separating the species into several equivalent classes, better known as the lumping technique. The aim of this study is to apply flow graph theory approach in finding solution for discrete lumped kinetic equation in heavy oils hydrocracking.

1.3 Objective

The objective of this paper is to apply flow graph theory approach for the solution of discrete lumped kinetic equation in hydrocracking of heavy oils.

CHAPTER 2 LITERATURE REVIEW

2.1 Hydrocracking of Heavy Oils

Hydrocracking of heavy oils is an important catalytic chemical process applied in petroleum refineries to treat oil residua. Its primary purpose is of breaking down high-molecular compound hydrocarbon in petroleum crude oils to more useful low molecular compound products such as gasoline, kerosene and diesel oil. The cracking process is usually carried out in hydrogen-rich atmosphere at 260-425 °C and pressure about 35-200 bar (Scherzer & Gruia, 1996). The process basically converts the high molecular weight heavy oils into lower molecular weight olefins and aromatic hydrocarbons where they are then hydrogenated. Any sulfur and nitrogen present are also hydrogenated and removed resulting in products that are free from them.

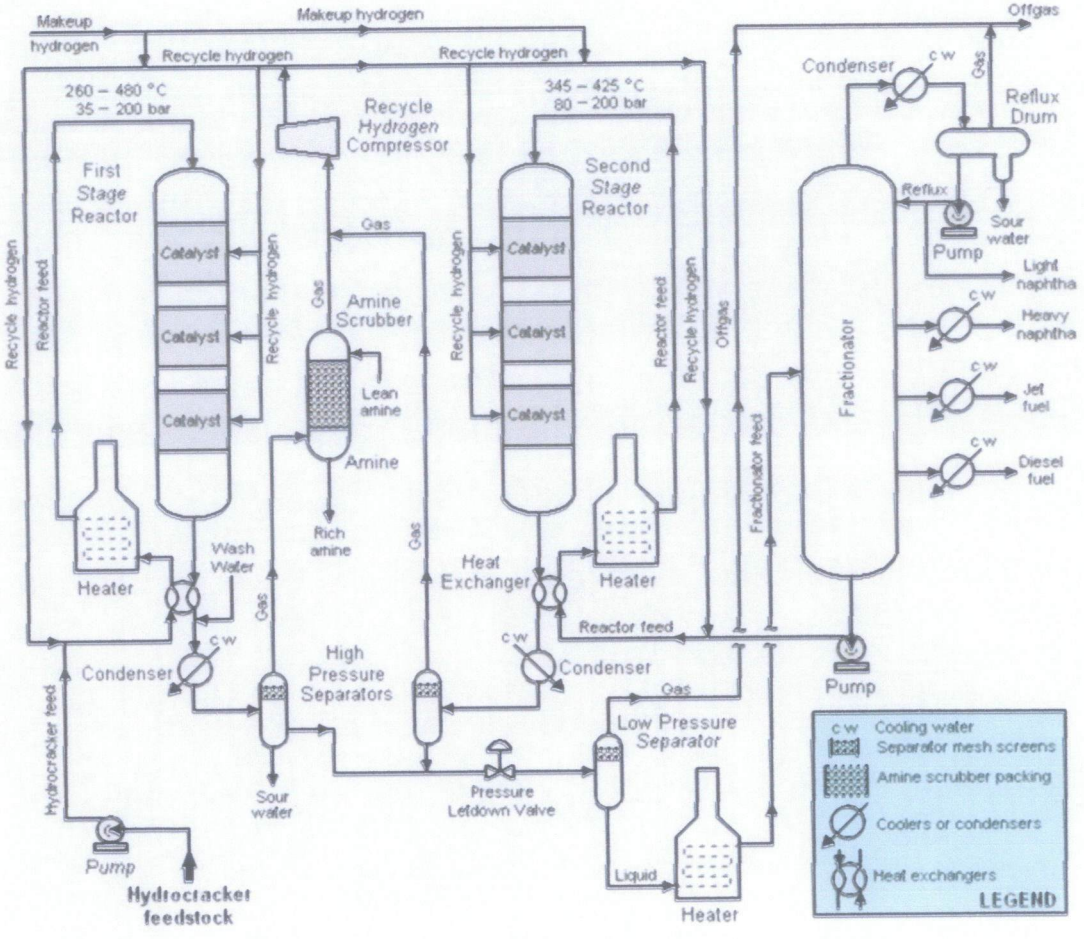


Figure 1: General Schematic Flow Diagram for Hydrocracking

Increasing demand for supply of middle distillates and increased production of heavy oils has made hydrocracking as a very important and significant secondary petroleum refinery process. The rates and selectivity of the cracking process depends heavily on the type of catalysts being used and on reaction severity, where most industrial processes utilized catalysts with both hydrogenation and acid functions.

There have been numerous technologies developed and patented for upgrading of heavy oils. Commercial processes mainly use two type of reactors namely fixed trickle-bed reactor (TBR) and ebullated bed reactor (EBR) (Choudhary & Saraf, 1975). Design and specifications of these reactors are relatively more complicated than that of ordinary fixed-bed gas reactor and are not readily available in public literature. The designs are often done with supports from experimental and industrial experiences. Another method to perform the design may be through the method of kinetic and reactor modeling where it is also useful for process simulations and optimization (Wei & Kuo, 1969).

2.2 Discrete Lumping

There has been much literature on the kinetic modeling of the hydrocracking process for heavy oils. One such important literature reported is of models based on pseudocomponents or known as discrete lumping (Krishna and Saxena, 1989). The models are made up of seven lumps in which different cut temperatures are considered where the pseudocomponents are regarded as light if it is formed from fractions with boiling points lower than cut temperatures. Experimental data are used to test the model and comparisons between predicted results and actual experimental data made.

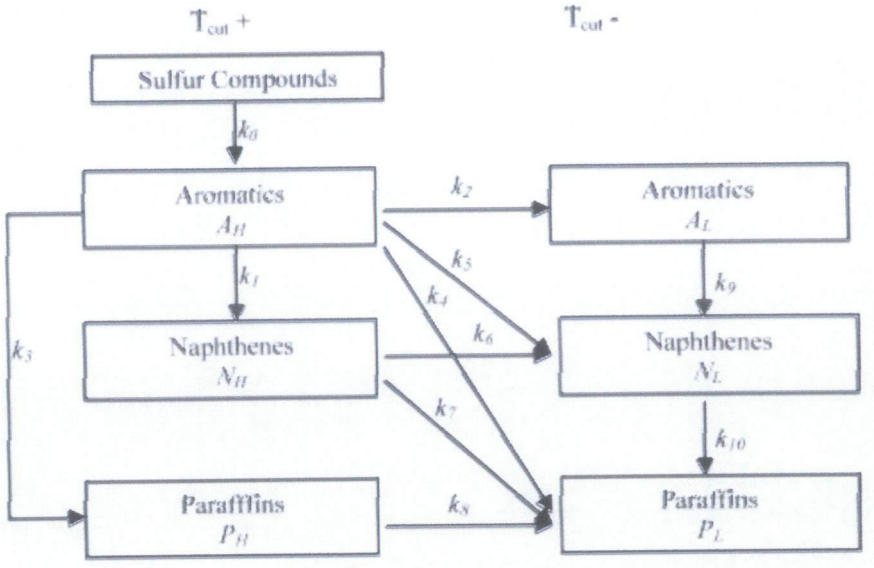


Figure 2. Detailed lumping reaction scheme for hydrocracking
Krisnhna and Saxena (1989)

Table 1. First Order Rate contants for the reaction network.

Kinetic constants (h^{-1})	T_{cut} (°C)					
	371	225	191	149	82	0
k_0	8.3000	–	–	–	–	–
k_1	1.2633	0.4943	0.4799	0.4624	0.4345	0.4000
k_2	0.6042	0.1809	0.1105	0.0397	0.0034	0.0000
k_3	0.0421	0.3131	0.2719	0.2593	0.2501	0.2302
k_4	0.5309	0.0211	0.0096	0.0095	0.0095	0.0095
k_5	0.0397	0.0383	0.0249	0.0131	0.0086	0.0000
k_6	1.1855	0.2772	0.2134	0.1117	0.0073	0.0000
k_7	0.1619	0.0474	0.0275	0.0275	0.0275	0.0275
k_8	0.4070	0.2391	0.1993	0.1518	0.0978	0.0299
k_9	0.2909	0.5434	0.5219	0.4509	0.4391	–
k_{10}	0.0818	0.0740	0.0709	0.0618	0.0608	–

From the models, Krishna and Saxena (1989) further proposed empirical correlations to predict value of decay rate for T50 with respect to residence time and also Peclet number. Moreover, Stangeland (1974) developed kinetic model for predicting hydrocracker yields using correlations based on boling points of each of pseudocomponents that characterize the cut.

Equations of the kinetic model for hydrocracking based on TBP of pseudocomponents

Model proposed by Stangeland [22]

$\frac{d}{dt}F_i(t) = -k_iF_i(t) + \sum_{j=1}^{i-1}P_{ij}k_jF_j(t)$	Mass balance
$k(T) = k_0[T + A(T^3 - T)]$	Cracking rate constant function
$PC_{ij} = [y_{ij}^2 + B(y_{ij}^3 - y_{ij}^2)](1 - [C_4]_j)$	Liquid product distribution function
$[C_4]_j = C\exp[-0.00693(1.8\,\mathrm{TBP}_j - 229.5)]$	Weight fraction of butane
$y_{ij} = \frac{\mathrm{TBP}_i - 2.5}{(\mathrm{TBP}_j - 50) - 2.5}$	Normalized boiling point temperature (TBP)
$P_{ij} = PC_{ij} - PC_{i-1,j}$	Actual fraction of lighter component

Model modified by Dassori and Pacheco [24]

$\sum_{i=1}^{j-2}P_{i,j}\mathrm{MW}_i = (\mathrm{MW}_j - n_j\mathrm{MW}_{H_2})$	Mass balance for each individual reaction
$PC_{ij} = [y_{ij}^2 + B_1y_{ij}^3 - B_2y_{ij}^2](1 - [C_4]_j)$	Modified product distribution function (with B_2)
$[C_4]_j = C\exp[-\omega(1.8\mathrm{TBP}_j - 229.5)]$	Modified weight fraction of butane (with ω)

Figure 3 Equations of the kinetic model for Hydrocracking based on TBP of pseudocomponents

There are several major disadvantages in this approach; the change in specifications of hydrocracker product, or in the number of products, requires the model to be reformulated and the data to be refitted. Another work (Mohanty et al., 1991) attemps Stangeland's kinetic model in a computer model for two stage commercial scale vacuum gas oil (VGO) hydrocracker. Estimation of the hydrocracking kinetic constants for the pseudocomponents are then done through following relationships:

$$k_i(T) = k_{365}K_i$$

Where K was adjusted with plant data using following relations:

$$K_i = 0.494 + 0.52 \times 10^{-2}\,\mathrm{TBP}_i - 2.185 \times 10^{-5}\,\mathrm{TBP}_i^2 + 0.312 \times 10^{-7}\,\mathrm{TBP}_i^3$$

The results of the findings which are calculated yields, hydrogen consumption, and outlet temperatures are obtained and comparisons with industrial data shows proper agreement.

