

Pszeudokomponensekből álló reakcióhálózat kinetikai azonosítása vákumgázolaj hidrokrakkolása során

Kinetic identification of reaction network consisting chemical lumps for vacuum gas oil hydrocracking

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Összefoglaló/ Summary

A hosszú szénláncú, nagy szénatomszámú szénhidrogének, mint például a finomítói vákuum lepárlási maradék, különböző növényi olajok vagy a használt sütőolaj hidrokrakkolásával hasznosítható motorhajtóanyagok, elsősorban biogázolajok állíthatók elő. Ezért ezen alapanyagok felhasználása környezetvédelmi és gazdasági szempontból is előnyös. Az alkalmas technológia kifejlesztéséhez szükség van a lejátszódó folyamatok modellezésére, ez azonban a nagyszámú lejátszódó reakció miatt gyakran nehézségekbe ütközik. Gyakran alkalmazott egyszerűsítésként lehetőség van nem az egyes kémiai komponensek, hanem a technológiai igényeknek megfelelő komponenscsoportok koncentrációváltozását leíró mérlegegyenleteket felírni. Ezen ún. lumped modellek alkalmazása elterjedt módszer a hidrokrakkolás modellezése során, azonban a modellek felírása gyakran próbálgatással, a lehetséges reakcióutak heurisztikus vizsgálatával történik.

Munkánkban egy olyan algoritmus fejlesztését kezdtük el, amely alkalmas lehet arra, hogy a komponenscsoportokat összekötő összes lehetséges reakció útvonal között keresve azonosítsa azt a legkisebb számú reakciót, melyek figyelembe vételével a csoportok koncentrációjának alakulása még megfelelő mértékben leírható. Az itt bemutatott módszer félig tekinthető automatizáltnak, azonban jelenlegi formájában is hatékonyan képes viszonylag nagyméretű reakcióhálózatok modell redukcióját elvégezni.

Through hydrocracking of long-chained hydrocarbons such as vacuum distillation residue from refineries, vegetable oils or waste cooking oil it is possible to produce serviceable fuels, mainly bio-gasoil with high quality. Therefore, utilization of these feedstocks is advantageous from both environmental and economical point of view. In order to develop a suitable production technology, it is necessary to model the processes taking place, yet this often meets difficulties because of the large number of reactions. A simpler and often adequate approach is to calculate concentration changes of certain component groups instead of individual components. The application of these so-called lumped models is a frequently used method during modeling of the hydrocracking process; however the construction of these models is often carried out with trial and error methods, investigating the possible reaction pathways using a heuristic approach.

In our work we started the development of an algorithm that would be capable to identify the smallest number of reactions that is necessary to describe concentration changes of lumps properly while searching among all possible reaction pathways. The method presented here is considered as a semi-automated one; nevertheless it is capable to carry out model reduction of reaction networks consisting of a fairly high number of possible pathways.

Introduction

Hydrocracking process, which involves catalytic cracking of long-chained hydrocarbon molecules, has a growing importance in oil industry. Important nonconventional feedstocks such as vacuum gas oil, various vegetable oils or even waste cooking oil can be utilized to produce fuels, mainly bio-gasoil with high quality [1].

Regardless of feedstock, its complexity and the several possible reactions that can take place during hydrocracking make the detailed kinetic modeling extremely difficult. Nonetheless, there are attempts present in the literature that deal with individual components. Zhang et al. studied hydrocracking of vacuum gas oil, modeling individual reactions while estimating the rate coefficients based on the structure of the species, applying quantum chemical and group contribution methods [2]. Browning et al. formulated a detailed kinetic model taking 217 lumps into consideration; still, the required number of kinetic parameters to be identified was

reduced to 17 with similarity considerations and probability matrices. This distribution approach raised some further interest recently, e.g. [3; 4].

Lumped models provide an alternative that does not require a detailed reaction network. Instead, macro scale information can be used as a starting point, usually the distillation curve of the system investigated. Based on that, various lumps can be formulated. One might consider “classical” oil fractions such as kerosene or gasoline, but lumping is possible in a greater degree as well resulting for example components with greater than 400°C normal boiling point. Both the advantage and disadvantage of this approach lie in its simplicity, as very little information is needed to calculate yields of relatively pure components, but the identified mechanism for the transition processes between individual lumps (often called reactions for the sake of simplicity) are specific to the feedstock and conditions present in the experimental system therefore cannot be simply transferred to other systems and ought to be identified for every system. The vast number of studies presented in literature supports this assumption. For example, Puro et al. developed a four-lump kinetic model to describe hydrocracking of vacuum residue from Maya crude oil [5]. 10 different reaction networks with increasing complexity were identified. Rate equation coefficients were reported in case of the most complex model. A similar model can be found for waste cooking oil feedstock [6]. Comparing this kinetic model with the former, it can be seen that while the chemical lumps are similar, different reaction pathways were taken into consideration, therefore it is not possible to compare the rate coefficients from obtained from the two cases. Additionally, in neither case the kinetic parameters followed strictly the Arrhenius equation. Hence, for lumped kinetic models it is often advantageous to determine the reaction rate coefficients at different temperatures independently and then calculate the frequency factor and activation energy of the reaction separately in a second regression step. This method explicitly covers the uncertainties of the temperature dependence of the reactions. However, this is not a necessity as there are modeling approaches with the limitation of rate equations following Arrhenius’ law present in the literature. e.g. [7; 8].

