Full Length Research Paper

Modeling of thermal cracking process in a crude oil refinery

Sepehr Sadighi and S. Reza. Seif Mohaddecy*

Project Manager, Catalysis and Nanotechnology Division, Catalytic Reaction Engineering Department, Research Institute of Petroleum Industry (RIPI) Iran

In a thermal cracking process, the molecular bonds of the liquid are broken to the lighter ones. Recently due to the availability of more heavy oils, the process interest was to yield light and middle distillate products. In this research, thermal cracking of vacuum residue in a commercial soaker-visbreaking plant is studied. The product of the process is characterized to the light gas (C_1, C_2), liquefied petroleum gases (C_3, C_4), gasoline (IBP-180°C), gas oil (180 to 320°C) and fuel (320$^+$°C). Then to model the visbreaking process, a six-lump kinetic network with fifteen reactions and thirty kinetic parameters is developed. In this model, visbreaking process is modeled as an equal distributed heater, and 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 reliable enough to simulate the performance of the reactor with the absolute average deviation ($AAD\%$) of 4.75%.

Key words: Kinetic model, visbreaking, lumped model.

INTRODUCTION

In the present day scenario the availability of more heavy crude oils has resulted in the increased production of atmospheric and vacuum residues and simultaneous decrease in light and middle distillate fractions (Singh et al., 2012). A visbreaker is a processing unit in oil refinery whose purpose is to reduce the quantity of residual oil produced in the distillation of crude oil and to increase the yield of more valuable middle distillates (heating oil and diesel) by the refinery. A visbreaker thermally cracks large hydrocarbon molecules in the oil by heating in a furnace to reduce its viscosity and to produce small quantities of light hydrocarbons (LPG and gasoline). The process name of "visbreaker" refers to the fact that the process reduces (that is, breaks) the viscosity of the residual oil. The process is non-catalytic (Gary et al., 1984; Speight et al., 2006).

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 (Joshi et al., 2008). Worldwide, about 200 visbreaking units are under operation, and Europe alone accounts for about 55% of the total visbreaking capacity (Joshi et al., 2008).

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 kinetics at a molecular level. Modern day rigorous

*Corresponding author. E-mail: Seifsr @ripi.ir.

simulators such as Aspen plus or Hysys from Aspen Technology do not have such restrictive limits on the total number of components, and it is possible to use a unique set of pseudo components for every petroleum assay stream (Sadighi et al., 2012). This approach increases the calculation time, however, and characterization of the streams and subsequent reports become unnecessarily complicated (Sadighi et al., 2012).

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 (for example, 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 discrete two-lump (Al-Soufi et al., 1988; Krishna et al., 1988; Di Carlo and Jenis, 1992), three-lump (Benito et al., 1995), 4-lump (Del Bianco et al., 1993; Trauth et al., 1992; Singh et al., 2012), five-lump (Kataria et al., 2004; AlHumaidan et al., 2013) and 7-lump (Xiao et al., 2002) approaches. In all these investigation, the experiments were carried out in a micro or pilot scale reactor. But, the common advantage of all of these presented models is their simplicity, less required computational time and the least needed structural information. Furthermore, the more sophisticated lumping models are continuous one that one of them was recently presented by Shadbahra et al. (2011).

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 fuel oil in a commercial soaker unit. The main advantage of this work is presenting a simple approach for the commercial visbreaking process in which the temperature profile of the furnace is also included in the model.

DATA GATHERING

Feed characterization

An Industrial 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.

Process description

The visbreaking feed is charged to the coil furnace at the temperature about 340°C. The visbreaking furnace is included of two sections fired independently. After the coil furnace, the two hot streams are drained into 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

Table 1. Feed characterization.

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

Distillation (ASTM D1160)	
Vol %	Temperature (°C)
IBP[1]	303
5	409
10	457
20	503
30	543
50	585

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

Coil specification	Unit	Value
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

soaker drum is quenched by the cold recycle stream to stop the cracking reactions, and so to inhibit the coke formation. Finally, 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.

