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Solution of linear differential equations in chemical kinetics through flow graph theory approach

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ABSTRACT

A flow graph theory is a method for finding the analytical solution of linear differential equations which arise in chemical kinetics through Cramer's method of determinants. This article presents the applicability of flow graph theory for deriving the analytical solution of kinetic equations which arise in modeling of complex reaction system such as hydrocracking of heavy oils. A discrete lumped model for hydrocracking of heavy oils was developed and analytical solution for the governing model equations was derived using Laplace transforms earlier. In this work, a new method involving flow graph theory was used instead of Laplace transforms. The kinetic equations which describe the performance of a hydrocracker are governed by linear differential equations and a general analytical solution was successfully derived using flow graph theory. The analytical solution obtained through flow graph theory is similar with the reported solution using Laplace transforms for the kinetic equations of hydrocracking of heavy oils. Furthermore, the relative errors between the experimental data and model calculations using analytical solution of the three lump hydrocracker model are reasonable except for few data points.

1. Introduction

A flow graph is a pictorial representation of reaction mechanisms involved in a chemically reacting system [1,2]. This approach determines the analytical solution of linear differential equations using Cramer's method of determinants [1–4]. In chemical kinetics, the linear differential equations arise as a result of mass balances of first order reactions which occur in either a batch reactor or an ideal plug flow reactor [3,4]. Analytical solution for the linear differential equations can be conveniently represented as a constant multiplied with a time dependent exponential function [1–4]. In flow graph theory, the constant is determined as ratio of determinants of the formation and consumption flow graphs. The consumption flow graph can be formulated on the basis of reaction stoichiometry. The formation flow graph is deduced from consumption flow graph by including the feed source terms and neglecting the final product with zero kinetic constant of the target product. This approach eliminates the usage of classical integration, Laplace transforms, and eigenvalue method for finding analytical solution of linear differential equations which arise in chemical kinetics and engineering [2,4].

A general analytical solution for the first order monomolecular irreversible reactions which occur in a batch reactor was derived using flow graph theory by Bhusare and Balasubramanian [3]. Recently, Nurul Amira and Balasubramanian [4] applied the flow graph theory for finding analytical solution of kinetic equations for the two and three species reversible reactions. In the present work, it was decided to demonstrate the applicability of the flow graph theory approach for finding analytical solution of kinetic equations for the cracking reactions. The illustrative example considered here is a discrete lumped model for hydrocracking of heavy petroleum fractions [5,6]. In hydrocracking, the high boiling point petroleum fractions such as vacuum gas oil or vacuum residue undergo carbon–carbon bond cleavage reactions and produce low boiling point petroleum fractions such as liquefied petroleum gas, naphtha and diesel in the presence of hydrogen gas over a bifunctional solid acid catalyst [7]. The kinetic equations for hydrocracking of heavy petroleum fractions were developed by assuming binary cracking kinetics. Earlier, Krishna and Balasubramanian [6] developed a general discrete lumped model for hydrocracking of heavy oils using true boiling point of the hydrocarbons as the basis. In this model, the cracking reactions which occur within the lumps are also considered along with the cracking reactions between the lumps. A general analytical solution of kinetic equations for hydrocracking of heavy oils was derived using Laplace transforms [6].

A flow graph theory is a recently emerging method for finding analytical solution of linear differential equations which arise in chemical kinetics. This approach is not applied for finding solution of kinetic equations of cracking kinetics which arises in hydrocracking of heavy oils. Therefore, this article presents the applicability of flow

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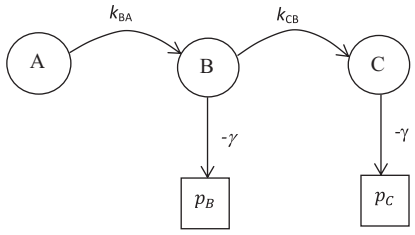

Fig. 1. A flow graph for the reaction $A \xrightarrow{k_{BA}} B \xrightarrow{k_{CB}} C$.

graph theory for finding solution of kinetic equations for hydrocracking of heavy oils.

2. Basis of flow graph theory

A flow graph in a signal system represents a network in which nodes are connected with directed edges. Each node in a signal flow graph indicates a system variable and each edge connecting two nodes acts as a signal multiplier. The direction of signal flow is represented by placing an arrow on the edge and transmittance of signal flow is indicated along the edge. The signal flow graph depicts how signals are transmitted from one system to another and provides the relationship between the systems.

In kinetics, a node represents a chemical component undergoing a structural transformation. An edge is a directed line segment joining two nodes. Weighting of an edge is a real gain between nodes and indicates the kinetic constant of a reaction. The reactant and product are represented as an input and output nodes, respectively. The input and output nodes have only outgoing and incoming edges, respectively. Furthermore, the mixed node has both outgoing and incoming edges.

The concept of flow graph in chemical kinetics is illustrated with the following example. The schematic representation of flow graph for the series reaction is depicted in Fig. 1. The label A in the flow graph represents a reactant and is an input node as a result of having only outgoing edge. The labels p_B and p_C denote the output nodes because of having only the incoming edges. Furthermore, the labels B and C are the mixed nodes, and have both incoming and outgoing edges. The transmittance shown in Fig. 1 is a kinetic constant, and the symbols k_{BA} and k_{CB} denote the kinetic constants for the nodes A and B, respectively. The detailed description for the flow graph theory in kinetics can be found elsewhere [1–4].