In this study a six-lump kinetic model was applied for modeling of vacuum gas oil hydrocracking process. The aim of our work is to thoroughly investigate the reaction network and reduce the number of kinetic parameters needed to be identified to describe concentration changes of the lumps without significantly decreasing model accuracy. In the following sections we present the complete reaction network and our developed algorithm for model reduction. The results show that the complete network can effectively be reduced without losing significant amount of information.

Investigating the complete reaction network

Here we consider the simulation of a single-tube reactor. Sadighi et al. reported measurement data for vacuum gas oil hydrocracking in a pilot scale single tube fixed bed reactor [7]. Six lumps were formed, namely Vacuum gas oil (VGO), Diesel (D), Kerosene (K), Heavy Naphtha (HN), Light Naphtha (LN) and Gas (G). This gives us a slightly realistic approach for modeling the hydrocracking process as the lumps broadly represent the desired products of the actual hydrocracking process. Experiments were carried out at four temperature values (380 °C, 400 °C, 410 °C and 420 °C) and four different LHSV values (0.5 h⁻¹, 1 h⁻¹, 1.5 h⁻¹ and 2 h⁻¹), resulting 16 experimental conditions for each lump (96 in total). Model of the pilot scale reactor is present in [8]. For the sake of simplicity, here we re-publish the six-lump kinetic model (including all forward reaction pathways, shown in Figure (1)) and governing equations as follows:

$$\frac{d(\underline{c} \cdot V)}{dz} = \eta \cdot \varepsilon \cdot \underline{A} \cdot \underline{c} \quad (1)$$

$$\underline{A} = a_{ij} = \begin{cases} -\sum_{l=1}^m k_{il}, & \text{if } i = j \\ k_{ji} & \text{if } i \neq j \end{cases} \quad (2)$$

$$k_i = k_{0,i} \cdot \exp\left(\frac{-E_{a,i}}{RT}\right) \quad (3)$$

$$\underline{c} = [c_F \ c_D \ c_K \ c_{HN} \ c_{LN} \ c_G]^T \quad (4)$$

Where η is the effectiveness factor of the heterocatalytic reactions, ε is the catalyst volume fraction, A is the conversion matrix of the reaction system, k_0 is the pre-exponential factor and E_a is the activation energy of the reaction, R is the gas constant and T is the temperature of the reactor in K. The values of η and ε are 0.8 and 0.264, respectively.

In short terms, the diagonal elements of the conservation matrix contain the negative sum of reaction rate coefficients for the reactions acts as a sink for the i^{th} component (m in total) and the off-diagonal elements contain the k values of reactions that produce the i^{th} component.

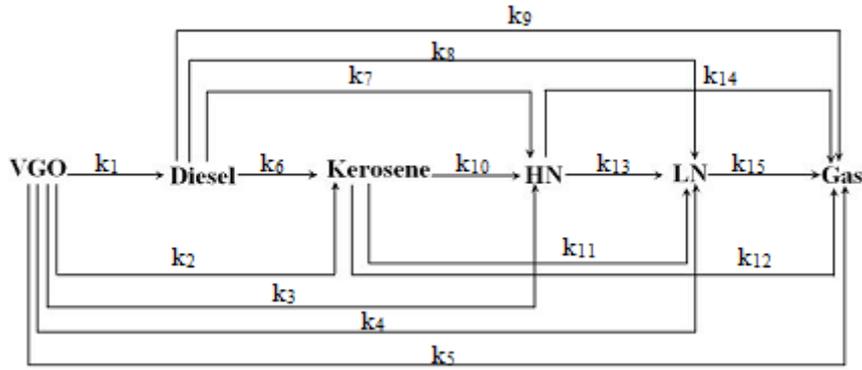


Figure 1. Complete six-lump reaction network.

In their work, Sadighi et al. identified the 30 parameters of the reaction network shown in Figure (1), namely the pre-exponential factor and activation energy for each reaction. It was shown that some reaction pathways are negligible (as the kinetic constants are relatively small), therefore a reduced network was defined manually and its parameters identified in a second parameter identification step.

