Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc
Petroleum & Coal 53 (1) 26-34, 2011

SIMULATION AND KINETIC MODELING OF VACUUM RESIDUE SOAKER-VISBREAKING

S. Reza. Seif Mohaddecy[1]* and Sepehr Sadighi[2]

[1]*Chemical Engineering Department, Arak Islamic Azad University, Arak, IRAN*
[2]*Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, UTM Skudai, Johor Bahru, 81310 Malaysia*

Received October 2, 2010, Accepted February 1, 2011

Abstract

In a refinery visbreaking is a complementary process to upgrade vacuum residue or bottom of barrels to the more precious stocks such as the fuel oil and gasoline. In this present work, visbreaking of vacuum residue in a commercial soaker-visbreaking plant is studied. The product of the visbreaking furnace is characterized to the light gas (C_1, C_2), LPG (C_3, C_4), gasoline (IBP-180^{o}C), gas oil (180-320^{o}C) and fuel (320^{+o}C). Afterwards to model the visbreaking process, a six-lump kinetic network with fifteen reactions and thirty kinetic parameters is developed. In this model, visbreaking furnace is modeled as a equal distributed heater whilst the soaker is modeled as a complete stirred tank reactor. After evaluating the rate of reactions by estimated kinetic parameters, it is confirmed that a reduced reaction network with seven reaction paths and fourteen kinetic parameters is appropriate to simulate the performance of the reactor with the same accuracy as complete network, which results the final AAD% of the model to 4.75%.

Key words: Visbreaking, Soaker; Lumped model; Upgrading.

1. Introduction

Visbreaking is a gentle non-catalytic thermal treatment which is used mainly to reduce the viscosity of heavy fractions such as atmospheric or vacuum residues for the production of gas, naphtha, distillates, and visbroken residue. Additionally, this process can be attractive to produce feedstock for catalytic cracking plants [2]. The process severity is controlled by the interchangeable operational variables (being essentially a first order reaction) such as temperature and the residence time [8]. There are two types of commercial visbreaking units: the coil or furnace type, and the soaker process. The coil-visbreaker is operated at high temperature and low residence time whilst in a soaker one by adding an adiabatic drum after the coil furnace, the product is held for a longer time so that the coil is kept at relatively lower temperature. Therefore, the heater duty and, in turn, the fuel consumption is only 70% of that for the coil-visbreaking process [7]. Worldwide, about 200 visbreaking units are under operation, and Europe alone accounts for about 55% of the total visbreaking capacity [7].

To effective design and perfect control of any process, a model is needed to predict product yields and qualities versus variables such as space velocity and temperature. However, the complexity of visbreaking feed and product makes it extremely difficult to characterize and describe its kinetic at a molecular level. One approach to simplify the problem is to consider the partition of the species into a few equivalent classes, the so-called lumps or lumping technique, and then assume each class is an independent entity. Developing simple kinetic models (e.g., power-law model) for complex catalytic reactions is a common approach as it can give basic information for reactor design and optimization. In this field, many investigations were reported in which visbreaking process was modeled with two-lump [1,6,9,], three-lump [2], 4-lump [4,14], five-lump [8] and 7-lump [15] approaches. In all these investigation, the experiments were carried out in a micro or pilot scale reactor.

The aim of this research is developing a simple yield predictor model, according to a six-lump reaction approach, to predict the most added value products consists of gas, LPG, gasoline, diesel and visbroken fuel oil in a commercial soaker unit. The main advantage of this

*corresponding author, mohaddecy@yahoo.com

work is its capability to predict LPG yield as an independent product. Another advantage is presenting a simple approach for the commercial visbreaking furnaces in which the temperature profile is also considered in the model.

2.Data gathering

2.1 Visbreaking feed

A commercial soker-visbreaker unit was chosen as a case study. This unit was designed to visbreak 20,000 barrel per day of a mixture of Vacuum Residuum and Slop Vacuum Gas Oil which are both taken from the vacuum tower; the composition of the fresh feed can vary slightly with time from start of run (SOR) to end of run (EOR). The specification of the combined feed, which was analyzed during this research, is shown in Table 1.