3. Illustrative example

In the following, the derivation of analytical solution for the kinetic equations of hydrocracking of heavy oils through flow graph theory approach is presented.

In hydrocracking, the discrete lumps are classified on the basis of true boiling point of the hydrocarbons. The typical lumps classification for hydrocracking of heavy oils is: (i) liquefied petroleum gas (< 315 K), naphtha (315–425 K), middle distillates (425–620 K) and residue (>620 K). In kinetic modeling, it was assumed that a molecule in the heavy lump undergoes a binary cracking reaction and produces two products which may lie either in the light lump or within a reactant lump [6]. Therefore, a general stoichiometry of the cracking reactions can be represented as

$$L_r \xrightarrow{k_{i,j,r}} L_i + L_j \tag{1}$$

where, r varies from N_L to 1, j vary from 1 to r and i vary from 1 to j, N_L is number of lumps considered, L_r is label of 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 product lumps i and j.

The kinetic equations for hydrocracking of heavy oils [6] were developed by assuming first order irreversible cracking kinetics and are given by

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

Eq. (2) can also be applied for determining the product distribution in thermal cracking of heavy petroleum fractions [8].

In Eq. (2), $\Omega_{r,i,j} = 4ij/r^2(r+1)^2$is exponential form of stoichiometric kernel for the distribution of products in the lumps r and i from the reactant lump j by virtue of a cracking reaction. The compensation factor$\delta_{r,i,j} = r/(i+r)$ is included for making the sum of weight fractions added to the two lumps is equal to unity at all instances of time. Furthermore, it was assumed that $k_{r,i,j} = k_{i,r,j}$ implying the symmetry of the kinetic constants included in Eq. (1). The detailed description for the derivation of Eq. (2) can be found elsewhere [6].

For deriving analytical solution, the coefficients in the first term on right-hand side for the formation of products within the lumps are conveniently grouped using the factor α_r. Similarly, the coefficients in the second term on right-hand side for the disappearance of hydrocarbons in a reactant lump are grouped using the factor β_r. Thus, these two factors are

$$\alpha_r = 2\sum_{j=1}^{r}\delta_{r,j,r}\Omega_{r,j,r}k_{r,j,r}, \text{ and} \tag{3a}$$

$$\beta_r = \sum_{i=1}^{r}\sum_{j=1}^{r}\Omega_{i,j,r}k_{i,j,r} \tag{3b}$$

Therefore, Eq. (2) can be conveniently written as

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

The matrix-vector form of Eq. (4) can be represented as

$$\dot{w}_L = Rw_L \tag{5}$$

where,

$$\dot{w}_L = \left(\frac{dw_{L_1}}{dt}, \frac{dw_{L_2}}{dt}, \cdots \frac{dw_{L_r}}{dt}, \cdots, \frac{dw_{L_{N_L-1}}}{dt}, \frac{dw_{L_{N_L}}}{dt}\right)^T,$$

$$w_L = (w_{L_1}, w_{L_2}, \cdots, w_{L_r}, \cdots, w_{L_{N_L-1}}, w_{L_{N_L}})^T \text{ and}$$

$$R = \begin{bmatrix}
\alpha_1-\beta_1 & 2\sum_{j=1}^{2}\delta_{1,j,2}\Omega_{1,j,2}k_{1,j,2} & \cdots & 2\sum_{j=1}^{r}\delta_{1,j,r}\Omega_{1,j,r}k_{1,j,r} & \cdots & 2\sum_{j=1}^{N_L-1}\delta_{1,j,N_L-1}\Omega_{1,j,N_L-1}k_{1,j,N_L-1} & 2\sum_{j=1}^{N_L}\delta_{1,j,N_L}\Omega_{1,j,N_L}k_{1,j,N_L} \\
0 & \alpha_2-\beta_2 & \cdots & 2\sum_{j=1}^{r}\delta_{2,j,r}\Omega_{2,j,r}k_{2,j,r} & \cdots & 2\sum_{j=1}^{N_L-1}\delta_{2,j,N_L-1}\Omega_{2,j,N_L-1}k_{2,j,N_L-1} & 2\sum_{j=1}^{N_L}\delta_{2,j,N_L}\Omega_{2,j,N_L}k_{2,j,N_L} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & \cdots & \alpha_r-\beta_r & \cdots & 2\sum_{j=1}^{N_L-1}\delta_{r,j,N_L-1}\Omega_{r,j,N_L-1}k_{r,j,N_L-1} & 2\sum_{j=1}^{N_L}\delta_{r,j,N_L}\Omega_{r,j,N_L}k_{r,j,N_L} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & \cdots & 0 & \cdots & \alpha_{N_L-1}-\beta_{N_L-1} & 2\sum_{j=1}^{N_L}\delta_{N_L-1,j,N_L}\Omega_{N_L-1,j,N_L}k_{N_L-1,j,N_L} \\
0 & 0 & \cdots & 0 & \cdots & 0 & \alpha_{N_L}-\beta_{N_L}
\end{bmatrix}$$