Table 2. Comparisons of calculated and plant data.

Comparison of calculated and plant data obtained by Mohanty et al. [23]

Data	Calculated results	Plant data	Error (%)
Total feed to second stage (kg/h)	183, 236	183, 385	−0.08
Hydrogen consumption (kg/h)			
First stage	2816	3267	−13.8
Second stage	1196	1363	−12.2
Reactor outlet temperature (°C)			
First stage	693.3	714 (max)	–
Second stage	677.7	700 (max)	–
High speed diesel (wt.%)	48.79	50.5	−3.46
Aviation turbine fuel (wt.%)	30.53	29.4	3.83
Naphtha (wt.%)	16.17	15.8	2.51
Butanes and lights (wt.%)	4.51	4.5	0.22

2.3 Flow Graph Theory

Flow graph method in chemical kinetics represents the image of reaction stoichiometry. The analytical solution for reactor performance which is governed by linear ordinary differential equations can be represented as the sum of constants multiplied with the time dependent exponential function. With respect to flow graph theory, the constants are the ratio of determinants of formation and consumption flow graphs where Cramer's method of determinants can be applied to determine the analytical solution of the first order monomolecular reaction system (Balasubramanian & Syakilla, 2013).

In chemical kinetics, the nodes in a flow graph are representing a component that is undergoing chemical transformation. The line segment joining two nodes is called an Edge and the weighting of the edge is the real gain between each node and represents the kinetic constants for a reaction. Input and output nodes are the reactant and products, respectively where else mixed node is a node which has both outgoing and incoming edges. Mixed nodes are usually the intermediate products in a chemical kinetics (Balasubramanian & Syakilla, 2013).

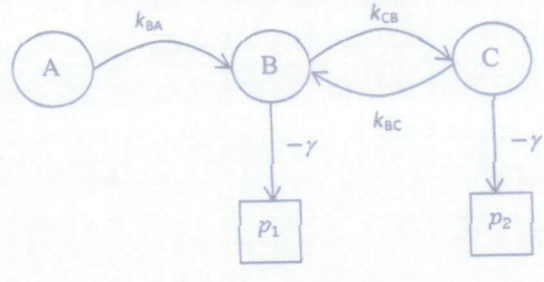


Figure 1. A flow graph for a reaction system.

Figure 4 A Flowgraph for a reaction system

The consumption determinant of a two species reacting system can be determined on the basis of a consumption flow graph.

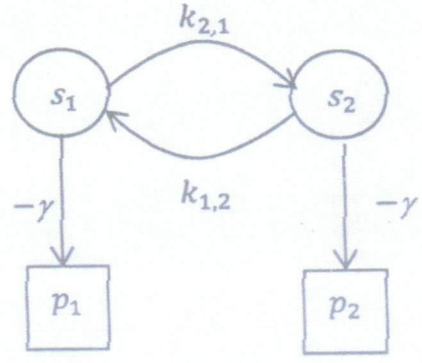


Figure 5 Consumption Flow Graph for 2 species reacting system

P1 and P2 may represent the formation of final products from s1 and s2 respectively with zero kinetic constants. The assumption is that every reacting species undergoes chemical reactions to produce final product with constant rate, even if it may be zero.

$$\Delta C = \begin{array}{c} \\ s_1 \\ s_2 \end{array} \begin{array}{c} \begin{array}{cc} s_1 & s_2 \end{array} \\ \begin{vmatrix} k_{2,1} - \gamma & -k_{1,2} \\ -k_{2,1} & k_{1,2} - \gamma \end{vmatrix} \end{array}$$

The diagonal elements represent the disappearance of reactant si to product in any possible ways with positive sign in front of it due to the transmittance of the edge are all outgoing from the node. The second element in first column represents formation of product s2 from reactant s1 with kinetic constant k2,1 and hence has negative sign as result of transmittance edge outgoing from s1 and incoming to s2.

$$\Delta C = \gamma^2 - \gamma(k_{2,1} + k_{1,2}) = (\gamma_1 - \gamma)(\gamma_2 - \gamma) = 0$$

The formation flow graph for two species reacting system is derived from the consumption flow graph but with consideration that the reacting species of interest is target one and new source input is added.

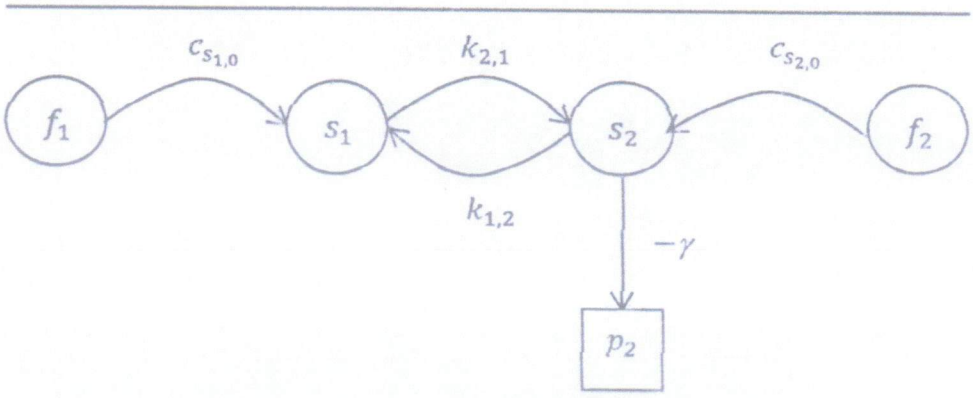


Figure 6 Formation Flow Graph for 2 species reacting system

F1 and F2 represent the source terms for reactant s1 and products s2 respectively. Initial concentrations $c_{s1,0}$ and $c_{s2,0}$ represent reactant and product respectively

$$\Delta f_{s_1} = \begin{array}{c} \\ s_1 \\ s_2 \end{array} \begin{array}{c} \begin{array}{cc} f & s_2 \end{array} \\ \begin{vmatrix} c_{s_{1,0}} & -k_{1,2} \\ c_{s_{2,0}} & k_{1,2} - \gamma \end{vmatrix} \end{array}$$

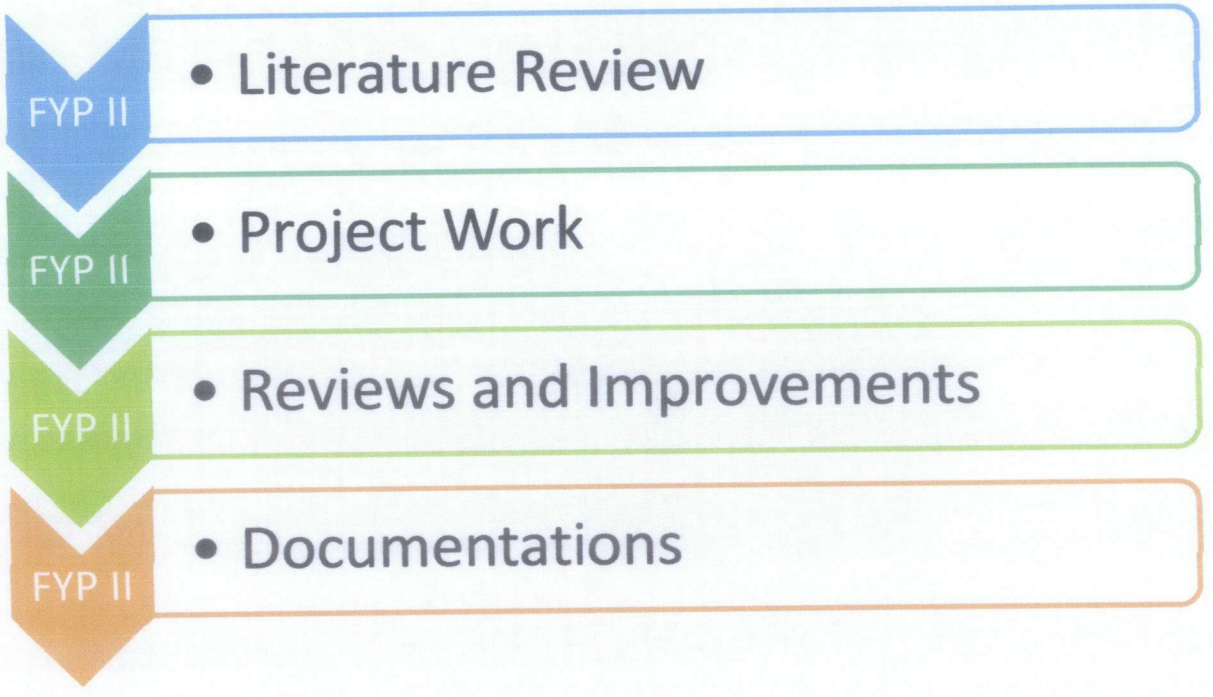
The elements of the first column represent the initial concentrations of the reacting species. This formation determinant is derived from previous consumption flow graph equation by replacing first column with the source terms according to Cramer's method.

$$\Delta f_{s_i}(\gamma_j) = c_{s_{1,0}}(k_{1,2} - \gamma_j) + c_{s_{2,0}} k_{1,2}, \text{ for } j = 1 \text{ and } 2$$

CHAPTER 3 RESEARCH METHODOLOGY

3.1 Project Flow Chart

In ensuring the smooth progression of the project, Gantt chart has been established in the pre-project stage in order to have a specific dateline indicator for the each task ahead that is required by the course. For the ease of planning, an outline using the waterfall model is established for the project tasks itself.