Table 1 Variation in properties of fresh vacuum gas oil

Property	Unit	Value
Sp.gr	-	1.006
Sulfur	wt%	3.19
Ni+Va	ppm	188

Distillation analysis (ASTM D1160)		
IBP	° C	303
5%	° C	409
10%	° C	457
20%	° C	503
30%	° C	543
50%	° C	585

2.2 Visbreaking Process

The visbreaking feed is charged to the coil furnace at the temperature about 340°C. The visbreaking furnace is constructed from two sections which are fired independently. After the coil furnace, the two hot streams coverage in a transfer line; then the mixed product is entered into the soaker drum. The specifications of cells and the soaker drum are presented in Table 2. The output product from the soaker drum is quenched by the cooled product to stop the more cracking reactions after the soaker to inhibit the coke formation. The combined stream is transferred to the fractionation tower and side strippers to separate the visbreaking products. The simplified process flow diagram of the described unit is depicted in Figure 1.

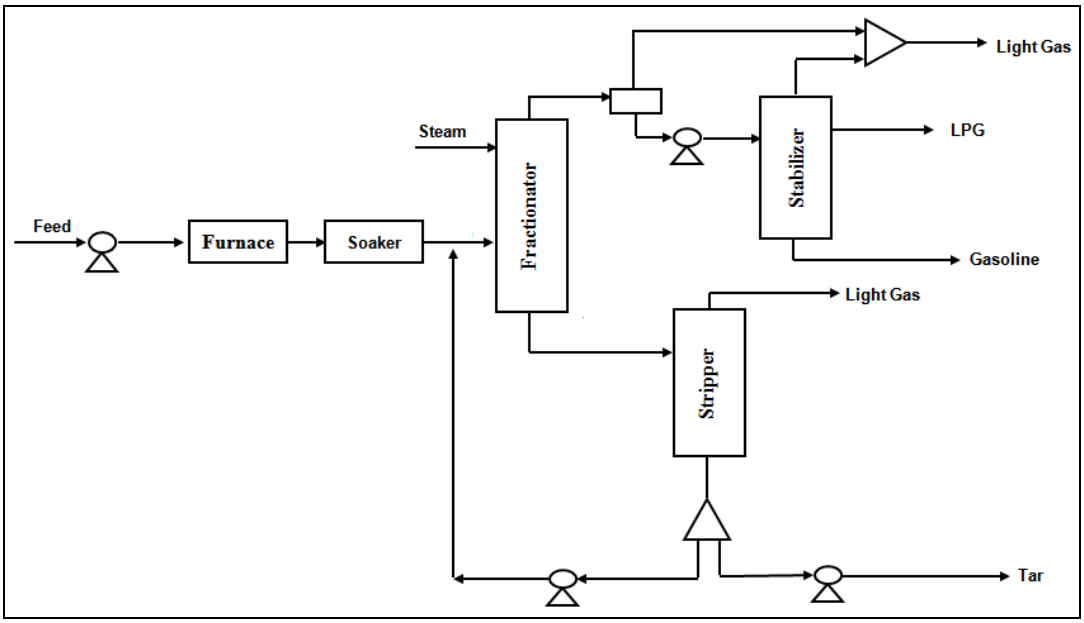

Figure 1 Block flow diagram of visbreaking process

Tab. 2 Specifications of the cell and soaker of the visbreaking unit

Coil specification		
Number of tubes	-	128
Number of convection tubes	-	76
Number of radiation tubes	-	52
Tube length	m	18.745
Outside diameter	m	0.114
Soaker specification		
Outside diameter	m	2.405
Length	m	16.5

Table 3 Feed flowrate and reactor operating condition

Case	Vacuum residue (kg/hr)	Inlet temperature (°C)	Outlet temperature (°C)
1	1.243E+05	326.5	439
2	1.286E+05	326	438.5
3	1.346E+05	324.4	440.7
4	1.193E+05	327.4	438.5
5	1.433E+05	324.8	441.3
6	1.313E+05	324.9	440.5
7	1.393E+05	324.8	439.3
8	1.156E+05	328.5	437.5
9	1.325E+05	324.8	440.5

During nine months of data gathering, nine set of data comprising of product flow rates, feed inlet temperature and soaker outlet temperature were gathered from the target commercial visbreaking process (see Table 3). As it is illustrated in Figure 2, light gases including C_1, C_2 and LPG, gasoline and tar are the output streams from the visbreaking plant. It is possible to take the gas oil product from the stripper tower, but it is usually blocked to mix up the gas oil as a cutter blend with the fuel oil. Performing mass balance around the unit showed that the error for all selected experiments was less than 2%, mainly related to the gross error for the measuring of the gas flow rates and maybe related to the coke formation. All products and feed samples were analyzed according to the ASTM standard procedures.