Alternatively, we would like to discuss a somewhat more sophisticated approach for kinetic parameter identification and model reduction. The complete reaction network contains 15 reactions; however, not all reaction pathways are necessarily needed to model the concentration changes in the reactor at various conditions. This consideration leads to a Mixed Integer Nonlinear Program (MINLP). There are three variables assigned to each reaction, a binary existence variable, and the associated pre-exponential factor and activation energy, the latter two normalized between 0 and 1, accordingly:

$$\underline{x} = \left[\underline{eXS}^T \quad \underline{k_0}^{linT} \quad \underline{E_a}^{linT} \right] \quad (5)$$

$$\underline{x}^{actual} = \underline{x} \circ (\underline{u}_b - \underline{l}_b) + \underline{l}_b \quad (6)$$

The notation “ \circ ” stands for the Hadamard-product of the two vectors. The lower and upper bounds for kinetic constants determined after some preliminary simulations as no a priori data is available for the system are

summarized in Table 1. Squared error between the measured and calculated concentrations summed up for each component at each temperature and LSHV value (Eq. (7)) was used as objective function:

$$f(x) = \sum_T \sum_{lump} \sum_{LHSV} (y_{meas} - y_{calculated})^2 \quad (7)$$

A linear inequality (Eq. (8)) was defined for numerical reasons stating that at least one reaction should be present in the reaction system:

$$\left[-\underline{exs}^T \quad 0 \cdot \underline{k_0}^{linT} \quad 0 \cdot \underline{E_a}^{linT} \right] \cdot \underline{x} \leq -1 \quad (8)$$

Table 1. Lower and upper bounds for kinetic constants.

Reaction		$k_0[\text{m}^3 \text{h}^{-1} \text{mcat}^{-3}]$		$E_a [\text{kcal mol}^{-1}]$	
		$\mathbf{l_b}$	$\mathbf{u_b}$	$\mathbf{l_b}$	$\mathbf{u_b}$
1.	VGO \rightarrow D	$5 \cdot 10^4$	$5 \cdot 10^5$	0	100
2.	VGO \rightarrow K	10^{13}	10^{14}		
3.	VGO \rightarrow HN	0	1		
4.	VGO \rightarrow LN	$5 \cdot 10^{10}$	$5 \cdot 10^{11}$		
5.	VGO \rightarrow G	10	10^3		
6.	D \rightarrow K	10^{10}	10^{11}		
7.	D \rightarrow HN	0	1		
8.	D \rightarrow LN	10	10^3		
9.	D \rightarrow G	10	10^3		
10.	K \rightarrow HN	10^6	10^7		
11.	K \rightarrow LN	10	10^3		
12.	K \rightarrow G	10	10^3		
13.	HN \rightarrow LN	10^4	10^5		
14.	HN \rightarrow G	0	1		
15.	LN \rightarrow G	$5 \cdot 10^4$	$5 \cdot 10^5$		

Model of the hydrocracking reactor was implemented in MATLAB 2011b as a set of ordinary differential equations (component balances). Component yields at the outlet of the reactor were computed for each LHSV and temperature values using a modified Rosenbrock formula of order 2 for stiff problems (ode23s) [9]. The optimization problem was formulated using the OPTimization Interface (OPTI) Toolbox [10], and solved with the supplied NOMAD (Nonlinear Optimization by Mesh Adaptive Direct Search) solver capable of handling binary constraints [11].

The obtained kinetic model is shown in Figure 1. It is clearly visible that only two from the 15 reactions could be eliminated using this algorithm. This may be explained by numerical issues, as the value of the objective function can be further reduced with increasing number of reactions. One way to overcome this is to include the number of existing reactions in the objective function using some weighted method; furthermore focusing on other indicators of the importance of a certain pathway.

The values of the actual reaction rate coefficients would appear a suitable indicator. The values of the obtained k_0 and E_a values are summarized in Table 2. Some of the estimated parameters reached the upper or lower bounds of the search space; however specifying the correct bounds is rather difficult as these pathways are not actual reactions. Furthermore, the performance of the optimization algorithm severely decreases when stretching the boundaries; therefore it was decided not to modify these limits. The reaction rate coefficients were calculated at the mean temperature and were compared to the largest k value in k_{rel} . This investigation suggests that while some of these 13 reactions do exist, their contribution to the changes in yields of various lumps are so small that they can be eliminated.