Literature Review

The early stage of the project is to gather information and resources on hydrocracking kinetic models and flow graph methods. Various literature sources will be implemented such as books, journals, conference texts, thesis papers, internet sources and others. The literature review is a very crucial stage as it defines the current understanding on the project that is going to be carried out and the limitations surrounding it

Project Work

The next stage of the project would be the understanding and study of the flow graph theory approach in solving the discrete lumped kinetic equation in hydrocracking of heavy oils.

Reviews and Improvements

Through carrying out the project work, constant reviews and improvements shall be made. This is of course facilitated by the help of supervisors in guiding the direction that the project should be going and to help in any road block that may be encountered. It is also important in order to ensure that the work done has second and third party opinion and free of any miscalculations or trivial error as possible.

Reviews and Improvements

The final part of the project would be documentations. Every work that has been done shall be documented according to the guidelines required by the university. The final dissertation shall be submitted to signal the end of this project.

CRACKING MODEL KINETIC EQUATION

In hydrocracking of heavy oils, the components are classified based on diverse range of true boiling point of each respective hydrocarbons. This method is called as discrete lumping and typical classification includes:

I) Liquefied petroleum gas (<315 K)
II) Naptha (315-425 K)
III) Middle distillates (425-620 K)
IV) Residue (>620 K)

In application of kinetic modeling, it was assumed that a molecule in heavy lump will undergoes binary cracking reaction and hence produces two products. These products may be in the light lumps, or within the reactant lumps. A general reaction stoichiometry of the cracking reactions may be written as:

$$L_r \longrightarrow L_i + L_j \qquad [1]$$

where, r varies from N_L to 1, i and j vary from 1 to r, N_L is number of lumps considered, L_r is label for the lump r, and $k_{i,j,r}$ is kinetic constant for binary cracking of hydrocarbons in the reactant lump r into two products which lie in the lumps i and j.

First order irreversible cracking reaction is considered in or der to develop a kinetic model for the hydrocracking process. Weight fractions of hydrocarbons w_{LI} in the lump *r* can be determined from following kinetic equation:

$$\frac{dw_{L_r}}{dt} = 2\sum_{j=r}^{N_L}\sum_{i=1}^{j} \delta_{r,i,j}\Omega_{r,i,j}k_{r,i,j}w_{L_j} - \sum_{i=1}^{r}\sum_{j=1}^{r}\Omega_{i,j,r}k_{i,j,r}w_{L_r} \qquad [2]$$

In Equation 2 above, $\delta_{r,i,j}=r/(i+r)$ is included in order to normalize the sum of weight fractions of all the lumps to unity at all times instances. $\Omega_{r,i,j}=4_{ij}/r^2(r+1)^2$ is an exponential form of stoichiometric kernel for distribution of products in the lumps r and i from the reactant lump j.

Also, it was assumed that $k_{i,r,j}=k_{i,r,j}$ implying the symmetry of the kinetic constants involved in the reaction stoichiometry.

In order to derive the explicit mathematical expression for the kinetic equation 2, the coefficients of rate equation for the formation of products within the lumps are conveniently grouped using the factor α_r. Similarly, the coefficients of rate equation for the disappearance of reactant lump into two products are grouped together by the factor β_r. Hence, these two factors are

$$\alpha_r = 2\sum_{j=1}^{r} \delta_{r,j,r}\Omega_{r,j,r}k_{r,j,r} \quad \text{and} \qquad \textbf{[3a]}$$

$$\beta_r = \sum_{i=1}^{r}\sum_{j=1}^{r} \Omega_{i,j,r}k_{i,j,r} \qquad \textbf{[3b]}$$

Therefore, the kinetic equation for the hydrocracking process can be written as

$$\frac{dw_{L_r}}{dt} = 2\sum_{j=r+1}^{N_L}\sum_{i=1}^{j} \delta_{r,i,j}\Omega_{r,i,j}k_{r,i,j}w_{L_j} + (\alpha_r - \beta_r)w_{L_r} \qquad \textbf{[4]}$$

The details of formulation of the discrete lumped kinetic model for hydrocracking of heavy oils is explained by *(Krishna,C.P. & Balasubramanian, P. (2009).*

DERIVATIONS OF EXACT SOLUTION

TWO LUMP MODEL

The stoichiometry of a two lump cracking model can be represented as

$$L_2 \xrightarrow{k_{1,2,2}} L_1 + L_2 \qquad L_1 \xrightarrow{k_{1,1,1}} 2L_1$$
$$L_2 \xrightarrow{k_{2,2,2}} 2L_2 \qquad [5]$$
$$L_2 \xrightarrow{k_{1,1,2}} 2L_1$$

The number of kinetic constants included in two lump model is four. The unit of kinetic constants involved in the aforementioned stoichiometry is h^{-1}. The kinetic equations for the cracking of hydrocarbons in the lumps L_2 and L_1 are

$$\frac{dw_{L_2}}{dt} = \left(2\sum_{j=1}^{2} \delta_{2,j,2}\Omega_{2,j,2}k_{2,j,2} - \sum_{i=1}^{2}\sum_{j=1}^{2} \Omega_{i,j,2}k_{i,j,2} \right) w_{L_2} \qquad [6]$$

$$\frac{dw_{L_1}}{dt} = 2\sum_{j=1}^{2} \delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2}w_{L_2} + \left(2\delta_{1,1,1}\Omega_{1,1,1}k_{1,1,1} - \Omega_{1,1,1}k_{1,1,1}\right) w_{L_1} \qquad [7]$$

The exact solution for the linear system of first order differential equations can be represented as sum of constants multiplied with the time dependent exponential functions. Therefore the exac solution for the kinetic equations of 6 and 7 may be expressed as

$$w_{L_i}(t) = \sum_{j=1}^{N_L} D_{i,j} \exp\left[\left(\alpha_j - \beta_j\right)t\right] \qquad [8]$$

In equation 8, the coefficient $D_{i,j}$ can be determined from the ratio of determinants of the formation and consumption flow graphs. These determinants are formulated on

the basis of formation and consumption flow graphs. The factors (α_j - β_r) included in the exponential functions are calculated from the solution of determinant of the consumption flow graph and are the function of kinetic constants included in a model. The formula for the calculation of $D_{i,j}$ can be represented as

$$D_{i,j} = \frac{\Delta f_{L_i}(\alpha_j, \beta_j)}{\Delta c(\alpha_j, \beta_j)} \quad \text{[9]}$$

where Δf_{Li} is formation determinant of the lump L_i and is constructed from the formation flow graph, and Δc is consumption determinant of the model and is constructed on the basis of consumption flow graph.

In equations 8 and 9, i varies from N_L to 1

Consumption Flow Graph.

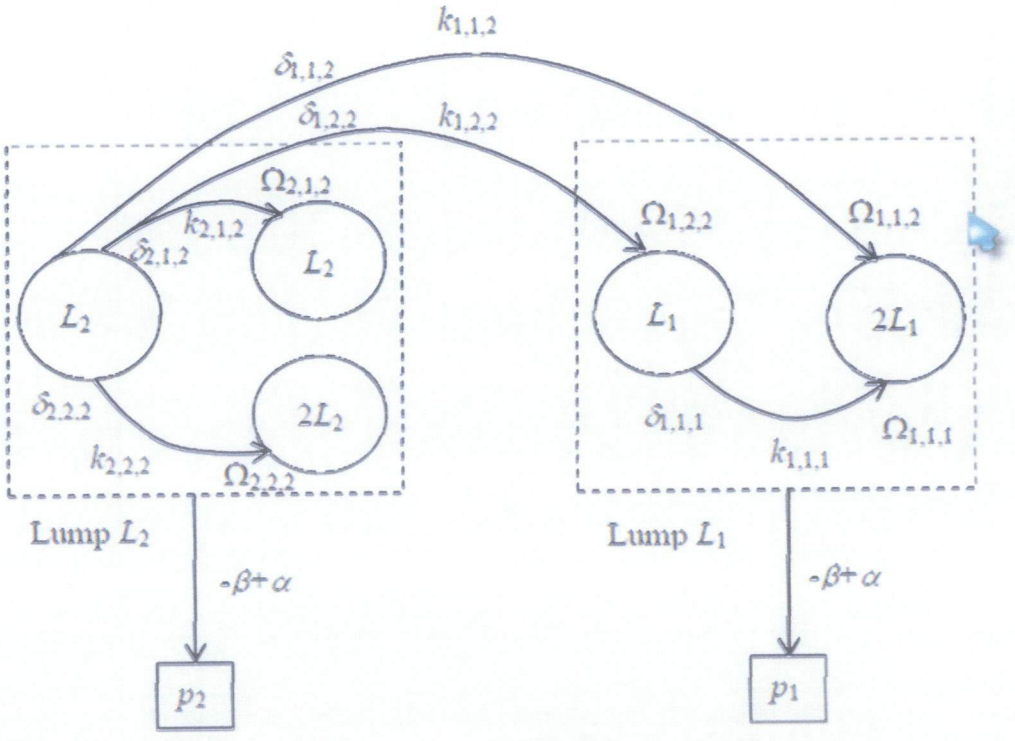


Figure 7 Consumption flow graph for two lump model

The consumption determinant for the two lump cracking model can be determined on the basis of consumption flow graph and is depicted in Figure 7. Here, the labels p_1 and p_2 represent the formation of final products from the lumps 1 and 2 respectively, with the zero kinetic constants. The cracking reactions between the two lumps and the reactions within the reactant lumps are also shown in Figure 7. Here, the kinetic constants $k_{1,1,2}$ and $k_{1,2,2}$ represent the formation of products in the lump L_1 from the reactant lump L_2 .The cracking reactions within the lumps L_1 and L_2 are denoted by the kinetic constants $k_{2,1,2}$, $k_{2,2,2}$ and $k_{1,1,1}$ respectively. The stoichiometric kernels ($\Omega_{1,1,2}$, $\Omega_{1,2,2}$, $\Omega_{2,1,2}$ and $\Omega_{2,2,2}$) and $\Omega_{r,i,j}$ represent the distribution of products from the reactant lumps L_2 and L_1 respectively. Furthermore, the factors $\delta_{i,j,2}$ and $\delta_{1,1,1}$ are included in the model to normalize the weight fraction distribution of the lumps. Thus, the sum of weight fraction of all the lumps must be equal to unity at all-time instances. The consumption determinant for the two lump model is given by