3.Visbreaking model

3.1 Kinetic model

This work considered seven lumps, i.e. vacuum residue (V), fuel (F), gas oil (D), gasoline (N), LPG and gas (G) to match all the main products in the commercial visbreaking unit. Because the type of the visbreaking unit was soaker, the rate of coking with time can be considered low [5], so that the coke as a main product was neglected. Fig. 2 shows the fifteen reaction pathways associated with this strategy, illustrating the complexity of the network if all possible pathways are considered. The model resulting from this strategy included thirty kinetic parameters which should be estimated using experimental data. However, some considerations are normally utilized to reduce the model complexity without sacrificing the accuracy [11,12,13].

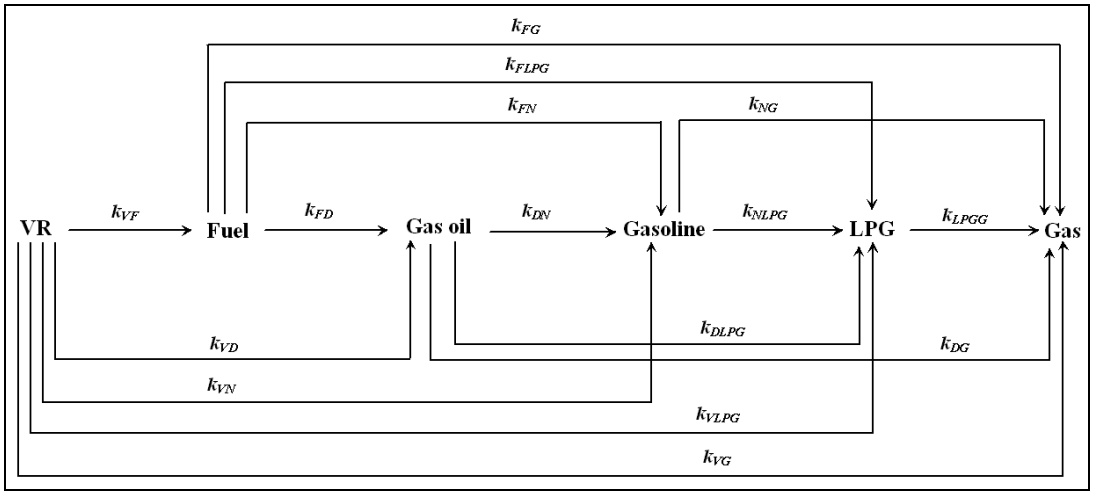

Figure 2 The complete six-lump kinetic model

For each reaction, a kinetic expression (R) is formulated as the function of the mass concentration of the reactants (*C*), furnace temperature (*T*) and kinetic parameters ($k_o$and *E*). The reaction of VGO hydrocracking to yield products is considered to be first order [2].

According to the above assumptions, the kinetic constants of the model were expressed as:

Vacuum gas oil (V): $$k_{Vj} = k_{0Vj} \exp(\frac{-E_{Vj}}{RT}) \quad (1)$$

where j in Eq. (1) represents all products lighter than the Vacuum residue lump;

Fuel (F): $$k_{Fj'} = k_{0Fj'} \exp(\frac{-E_{Fj'}}{RT}) \quad (2)$$

where j' in Eq. (2) represents all products lighter than the Fuel lump;

Gas oil (D): $$k_{Dj''} = k_{0Dj''} \exp(\frac{-E_{Dj''}}{RT}) \quad (3)$$

where j'' in Eq. (3) represents all products lighter than the light-diesel lump;