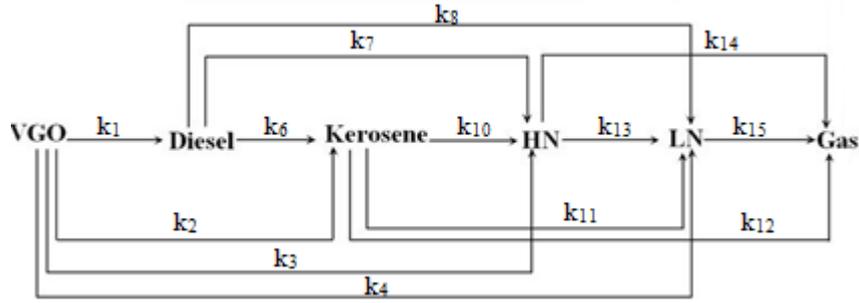


Figure 2. Reaction network solution of the MINLP problem.

Table 2. Identified kinetic parameters in the MINLP problem.

Reaction	k_0 [$\text{m}^3 \text{h}^{-1} \text{mcat}^{-3}$]	E_a [kcal mol^{-1}]	k (at T_{mean}) [$\text{m}^3 \text{h}^{-1} \text{mcat}^{-3}$]	k_{rel} [-]
1. VGO \rightarrow D	$2.58 \cdot 10^5$	13.54	10.67	0.073
2. VGO \rightarrow K	$8.92 \cdot 10^{13}$	40.78	5.59	0.038
3. VGO \rightarrow HN	0.87	1.49	0.29	0.002
4. VGO \rightarrow LN	$3.54 \cdot 10^{11}$	33.60	4.66	0.032
6. D \rightarrow K	$9.97 \cdot 10^{10}$	31.62	5.78	0.040
7. D \rightarrow HN	0.98	0	0.98	0.007
8. D \rightarrow LN	771.25	8.26	1.63	0.011
10. K \rightarrow HN	10^7	19.13	6.4	0.044
11. K \rightarrow LN	10.07	67.20	$1.74 \cdot 10^{-21}$	$1.19 \cdot 10^{-23}$
12. K \rightarrow G	808.15	85.19	$2.12 \cdot 10^{-25}$	$1.45 \cdot 10^{-27}$
13. HN \rightarrow LN	10^5	14.40	2.17	0.015
14. HN \rightarrow G	1	0	1	0.007
15. LN \rightarrow G	$5.06 \cdot 10^4$	7.83	146.21	1

Model reduction and comparison

Consequently, reactions where k_{rel} was less than the threshold value 0.01 were eliminated from the reaction network. The derived kinetic model is shown in Figure 3. It can be seen that only eight reaction steps remains when using this particular threshold, resulting in a much simpler kinetic model. The accuracy of the reduced model was quantitatively evaluated by determining the correlation factor between the measured and calculated values (Eq. (9)). The calculated correlation factors for each component and the complete system are listed in Table 3.

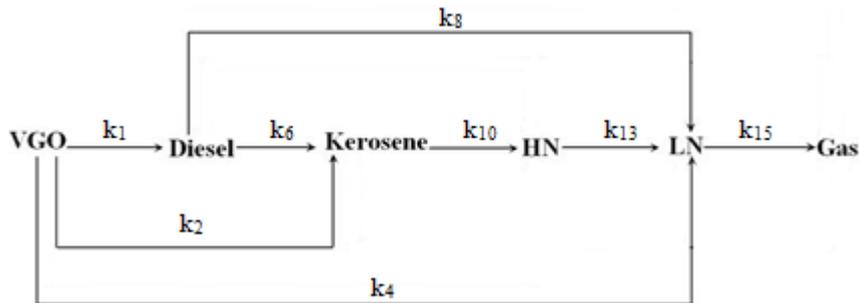


Figure 3. Reduced reaction network.

The accuracy of the model varies highly in case of different lumps. It can be considered as accurate in case of VGO, K and G lumps, while the accuracy is only moderate for D and HN and the identified kinetic parameter set was unable to predict the yield of LN. A possible solution for this problem is the modification of the objective

function in order to address the concentration changes more accurately for all components that need further consideration.

Table 3. Pearson correlation factors between measured and calculated values.

	VGO	D	K	HN	LN	G	Overall
Complete kinetic model	0.8934	0.4268	0.9597	0.7746	0.0441	0.8472	0.9333
Reduced kinetic model	0.8952	0.4068	0.9570	0.8494	0.0440	0.8474	0.9343

Conclusions and future work

In this study, we have presented the results of a development phase algorithm that would be capable to reduce kinetic networks automatically in case of lumped models describing hydrocracking process. This problem, where not only the kinetic parameters but also the existence of a reaction is a variable in the objective function, leads to the field of reaction network engineering. Solving the inverse problem, where the time series profiles of some components are known and the objective is to reconstruct the chemical reaction network, is a well-known technique that has its applications mainly in biochemistry and bioinformatics. However, those methods have not yet been applied in case of lumped models. Therefore it would be beneficial to thoroughly investigate the possible connections between the two fields of research, e.g. compute the sparsest realization of the chemical network, or apply an extended Kalman-filter to find the suitable kinetic parameters.

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