$$\Delta c = \begin{array}{c} \\ L_2 \\ L_1 \end{array} \begin{array}{c} \begin{array}{cc} L_2 & L_1 \end{array} \\ \begin{vmatrix} \sum_{i=1}^{2}\sum_{j=1}^{2}\Omega_{i,j,2}k_{i,j,2} - 2\sum_{j=1}^{2}\delta_{2,j,2}\Omega_{2,j,2}k_{2,j,2} - \beta + \alpha & 0 \\ -2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2} & \Omega_{1,1,1}k_{1,1,1} - 2\delta_{1,1,1}\Omega_{1,1,1}k_{1,1,1} - \beta + \alpha \end{vmatrix} \end{array}$$

[10]

In equation 10, the first and second terms of diagonal elements represent the disappearance of hydrocarbons in a reactant lump L_i to the products on all possible ways with the positive sign in front of it and the formation of products within the reactant lump L_i with the negative sign in front of it, respectively. The second element in the first column represents the formation of products in the lump L_1 from the reactant lump L_2 by the virtue of cracking reactions with the kinetic constants $k_{1,1,2}$*(j=1 and 2)*. Here, this element has a negative sign in front of it as a result of transmittance of the edge outgoing from the lump L_2 and incoming to the lump L_1. Furthermore the first element of the second column is zero as a result of irreversible cracking reaction considered in a kinetic model.

The values of $(\alpha - \beta)$ are determined by making $\Delta c=0$. That is

$$\Delta c = \left(\sum_{i=1}^{2}\sum_{j=1}^{2}\Omega_{i,j,2}k_{i,j,2} - 2\sum_{j=1}^{2}\delta_{2,j,2}\Omega_{2,j,2}k_{2,j,2} - \beta + \alpha \right)\left(\Omega_{1,1,1}k_{1,1,1} - 2\delta_{1,1,1}\Omega_{1,1,1}k_{1,1,1} - \beta + \alpha\right) = 0$$

[11]

The roots of equation 11 are

$$\alpha_1 - \beta_1 = 2\delta_{1,1,1}\Omega_{1,1,1}k_{1,1,1} - \Omega_{1,1,1}k_{1,1,1} \qquad \textbf{[12a]}$$

$$\alpha_2 - \beta_2 = 2\sum_{j=1}^{2}\delta_{2,j,2}\Omega_{2,j,2}k_{2,j,2} - \sum_{i=1}^{2}\sum_{j=1}^{2}\Omega_{i,j,2}k_{i,j,2} \qquad \textbf{[12b]}$$

For the two lump model, equation 11 is a second order polynomial in of $(\alpha - \beta)$ and for N_L lump cracking model, the consumption expression can be represented as n^{th} order polynomial in $(\alpha - \beta)$. The expression for the consumption determinant can be

conveniently represented as the product of difference of the factors (α_i - β_i) . Therefore a general formula for finding the consumption determinant on the basis on consumption flow graph of the discrete lumped kinetic model for the hydrocracking process is

$$\Delta c(\alpha_i, \beta_i) = \prod_{\substack{j=1 \\ j \neq i}}^{N_L} (\beta_j - \beta_i + \alpha_i - \alpha_j) \neq 0 \qquad [13]$$

where i = N_L, N_L-1, …., 1.

Formation Flow Graph

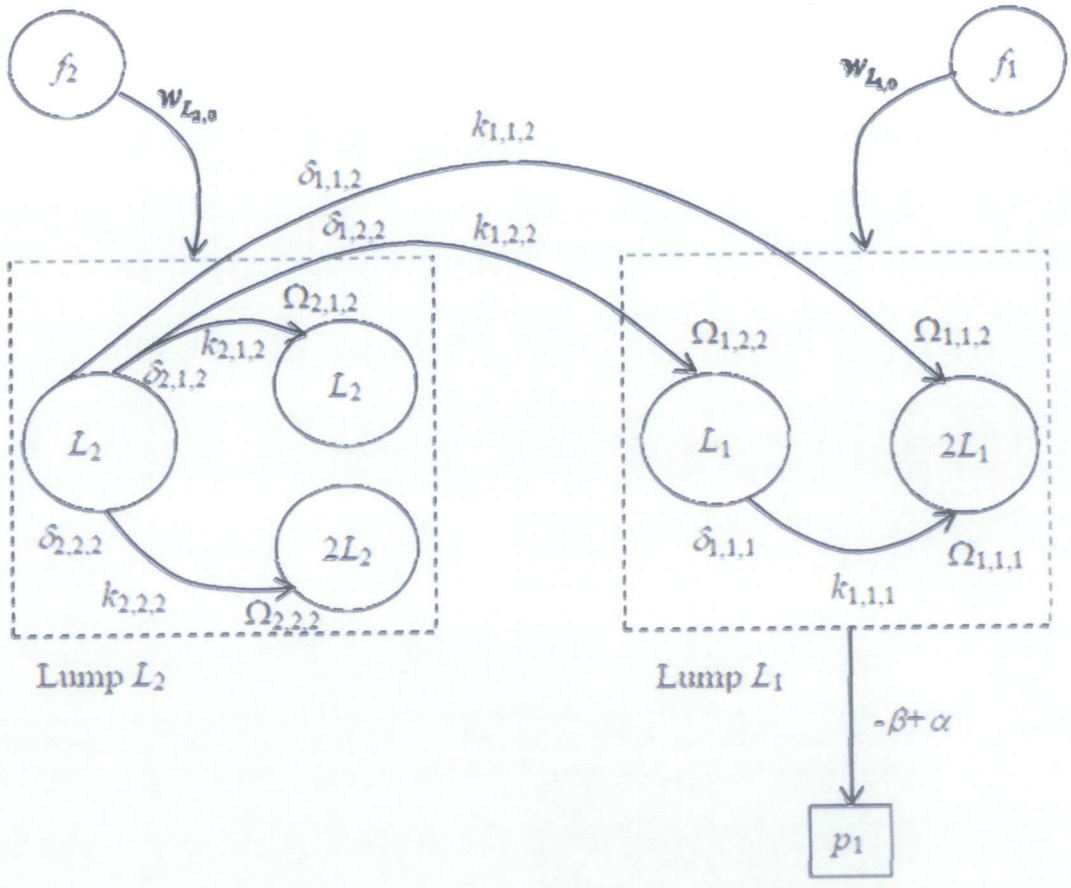


Figure 8 Formation flow graph for two lump model

For the two lump model. The formation flow graph is deduced from the consumption flow graph (Figure 7) with the consideration that the reacting lump of interest is a target one and a new source feed is added. The formation flow graph for the lump L_2 is shown in Figure 8. Here the labels $f1$ and $f2$ represent the feed source terms for the lumps L_1 and L_2 with the initial weight fractions $w_{L1,0}$ and $w_{L2,0}$, respectively. Thus the formation determinant of the lump L_2 in the two cracking model can be represented as

$$\Delta f_{L_2} = \begin{array}{c} \\ L_2 \\ L_1 \end{array} \begin{array}{c} f \\ \begin{vmatrix} w_{L_{2,0}} \\ w_{L_{1,0}} \end{vmatrix} \end{array} \begin{array}{c} L_1 \\ \begin{vmatrix} 0 \\ \Omega_{1,1,1}k_{1,1,1} - 2\delta_{1,1,1}\Omega_{1,1,1}k_{1,1,1} - \beta + \alpha \end{vmatrix} \end{array} \qquad [14]$$

The elements for the first column of the above-mentioned formation determinant represent the initial feed weight fraction of the lumps considered. Equation 14 is deduced from equation 10 by replacing the first column with the feed source terms according to Cramer's method of determinants. The expression for the formation determinant of the luml L_2 is

$$\Delta f_{L_2}(\alpha_i, \beta_i) = w_{L_{2,0}}(\Omega_{1,1,1}k_{1,1,1} - 2\delta_{1,1,1}\Omega_{1,1,1}k_{1,1,1} - \beta_i + \alpha_i) \quad \text{for } i = 1, \text{ and } 2 \quad \textbf{[15]}$$

The coefficients $D_{i,j}$ for the lump L_2 are calculated by substituting equation 13 and 15 in equation 9. The resulting coefficients are

$$D_{2,2} = \frac{\Delta f_{L_2}(\alpha_2, \beta_2)}{\Delta c(\alpha_2, \beta_2)} = \frac{w_{L_{2,0}}(\beta_1 - \beta_2 + \alpha_2 - \alpha_1)}{(\beta_1 - \beta_2 + \alpha_2 - \alpha_1)} = w_{L_{2,0}} \quad \textbf{[16a]}$$

$$D_{2,1} = \frac{\Delta f_{L_2}(\alpha_1, \beta_1)}{\Delta c(\alpha_1, \beta_1)} = 0 \quad \textbf{[16b]}$$