Gasoline (N): $$k_{Nj'''} = k_{0Nj'''} \exp(\frac{-E_{Nj'''}}{RT}) \quad (4)$$

where j''' in Eq. (4) represents all products lighter than kerosene; and

LPG (LPG): $$k_{LPGG} = k_{0LPGG} \exp(\frac{-E_{LPGG}}{RT}) \quad (5)$$

In Equations (1) to (5), T and R are the absolute value of the coil temperature of the visbreaking furnace and the ideal gas constant, respectively. Thus, the reaction rates (R) can be formulated as the following:

Vacuum residue (R_V): $$R_V = \sum_{j=V}^{G} k_{Vj} C_V \quad (6)$$

Fuel (R_F): $$R_F = k_{VF} C_V - \sum_{j=F}^{G} k_{Fj} C_F \quad (7)$$

Gas oil (R_D): $$R_D = k_{VD} C_V + k_{FD} C_F - \sum_{j=D}^{G} k_{Dj} C_D \quad (8)$$

Gasoline (R_N): $$R_N = \sum_{j=V}^{D} k_{jN} C_j - \sum_{j=N}^{G} k_{Nj} C_N \quad (9)$$

LPG (R_{LPG}): $$R_{LPG} = \sum_{j=V}^{N} k_{jLPG} C_j - k_{LPGG} C_{LPG} \quad (10)$$

Gas (R_G): $$R_G = \sum_{j=V}^{G} k_{jG} C_j \quad (11)$$

3.2 Mass Balance Equations

A soaker-visbreaking unit can be considered as two separated reactive equipment .The first part is the coils of the furnace which can be considered as an ideal plug-flow one in which the end effects were neglected [7], and the second is the soaker drum which can be considered as complete mixed reactor. So, the mass balance equation for the coil and soaker drum can be given as follows.

For the coil:
$$\frac{\partial(\upsilon C_j)}{\partial V_C} \pm R_j = 0 \tag{12}$$

For the soaker drum:
$$\frac{\Delta(\upsilon C_j)}{V_D} \pm R'_j = 0 \tag{13}$$

In Eqs. (12) and (13), j ranges from the vacuum residue lump (*V*) to the gas (*G*), *C* is the mass concentration of the lump, V_C is the volume of coil, V_D is the volume of drum; a negative sign indicates reactant (feed or VGO) and a positive sign products.

For the coil:
$$\frac{\partial(\rho\nu)}{\partial V_c} = 0 \tag{14}$$

For the soaker drum:
$$\frac{\Delta(\rho\nu)}{V_D} = 0 \tag{15}$$

$$X_j = \frac{C_j.\nu}{F_m} \tag{17}$$

$$\frac{1}{\rho} = \sum_{j=V}^{G} \frac{X_j}{\rho_j} \tag{18}$$

In Equations (14) to (18), ρ and ν are the stream density and volumetric flow rate through the reactor, respectively, F_m is the mass flow rate of the stream passing through the coil and X_j and ρ_j are the mass fraction and density of lump *j*, respectively.

After calculating the mass concentration and volumetric flow rate of each lump in the effluent stream of the reactor, the product yields can be found as the following:

$$Y_j = \frac{C_{j_{out}}.\upsilon_{out}}{F_m} \tag{19}$$

In Eq. (19), R_s is the recycle fraction of the lumps, which is mixed with the fresh feed.

3.3 Coil temperature model

In this work, it is supposed that there is an equal heat flux throughout the furnace to close the overall heat balance. Therefore, the following expression can be written for the temperature profile through the furnace tubes:

$$\frac{\partial T}{\partial z} = \frac{F_m.\left[(\sum_{j=G}^{V} X_j Cp_j.T)_{out} - (\sum_{j=G}^{V} X_j Cp_j.T)_{in}\right]}{L_t} \tag{20}$$

where T is the fluid temperature flowing the coil (reaction temperature), L_t is the total length of the tubes and Cp_j is the heat capacity of lump *j;* T_{co} and T_O are coil inlet and outlet temperatures, respectively.

Because the difference between the inlet and outlet temperature of the soaker drum in the understudy plant was negligible, it is modeled like an isothermal reactor that its temperature is equal to the coil outlet temperature.

3.4 Parameter Estimation

To estimate the kinetic parameters, the sum of squared errors,*SQE* , as given below, is minimized:

$$SQE = \sum_{n=1}^{N_t} \sum_{j=V}^{G} (Y_{jn}^{meas} - Y_{jn}^{pred})^2 \quad (21)$$

In Eq. (21), N_t, Y_{jn}^{meas} and Y_{jn}^{pred} are the number of test runs, the measured product yield and the yield predicted by the model, respectively.

The visbreaking model according to Equations (1) to (20) was coded and solved simultaneously using the Aspen Custom Modeler (ACM) programming environment (AspenTech, 2004) to evaluate the product yields (Y_{jn}). Then, to estimate kinetic parameters, Eq. (21) was minimized by sequential application of the NL2Sol and Nelder-Mead algorithms, which are both found in the Aspen Custom Modeler software.

To compare the simulated and measured product values, absolute average deviations (*AAD*) [11] were calculated by the following equation:

$$AAD\% = 100 \frac{\sum_{n=1}^{N_t} \sum_{j=F}^{G} \sqrt{\frac{(Y_{jn}^{meas} - Y_{jn}^{pred})^2}{Y_{jn}^{meas^2}}}}{N_t}\% \quad (22)$$

4. Results and Discussions

During the field study, nine sets of data consisting of flow rate of products, composition of gaseous products, distillation curve of cuts and soaker temperature were gathered from the target soaker-visbreaking plant. The Petro-sim process simulator was employed to lump the feed and products into components with the specific boiling-point ranges and properties, presented in Table 4, including gas (C_1&C_2), LPG (C_3&C_4), gasoline (IBP-180°C), gas oil (180-320°C), fuel(320^+°C) and vacuum residue. Hence, the process flow diagram of the visbreaking simulator can be shown as Fig. 3.

Table 4 Average properties of the visbreaking lumps

	IBP-FBP (°C)	Sp.gr	Heat capacity (kj/kg.°C)
Gas	C_1&C_2	0.364	1.86
LPG	C_3&C_4	0.55	1.97
Gasoline	IBP-180	0.739	2.4
Gas oil	180-320	0.806	2.6
Fuel	320^+	0.999	2.95

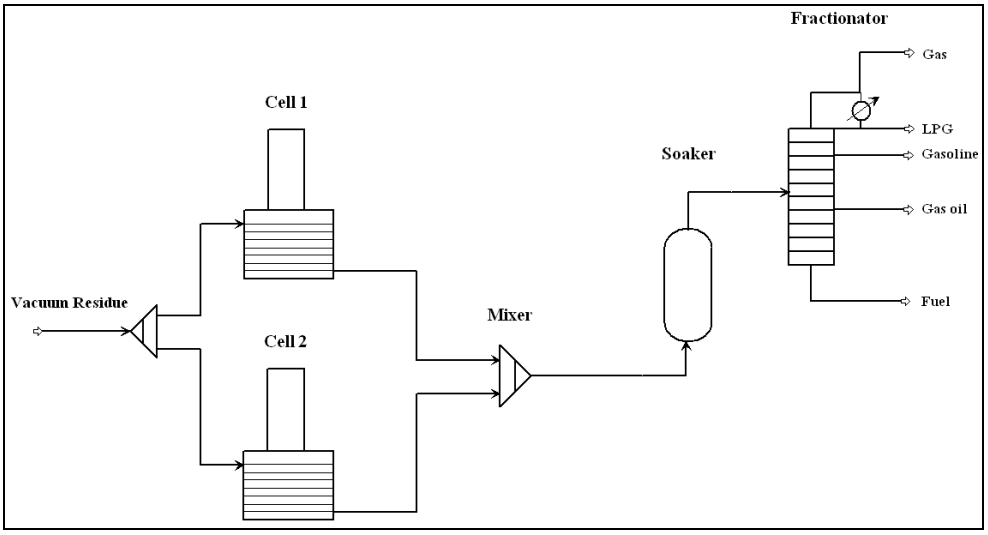

Figure 3 The scheme of the process flow diagram of visbreaking simulator

The thirty kinetic parameters for the assumed model (Fig.1) were estimated, using measured industrial data, reported in Table 5. In this table, the ratio of magnitude of all rate constants to the highest one (k_{VF} or vacuum residue to fuel) were calculated. After parameter estimation and simulation, the *AAD%* was 4.75% in comparison to the measured data.