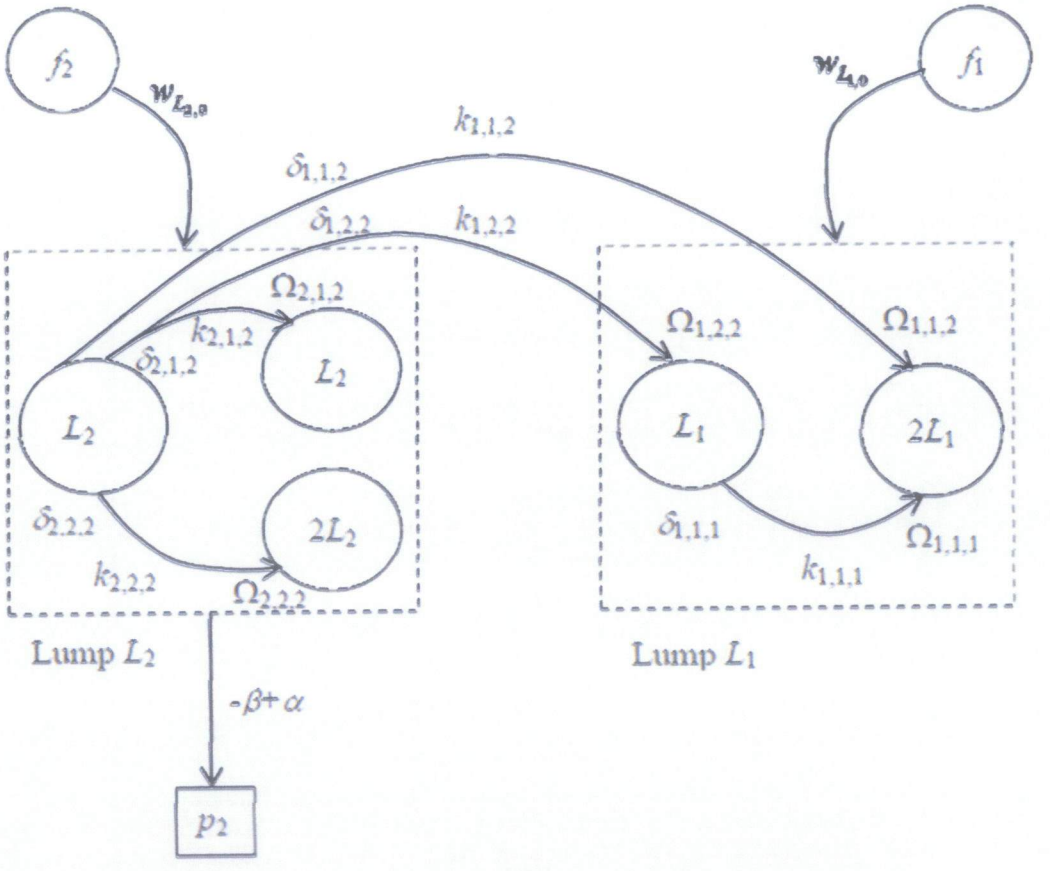


Figure 9 Formation flow graph for two lump model: Lump L1

The formation flow graph of the lump L_1 is depicted in Figure 9 and the formation determinant of the lump L_1 is deduced by replacing the second column of Equation 10 with the feed source terms. Thus, the formation determinant of the lump L_1 is given by

$$\Delta f_{L_1} = \begin{array}{c} \\ L_2 \\ L_1 \end{array} \begin{array}{c} \begin{array}{cc} L_2 & f \end{array} \\ \begin{vmatrix} \sum_{i=1}^{2}\sum_{j=1}^{2}\Omega_{i,j,2}k_{i,j,2} - 2\sum_{j=1}^{2}\delta_{2,j,2}\Omega_{2,j,2}k_{2,j,2} - \beta + \alpha & w_{L_{2,0}} \\ -2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2} & w_{L_{1,0}} \end{vmatrix} \end{array} \qquad [17]$$

Equation 17 results the following expression for finding the determinant of the formation flow graph of the lump L_1.

$$\Delta f_{L_1}(\alpha_i,\beta_i) = w_{L_{1,0}}\left(\sum_{i=1}^{2}\sum_{j=1}^{2}\Omega_{i,j,2}k_{i,j,2} - 2\sum_{j=1}^{2}\delta_{2,j,2}\Omega_{2,j,2}k_{2,j,2} - \beta_i + \alpha_i\right) + w_{L_{2,0}}2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2}$$

[18]

The coefficients $D_{i,j}$ for the lump L_1 are calculated by substituting equations 13 and 18 into equation 9, and resulting expressions can be written as

$$D_{1,2} = \frac{\Delta f_{L_1}(\alpha_2,\beta_2)}{\Delta c(\alpha_2,\beta_2)} = \frac{2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2}D_{2,2}}{(\beta_1 - \beta_2 + \alpha_2 - \alpha_1)} \qquad \textbf{[19a]}$$

$$D_{1,1} = \frac{\Delta f_{L_1}(\alpha_1,\beta_1)}{\Delta c(\alpha_1,\beta_1)} = w_{L_{1,0}} - \frac{2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2}D_{2,2}}{(\beta_1 - \beta_2 + \alpha_2 - \alpha_1)} = w_{L_{1,0}} - D_{1,2} \qquad \textbf{[19b]}$$

The exact solution for the two lumps L2 and L1 are obtained by substituting equations 12, 16 and 19 in equation 8. The resulting explicit mathematical expressions for the two lump model are

$$w_{L_2}(t) = D_{2,2}\exp[(\alpha_2 - \beta_2)t], \qquad \textbf{[20]}$$

$$w_{L_1}(t) = \sum_{m=1}^{2} D_{1,m}\exp[(\alpha_m - \beta_m)t] \qquad \textbf{[21]}$$

THREE LUMP MODEL

$$L_3 \xrightarrow{k_{1,3,3}} L_1 + L_3 \qquad L_2 \xrightarrow{k_{1,2,2}} L_1 + L_2 \qquad L_1 \xrightarrow{k_{1,1,1}} 2L_1$$
$$L_3 \xrightarrow{k_{2,3,3}} L_2 + L_3 \qquad L_2 \xrightarrow{k_{2,2,2}} 2L_2$$
$$L_3 \xrightarrow{k_{3,3,3}} 2L_3 \qquad L_2 \xrightarrow{k_{1,1,2}} 2L_1$$
$$L_3 \xrightarrow{k_{1,2,3}} L_1 + L_2$$
$$L_3 \xrightarrow{k_{2,2,3}} 2L_2$$
$$L_3 \xrightarrow{k_{1,1,3}} 2L_1$$

[22]

The number of kinetic constants included in the three lump cracking model is ten. The unit of the kinetic constants involved in the aforementioned stoichiometry is h^{-1}. The kinetic equation for the lumps L_3, L_2 and L_1 in hydrocracker are

$$\frac{dw_{L_3}}{dt} = \left(2\sum_{j=1}^{3} \delta_{3,j,3}\Omega_{3,j,3}k_{3,j,3} - \sum_{i=1}^{3}\sum_{j=1}^{3} \Omega_{i,j,3}k_{i,j,3} \right) w_{L_3} \qquad \textbf{[23]}$$

$$\frac{dw_{L_2}}{dt} = 2\sum_{j=1}^{3} \delta_{2,j,3}\Omega_{2,j,3}k_{2,j,3}w_{L_3} + \left(2\sum_{j=1}^{2} \delta_{2,j,2}\Omega_{2,j,2}k_{2,j,2} - \sum_{i=1}^{2}\sum_{j=1}^{2} \Omega_{i,j,2}k_{i,j,2} \right) w_{L_2} \qquad \textbf{[24]}$$

$$\frac{dw_{L_1}}{dt} = 2\sum_{j=2}^{3}\sum_{i=1}^{j} \delta_{1,j,j}\Omega_{1,j,j}k_{1,j,j}w_{L_j} + \left(2\delta_{1,1,1}\Omega_{1,1,1}k_{1,1,1} - \Omega_{1,1,1}k_{1,1,1}\right) w_{L_1} \qquad \textbf{[25]}$$

In the following the derivation of exact solution for equations 23-5 through flow graph theory approach is detailed.

Consumption Flow Graph

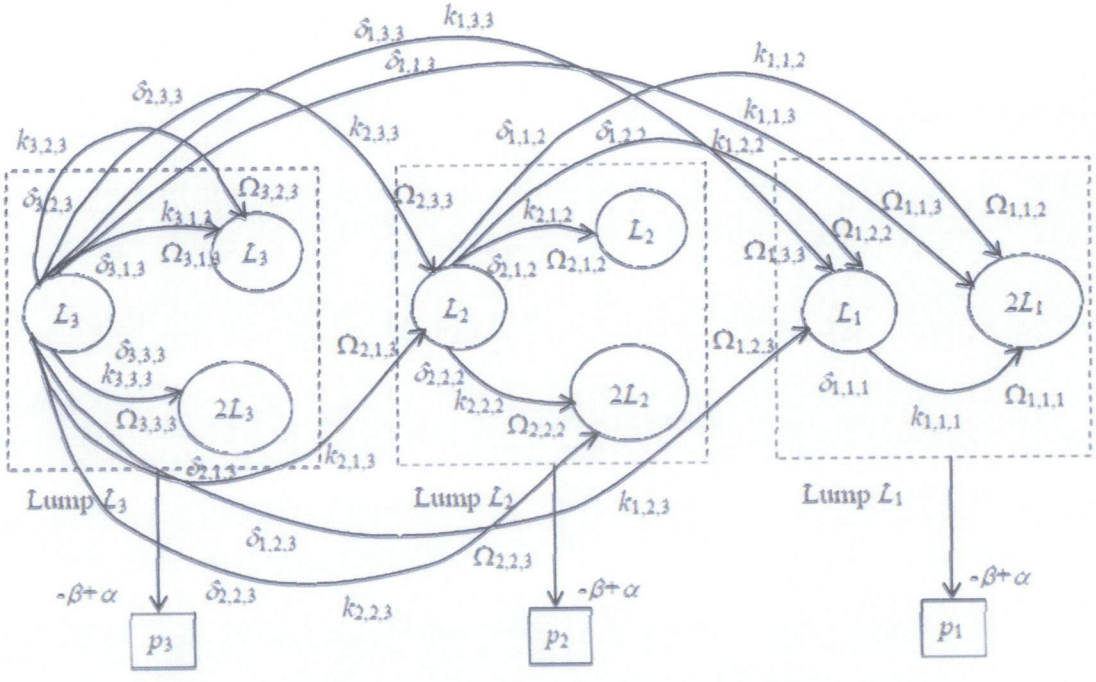


Figure 10 Consumption flow graph for three lump model

The consumption flow graph of the three lump cracking model is depicted in Figure 10. This flow graph is formulated on the basis of reaction stoichiometry shown in equation 22. The consumption determinant is written based on the consumption flow graph as shown in Figure10 and is given below