Table 5 Kinetic parameters for the reaction network

Frequency Factor k_0 [$m^3.hr^{-1}.m^3\ cat^{-1}$]		Activation Energy E [kcal/mol]		Rate $k_o \exp(-E/RT_{mean})$	Order (to k_{VF})
k_{0VF}	243082	E_{VF}	8.70	520.98	1
k_{0VD}	6785.12	E_{VD}	11.10	2.66	5.11E-03
k_{0VN}	0	E_{VN}	31.11	0	0
k_{0VLPG}	0	E_{VLPG}	30.91	0	0
k_{0FG}	3034.89	E_{FG}	31.29	7.63E-07	1.46E-09
k_{0FD}	0	E_{FD}	29.08	0	0
k_{0FN}	91224.183	E_{FN}	19.53	0.093	1.78E-04
k_{0FLPG}	2184.96	E_{FLPG}	31.01	6.70E-07	1.29E-09
k_{0FG}	15776.3	E_{FG}	19.30	0.019	3.63E-05
k_{0DN}	0	E_{DN}	29.32	0	0
k_{0DLPG}	0	E_{DLPG}	29.26	0	0
k_{0DG}	1766.11	E_{DG}	30.66	6.91E-07	1.33E-09
k_{0NLPG}	1344.11	E_{NLPG}	12.12	0.256	4.92E-04
k_{0NG}	1.03799	E_{NG}	16.97	6.45E-06	1.24E-08
k_{0LPGG}	1344.11	E_{LPGG}	31.15	0	0

From Table 5 it can be concluded that I) the selectivity of the process to convert vacuum residue to fuel is the strongest reaction. Moreover, the fuel product is fairly stable (k_{FD} ~0 and k_{FN} is low); therefore these phenomena can justify the highest yield of fuel in the visbreaking process, II) Gas oil is fairly stable in the visbreaking process (k_{DN}, k_{DLPG} ~0), III) most of the produced gas and LPG of the visbreaking product are from thermal cracking of gasoline which can be the reason for low yield of gasoline in the visbreaking process, and IV) LPG cannot be converted to gas in the visbreaking process which is rational due to the stability of C_3 and C_4 chains.

After eliminating the low rate reaction paths (~0) and predicting the yields again, the *AAD%* of resulted reduced model were found to be still 4.75% which can be considered acceptable thus justifying the removal of the less important reactions.

The simplified reaction-path network for the seven-lump hydrocracking model is shown in the Fig. 4, designated the reduced model.

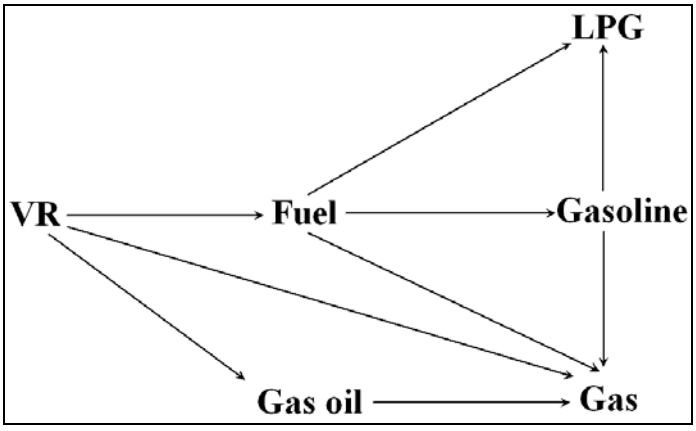

Figure 4 The complete six-lump kinetic model

Figs. 5, 6 and 7 show the comparison between the measured and predicted product yields. As it can be observed, acceptable mappings are realized.

The *AAD%* of all lumps is presented in Table 6. As it can be observed, the simulated yields for the nine commercial data, for the vacuum residue, fuel, gas oil and gasoline are in good agreement with the actual data. It was thought that the high *AAD%* for the LPG and gas lumps were for the reason of the difficulty of their measurement in the commercial unit, creating large gross error. In addition, there are existed several vents in the gas system for which flow rates were not reported in the test runs. Because, the yield of these lumps, especially LPG and gas, were low, a little deviation could make a flagrant *AAD%*.

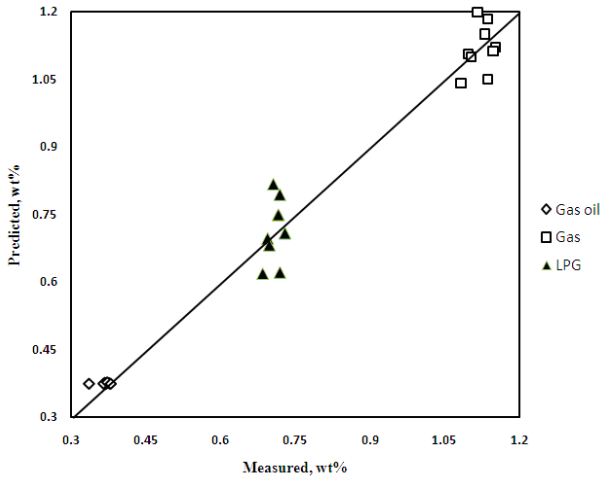

Fig. 5 Comparison between the measured yields and the predicted yields of gas, LPG and gas oil.

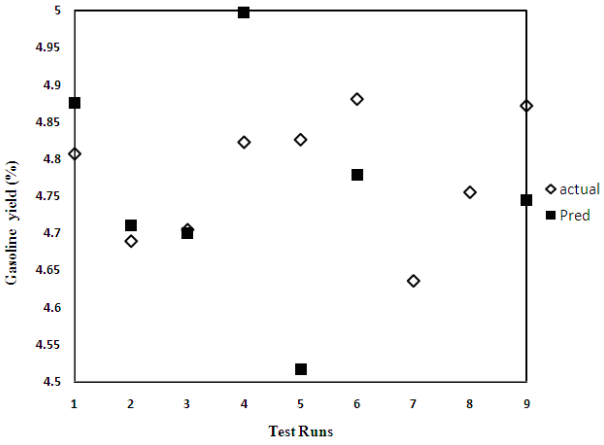

Fig. 6 Comparison between the measured yields and the predicted yield of gasoline.

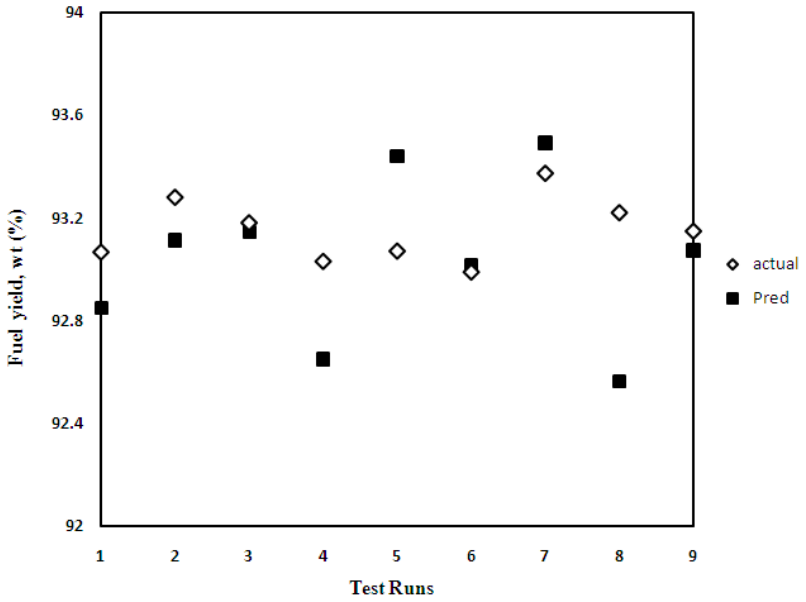

Figure 7 Comparison between the measured yields and the predicted yield of fuel

Table 6 AAD% of model prediction in comparison to measured data

Lump	*AAD%*	*Lump*	*AAD%*
Fuel	0.24	LPG	10.52
Gas oil	2.49	Gas	7.57
Gasoline	6.24	Ave%	4.75

5. Conclusions

In this study, a new six-lump kinetic model for a commercial vacuum residue visbreaker was proposed. The model was included of vacuum residue, fuel oil, gas oil, gasoline, LPG and light gas as the lumps. The advantages of the model over the previous works were considering the gas and LPG as different lumps which can be helpful for the better economical evaluation of the process. It is an important aspect related to the requirement of a refinery to re-optimization of operating conditions.