$$\Delta c = \begin{array}{c} \\ L_3 \\ L_2 \\ L_1 \end{array} \begin{vmatrix} L_3 & L_2 & L_1 \\ \left(\sum_{j=1}^{3}\sum_{j=1}^{3}\Omega_{1,j,3}k_{1,j,3} - 2\sum_{j=1}^{3}\delta_{1,j,3}\Omega_{1,j,3}k_{1,j,3} - \beta+\alpha\right) & 0 & 0 \\ -2\sum_{j=1}^{3}\delta_{2,j,3}\Omega_{2,j,3}k_{2,j,3} & \left(\sum_{j=1}^{2}\sum_{j=1}^{2}\Omega_{1,j,2}k_{1,j,2} - 2\sum_{j=1}^{2}\delta_{2,j,2}\Omega_{2,j,2}k_{2,j,2} - \beta+\alpha\right) & 0 \\ -2\sum_{j=1}^{3}\delta_{1,j,3}\Omega_{1,j,3}k_{1,j,3} & -2\sum_{j=1}^{3}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2} & \left(\Omega_{1,1,1}k_{1,1,1} - 2\delta_{1,1,1}\Omega_{1,1,1}k_{1,1,1} - \beta+\alpha\right) \end{vmatrix}$$

[26]

In the aforementioned consumption determinant, the first and second terms of diagonal elements represent the disappearance of reactant in all possible ways with positive sign in front of it and the formation of products within the reactant lump with negative sign in front of it, respectively. The subdiagonal elements denote the

formation of cracked products in the light lump L_i and from the heavy lump L_j (i<j) with negative sign in front of it. The superdiagonal elements are zero as a result of irreversible cracking reactions according to the stoichiometric equation 22. Thus, a general exact solution is possible for the discrete lumped model presented in this article. The values for $(\alpha_i - \beta_i)$ are determined by making $\Delta c=0$ and the resulting expressions for $(\alpha_i - \beta_i)$ are

$$\alpha_3 - \beta_3 = 2\sum_{j=1}^{3} \delta_{3,j,3}\Omega_{3,j,3}k_{3,j,3} - \sum_{i=1}^{3}\sum_{j=1}^{3} \Omega_{i,j,3}k_{i,j,3} \qquad \textbf{[27a]}$$

$$\alpha_2 - \beta_2 = 2\sum_{j=1}^{2} \delta_{2,j,2}\Omega_{2,j,2}k_{2,j,2} - \sum_{i=1}^{2}\sum_{j=1}^{2} \Omega_{i,j,2}k_{i,j,2} \qquad \textbf{[27b]}$$

$$\alpha_1 - \beta_1 = 2\delta_{1,1,1}\Omega_{1,1,1}k_{1,1,1} - \Omega_{1,1,1}k_{1,1,1} \qquad \textbf{[27c]}$$

A general expression for determining the factors $(\alpha_r - \beta_r)$ can be written on the basis of equation 27 and is given by

$$\alpha_r - \beta_r = 2\sum_{j=1}^{r} \delta_{r,j,r}\Omega_{r,j,r}k_{r,j,r} - \sum_{i=1}^{r}\sum_{j=1}^{r} \Omega_{i,j,r}k_{i,j,r} \qquad \textbf{[28]}$$

Formation Flow Graph

The formation determinant of the lump L_3 can be determined on the basis of the formation flow graph shown in Figure 11.

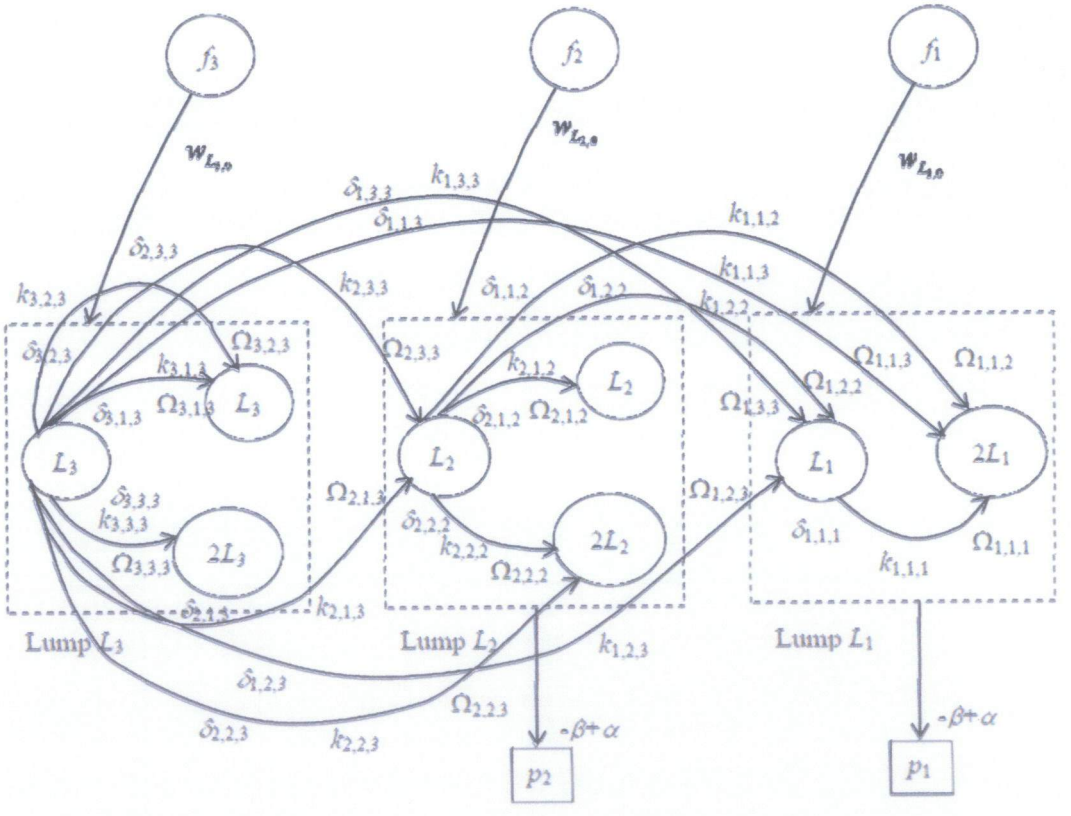


Figure 11 Consumption flow graph for three lump model: Lump L3

The formation determinant of the lump L_3 is deduced from equation 26 by replacing the first column with the feed source terms according to Cramer's method of determinants. Thus the formation determinant of the lump L_3 in the three lump model is

$$\Delta f_{L_i} = \begin{array}{c} \\ L_3 \\ L_2 \\ L_1 \end{array} \begin{array}{c} f \\ \begin{vmatrix} w_{L_{3,0}} & 0 & 0 \\ w_{L_{2,0}} & \left(\sum_{i=1}^{2}\sum_{j=1}^{2}\Omega_{i,j,2}k_{i,j,2} - 2\sum_{j=1}^{2}\delta_{2,j,2}\Omega_{2,j,2}k_{2,j,2} - \beta + \alpha\right) & 0 \\ w_{L_{1,0}} & -2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2} & \left(\Omega_{1,1,1}k_{1,1,1} - 2\delta_{1,1,1}\Omega_{1,1,1}k_{1,1,1} - \beta + \alpha\right) \end{vmatrix} \end{array} \quad \begin{array}{c} \\ L_3 \\ L_2 \\ L_1 \end{array}$$

[29]

Equation 29 results

$$\Delta f_{L_3}(\alpha_i, \beta_i) = w_{L_{3,0}}(\beta_2 - \alpha_2 - \beta_i + \alpha_i)(\beta_1 - \alpha_1 - \beta_i + \alpha_i) \quad \text{for } i = 1, 2 \text{ and } 3 \qquad \textbf{[30]}$$

The coefficients $D_{i;j}$ for the lump L_3 are calculated by substituting equations 13 and 30 in equation 9, and the resulting expressions are as follows

$$D_{3,3} = \frac{\Delta f_{L_3}(\alpha_3, \beta_3)}{\Delta c(\alpha_3, \beta_3)} = \frac{w_{L_{3,0}}(\beta_2 - \beta_3 + \alpha_3 - \alpha_2)(\beta_1 - \beta_3 + \alpha_3 - \alpha_1)}{(\beta_1 - \beta_3 + \alpha_3 - \alpha_1)(\beta_2 - \beta_3 + \alpha_3 - \alpha_2)} = w_{L_{3,0}} \qquad \textbf{[31a]}$$

$$D_{3,2} = \frac{\Delta f_{L_3}(\alpha_2, \beta_2)}{\Delta c(\alpha_2, \beta_2)} = 0 \qquad \textbf{[31b]}$$

$$D_{3,1} = \frac{\Delta f_{L_3}(\alpha_1, \beta_1)}{\Delta c(\alpha_1, \beta_1)} = 0 \qquad \textbf{[31c]}$$

Similarly the formation flow graph of the lump L_2 in the three lump model is depicted in Figure12.