Nine sets of industrial data gathered from a soaker-visbreaking unit were used to estimate the apparent activation energies and frequency factors. For the modeling of the visbreaking furnace, it was supposed that there was an equal heat flux throughout the furnace to close the overall heat balance. Moreover, the furnace and soaker drum were simulated as a plug ideal flow and a completely mixed reactors, respectively.

Product yields predicted by this model showed a good agreement with commercial test runs, with an absolute average deviation of about 4.75%. Results confirmed that the prediction was more accurate for heavy products than the light ones (gas and LPG). It was thought that the higher deviation for gas and LPG was probably because of difficulties in measuring all gaseous flows of the visbreaking process.

References

[1] Al Soufi, H. H., Savaya, Z. F., Moahmmed, H. K. and Al-Azami, I. A., "Thermal conversion (visbreaking) of heavy Iraqi residue", Fuel,1998, 67.

[2] Benito, A.M., Martinez, M.T., Fernandez, I. and Miranda, J.L., "Visbreaking of an asphaltenic coal residue", Fuel, 1995,74.

[3] Clarke, G. M. and Kempson, R. E., "Introduction to the design and Analysis of Experiments", London: Arnold,1997.

[4] Del Bianco, A., Anelli, P. M., Beltrame, P. L. and Carniti, P., "Thermal cracking of petroleum residues 1. Kinetic analysis of the reaction", Fuel,1993, 72.

[5] Dente, M., Bozzano, G. and Bussani, G., "A comprehensive program for visbreaking simulation: product amounts and their properties prediction", Computers Chem. Eng.,1997, 21.

[6] Di Carlo, S. and Janis, B., "Composition and visbreakability of petroleum residues", Chem. Eng. Sci.,1992, 47.

[7] Joshi, J.B., Pandit, A.B., Kataria, K.L., Kulkarni, R.P., Sawarkar, A.N., Tandon, D., Ram, Y. and Kumar, M.M., "Petroleum Residue Upgrading via Visbreaking: A Review", Ind. Eng. Chem. Res.,2008, 47.

[8] Kataria, K.L, Kulkarni, R.P., Pandit, A.B., Joshi, J.B. and Kumar, M., "Kinetic Studies of Low Severity Visbreaking", Ind. Eng. Chem. Res.,2004, 43.

[9] Krishna, R., Kuchhal, Y. K., Sarna, G. S. and Singh, I. D., "Visbreaking studies on Aghajari long residue", Fuel, 1988, 67.

[10] Montgomery, D. C. "Design and Analysis of Experiments", New York: John Wiley & Sons ,2001.

[11] Sadighi S., Ahmad A. and Mohaddecy S.R., "6-Lump Kinetic Model for a Commercial Vacuum Gas Oil Hydrocracke", Int. J. Chem. Reactor Eng.,,2010,8.

[12] Sadighi, S., Arshad, A., & Irandoukht, A., "Modeling a Pilot Fixed-bed Hydrocracking Reactor via a Kinetic Base and Neuro-Fuzzy Method". Journal of Chemical Engineering Japan, 2010b,43 (2), 174.

[13] Sadighi, S., Arshad, A., & Irandoukht, A., "Kinetic Study on a Commercial Amorphous Hydrocracking Catalyst by Weighted Lumping Strategy". International Journal of Chemical Reactor Engineering, 2010c,8 (A60).

[14] Trauth, D. M., Yasar, M., Neurock, M., Nasigam, A., Klein, M. and Kukes, S. G., "Asphaltene and Resid Pyrolysis: Effect of Reaction Environment", Fuel Sci. Technol. Int.,1992,10(7).

[15] Xiao, J., Wang, L., Chen, Q. and Wang, D., "Modeling for Product Distribution in Thermal conversion of Heavy Oil", Pet. Sci. Technol.,2002, 20.