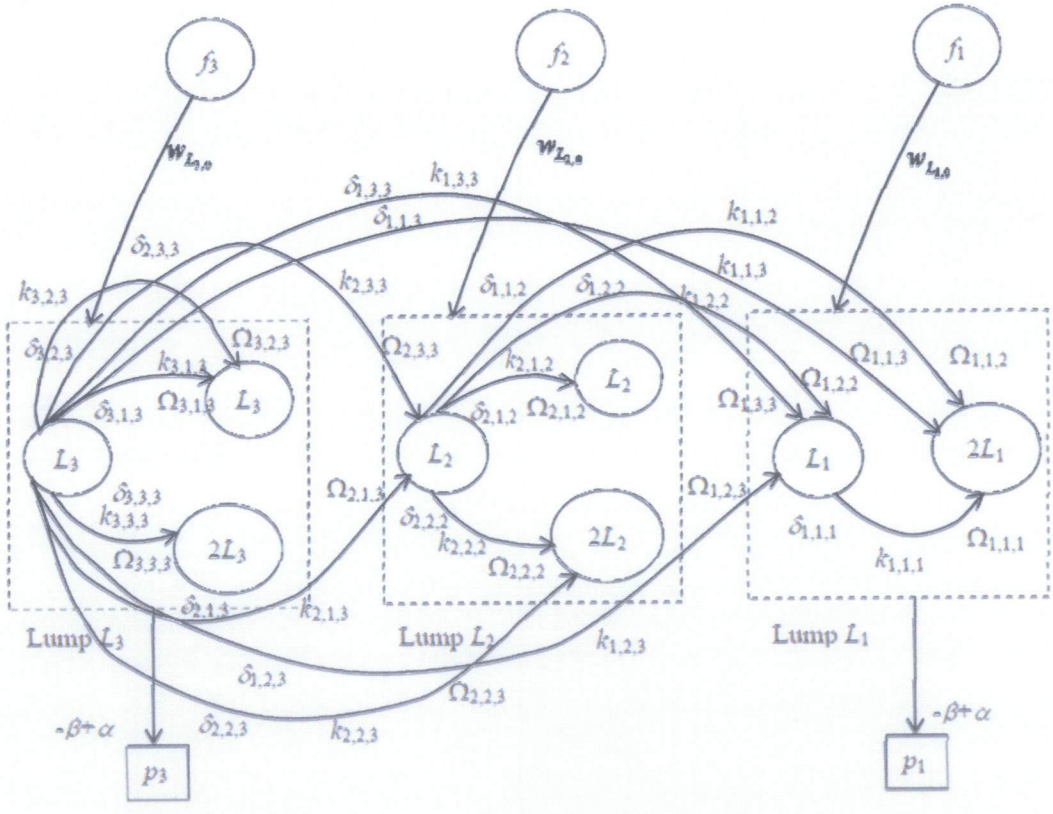


Figure 12 Consumption flow graph for three lump model: Lump L2

The formation determinant of the lump L_2 is formulated on the basis of formation flow graph shown in Figure 12 and is given by

$$\Delta f_{L_2} = \begin{array}{c} \\ L_3 \\ L_2 \\ L_1 \end{array} \begin{array}{c} \begin{array}{ccc} L_3 & f & L_1 \end{array} \\ \begin{vmatrix} \left(\sum_{i=1}^{3}\sum_{j=1}^{3}\Omega_{i,j,3}k_{i,j,3} - 2\sum_{j=1}^{3}\delta_{3,j,3}\Omega_{3,j,3}k_{3,j,3} - \beta+\alpha\right) & w_{L_{3,0}} & 0 \\ -2\sum_{j=1}^{3}\delta_{2,j,3}\Omega_{2,j,3}k_{2,j,3} & w_{L_{2,0}} & 0 \\ -2\sum_{j=1}^{3}\delta_{1,j,3}\Omega_{1,j,3}k_{1,j,3} & w_{L_{1,0}} & \left(\Omega_{1,1,1}k_{1,1,1} - 2\delta_{1,1,1}\Omega_{1,1,1}k_{1,1,1} - \beta+\alpha\right) \end{vmatrix} \end{array} \quad \textbf{[32]}$$

Through simplifications of the above equation 32, we get

$$\Delta f_{L_2}(\alpha_i,\beta_i) = w_{L_{2,0}}(\beta_3-\alpha_3-\beta_i+\alpha_i)(\beta_1-\alpha_1-\beta_i+\alpha_i) + w_{L_{3,0}}2\sum_{j=1}^{3}\delta_{2,j,3}\Omega_{2,j,3}k_{2,j,3}(\beta_1-\alpha_1-\beta_i+\alpha_i) \quad \text{for } i = 1, 2 \text{ and } 3 \qquad \textbf{[33]}$$

The coeeficients $D_{i,j}$ for the lump L_2 in three lump model are calculated by substituting equations 13 and 33 into equation 9. The resulting coefficients are

$$D_{2,3} = \frac{\Delta f_{L_2}(\alpha_3,\beta_3)}{\Delta c(\alpha_3,\beta_3)} = \frac{2\sum_{j=1}^{3}\delta_{2,j,3}\Omega_{2,j,3}k_{2,j,3}w_{L_{3,0}}}{(\beta_2-\beta_3+\alpha_3-\alpha_2)} \qquad \textbf{[34a]}$$

$$D_{2,2} = \frac{\Delta f_{L_2}(\alpha_2,\beta_2)}{\Delta c(\alpha_2,\beta_2)} = w_{L_{2,0}} - \frac{2\sum_{j=1}^{3}\delta_{2,j,3}\Omega_{2,j,3}k_{2,j,3}w_{L_{3,0}}}{(\beta_2-\beta_3+\alpha_3-\alpha_2)} = w_{L_{2,0}} - D_{2,3} \qquad \textbf{[34b]}$$

$$D_{2,1} = \frac{\Delta f_{L_2}(\alpha_1,\beta_1)}{\Delta c(\alpha_1,\beta_1)} = 0 \qquad \textbf{[34c]}$$

Furthermore, the formation flow graph of the lump L_1 is shown in Figure 13.

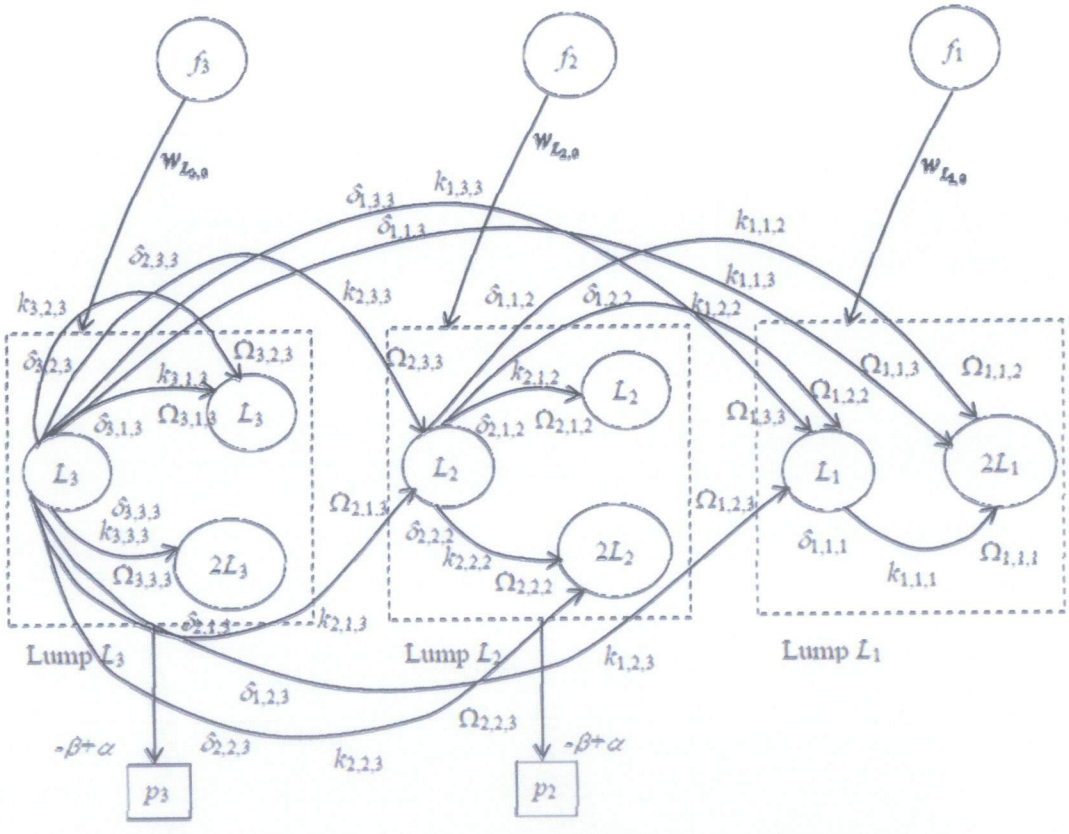


Figure 13 Consumption flow graph for three lump model: Lump L1

The formation determinant of the lump L_1 in three lump model can be written as

$$\Delta f_{L_1} = \begin{array}{c} \\ L_3 \\ L_2 \\ L_1 \end{array} \begin{vmatrix} L_3 & L_2 & f \\ \left(\sum_{i=1}^{3}\sum_{j=1}^{3}\Omega_{i,j,3}k_{i,j,3} - 2\sum_{j=1}^{3}\delta_{3,j,3}\Omega_{3,j,3}k_{3,j,3} - \beta + \alpha\right) & 0 & w_{L_{3,0}} \\ -2\sum_{j=1}^{3}\delta_{2,j,3}\Omega_{2,j,3}k_{2,j,3} & \left(\sum_{i=1}^{3}\sum_{j=1}^{3}\Omega_{i,j,2}k_{i,j,2} - 2\sum_{j=1}^{3}\delta_{2,j,2}\Omega_{2,j,2}k_{2,j,2} - \beta + \alpha\right) & w_{L_{2,0}} \\ -2\sum_{j=1}^{3}\delta_{1,j,3}\Omega_{1,j,3}k_{1,j,3} & -2\sum_{j=1}^{3}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2} & w_{L_{1,0}} \end{vmatrix}$$

[35]

Equation 35 results the following expression for the formation determinant of the lump L_1

$$\Delta f_{L1}(\alpha_i,\beta_i) = (\beta_3-\alpha_3-\beta_i+\alpha_i)\left[w_{L_{1,0}}(\beta_2-\alpha_2-\beta_i+\alpha_i)+w_{L_{2,0}}2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2}\right]$$

$$+w_{L_{3,0}}\left[2\sum_{j=1}^{3}\delta_{2,j,3}\Omega_{2,j,3}k_{2,j,3}2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2}\right. \qquad \text{for } i = 1,\ 2 \text{ and } 3$$

$$\left.+2\sum_{j=1}^{3}\delta_{1,j,3}\Omega_{1,j,3}k_{1,j,3}(\beta_2-\alpha_2-\beta_i+\alpha_i)\right] \qquad \textbf{[36]}$$

The coefficients $D_{i,j}$ for the lump L_1 in the three lump cracking model are determined by substituting equations 13 and 36 into equation 9. Hence, the resulting coefficients are

$$D_{1,3} = \frac{\Delta f_{L_1}(\alpha_3,\beta_3)}{\Delta c(\alpha_3,\beta_3)} = \frac{2\sum_{i=2}^{3}\sum_{j=1}^{i}\delta_{1,j,j}\Omega_{1,j,j}k_{1,j,j}D_{i,3}}{(\beta_1-\beta_3+\alpha_3-\alpha_1)} \qquad \textbf{[37a]}$$

$$D_{1,2} = \frac{\Delta f_{L_1}(\alpha_2,\beta_2)}{\Delta c(\alpha_2,\beta_2)} = \frac{2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2}}{(\beta_1-\beta_2+\alpha_2-\alpha_1)}\left[w_{L_{2,0}}-\frac{2\sum_{j=1}^{3}\delta_{2,j,3}\Omega_{2,j,3}k_{2,j,3}w_{L_{3,0}}}{(\beta_2-\beta_3+\alpha_3-\alpha_2)}\right]$$

$$= \frac{2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2}D_{2,2}}{(\beta_1-\beta_2+\alpha_2-\alpha_1)} \qquad \textbf{[37b]}$$

$$D_{1,1} = \frac{\Delta f_{L_1}(\alpha_1,\beta_1)}{\Delta c(\alpha_1,\beta_1)} = w_{L_{1,0}}-\frac{2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2}}{(\beta_1-\beta_2+\alpha_2-\alpha_1)}\left[w_{L_{2,0}}-\frac{2\sum_{j=1}^{3}\delta_{2,j,3}\Omega_{2,j,3}k_{2,j,3}w_{L_{3,0}}}{(\beta_2-\beta_3+\alpha_3-\alpha_2)}\right]$$

$$-\frac{2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2}\dfrac{2\sum_{j=1}^{3}\delta_{2,j,3}\Omega_{2,j,3}k_{2,j,3}w_{L_{3,0}}}{(\beta_2-\beta_3+\alpha_3-\alpha_2)}+2\sum_{j=1}^{3}\delta_{1,j,3}\Omega_{1,j,3}k_{1,j,3}w_{L_{3,0}}}{(\beta_1-\beta_3+\alpha_3-\alpha_1)}$$

$$= w_{L_{1,0}}-\sum_{j=2}^{3}D_{1,j} \qquad \textbf{[37c]}$$

The exact solution for kinetic equations of the three lump model are obtained by substituting the expressions for $D_{i,j}$ and (α_i - β_i) in equation 8. The resulting explicit time dependent weight fractions expressions for lumps L_3, L_2 and L_1 are

$$w_{L_3}(t) = D_{3,3}\exp[(\alpha_3 - \beta_3)t] \quad [38]$$

$$w_{L_2}(t) = \sum_{m=2}^{3} D_{2,m}\exp[(\alpha_m - \beta_m)t] \quad [39]$$

$$w_{L_1}(t) = \sum_{m=1}^{3} D_{1,m}\exp[(\alpha_m - \beta_m)t] \quad [40]$$

A general exact solution for the discrete lumped kinetic equation in hydrocracking of heavy oils can be deduced from equations 20-21 and 38-40, and is given by

$$w_{L_r}(t) = \sum_{m=r}^{N_L} D_{r,m}\exp[(\alpha_m - \beta_m)t] \quad [41]$$

The factors (α_m - β_m) in equation 41 must be calculated using equation 28. The general expressions to determine the coefficient $D_{r,m}$ can be deduced from equations 16,19,31,34, and 37. They are

$$D_{r,r} = w_{L_r,0} - \sum_{m=r+1}^{N_L} D_{r,m} \quad \text{for } r = m, \text{ and} \quad [42]$$

$$D_{r,m} = \frac{2\sum_{j=r+1}^{m}\sum_{i=1}^{j}\delta_{r,i,j}\Omega_{r,i,j}k_{r,i,j}D_{j,m}}{(\beta_r - \beta_m + \alpha_m - \alpha_r)} \quad \text{for } r < m \quad [43]$$

NO	DETAIL WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Literature Review and Background Study														
2	Submission of Progress Report														
3	Project Work Continues														
4	Pre-EDX														
5	Submission of Draft Report														
6	Submission of Dissertation (soft bound)														
7	Submission of Technical Paper														
8	Oral Presentation														
9	Submission of Project Dissertation (Hard Bound)														

3.2 Gantt Chart

.0 RESULTS AND DISCUSSIONS

$$w_{L_r}(t) = \sum_{m=r}^{N_L} D_{r,m} \exp[(\alpha_m - \beta_m)t] \quad [41]$$

$$D_{r,r} = w_{L_r,0} - \sum_{m=r+1}^{N_L} D_{r,m} \text{ for } r = m, \text{ and} \quad [42]$$

$$D_{r,m} = \frac{2\sum_{j=r+1}^{m}\sum_{i=1}^{j} \delta_{r,i,j}\Omega_{r,i,j}k_{r,i,j}D_{j,m}}{(\beta_r - \beta_m + \alpha_m - \alpha_r)} \text{ for } r < m \quad [43]$$

The derived general exact solution (eq 41) for the kinetic equation 2 is consistent with the exact olution reported in the literature by using Laplace transforms. The time dependent behavior of he cracked products in the three lump hydrocracker model was calculated using equations 41-43 vith the kinetic constants presented in table 1 at 703K.

Table 3 Kinetic constants of hydrocracker

kinetic constant	value (h^{-1})
$k_{1,1,1}$	0.001
$k_{1,1,2}$	0.147
$k_{2,1,2}$	0.230
$k_{2,2,2}$	0.230
$k_{1,1,3}$	0.408
$k_{2,1,3}$	2.859
$k_{2,2,3}$	2.859
$k_{3,1,3}$	2.252
$k_{3,2,3}$	2.252
$k_{3,3,3}$	2.252

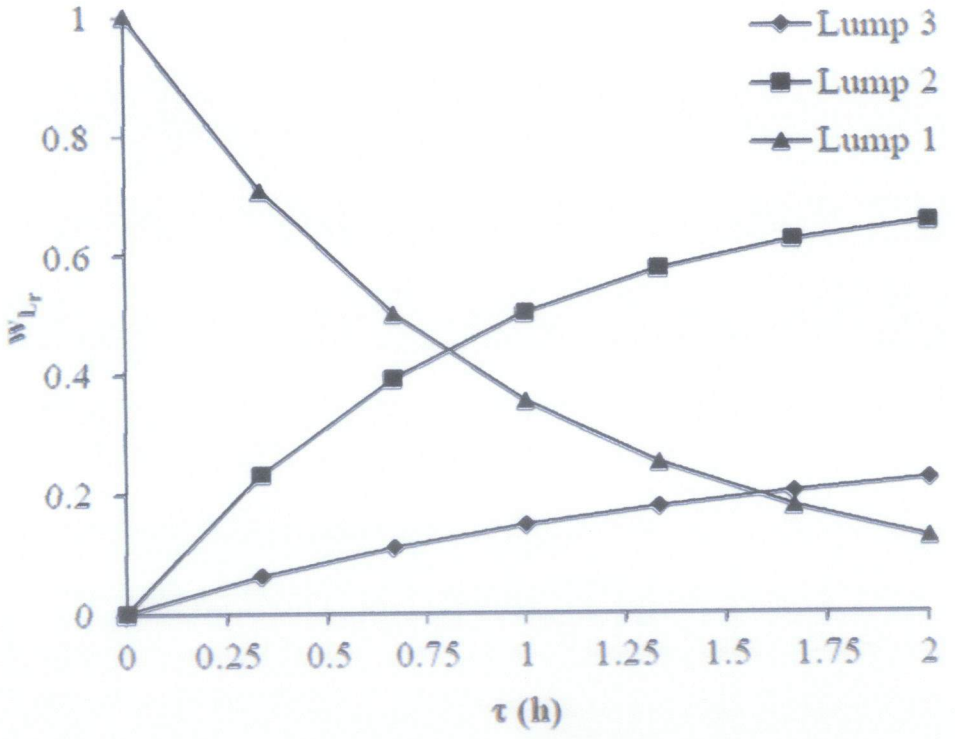


Figure 14 Graph of weight fraction distribution of lumps

The weight fraction distribution of the lumps at 723 in the three lump hydrocracker model is depicted in Figure 14. The calculated stoichiometric kernel, *D* coefficient matrix, weight fraction of the lumps using exact solution and numerical methods are presented in the supporting information.

5.0 CONCLUSIONS AND RECOMMENDATIONS

In conclusion, this research aims to apply the flow graph theory approach for the solution of discrete lumped kinetic equation in hydrocracking of heavy oils. This progress report details the project activities and milestones that have been set in order to achieve that result.

Discrete lumped model for hydrocracking of heavy oils is governed by the first order linear differential equations. In this article, a general exact solution of the kinetic equation for hydrocracking of heavy oils is derived using flow graph theory approach. This method utilized the Cramer's rule of determinants for finding the solution of kinetic equation. The superdiagonal elements of the consumption determinant are zero for the hydrocracker model presented in this article. As a result, the derivation of a general exact solution for the kinetic equation 2 is feasible. Furthermore, the exact solution obtained for the hydrocracker model through flow graph theory approach is consistent with the reported results available in the literature using Laplace transforms.

Previous literature research has shown that heavy oils hydrocracking is a very important field in petroleum refineries and the authors believe that the work done in this paper would be of beneficial use to the industry and community alike.

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