During one year of data gathering, nine sets of data including product flow rates, feed inlet temperature and soaker outlet temperature were gathered from the target visbreaking process (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. Performing mass balance around the unit proved that the error for all experiments was less than 2%, mainly related to the gross error for the measuring of the gaseous products and maybe related to the coke formation. Moreover, the boiling range of VGO feed, fuel and gas oil samples are analyzed according to the ASTM D1160 standard procedure (ASTM Standard D1160-06, 2009) whilst the one for the gasoline sample is analyzed according to the ASTM D86 method (ASTM Standard D86-08a, 2009).

KINETIC MODEL

This work considers six lumps, that is, vacuum residue (V), fuel (F), gas oil (D), gasoline (N), LPG and gas (G) to match all main
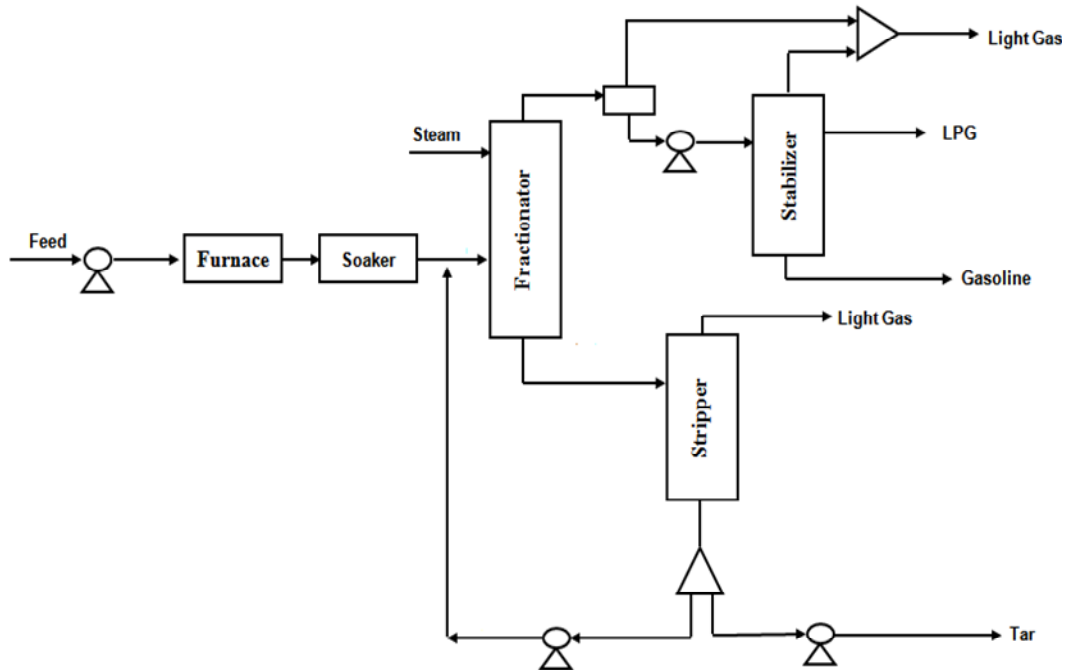
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[1] Initial Boiling Point

Figure 1. Block flow diagram of visbreaking process.

Table 3. Feed flow rate and reactor operating condition.

Case	Vacuum residue (kg/h)	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

products in the commercial process. The rate of coke formation with time can be considered low for a soaking visbreaker (Dente et al., 1997), and so the coke as a main product can be neglected. Figure 2 shows the fifteen reaction pathways associated with this strategy, illustrating the complexity of the network if all possible pathways are considered. So, the model consists of thirty kinetic parameters which should be estimated using experimental data. However, some considerations can be normally utilized to reduce the model complexity without sacrificing the accuracy (Sadighi et al., 2010b, c).

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_0 and E). The reaction of VGO hydrocracking to yield products is assumed first order (Benito et al., 1995).

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

Vacuum residue (V):
$$k_{Vj} = k_{0Vj} \exp(\frac{-E_{Vj}}{RT}) \tag{1}$$

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

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

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

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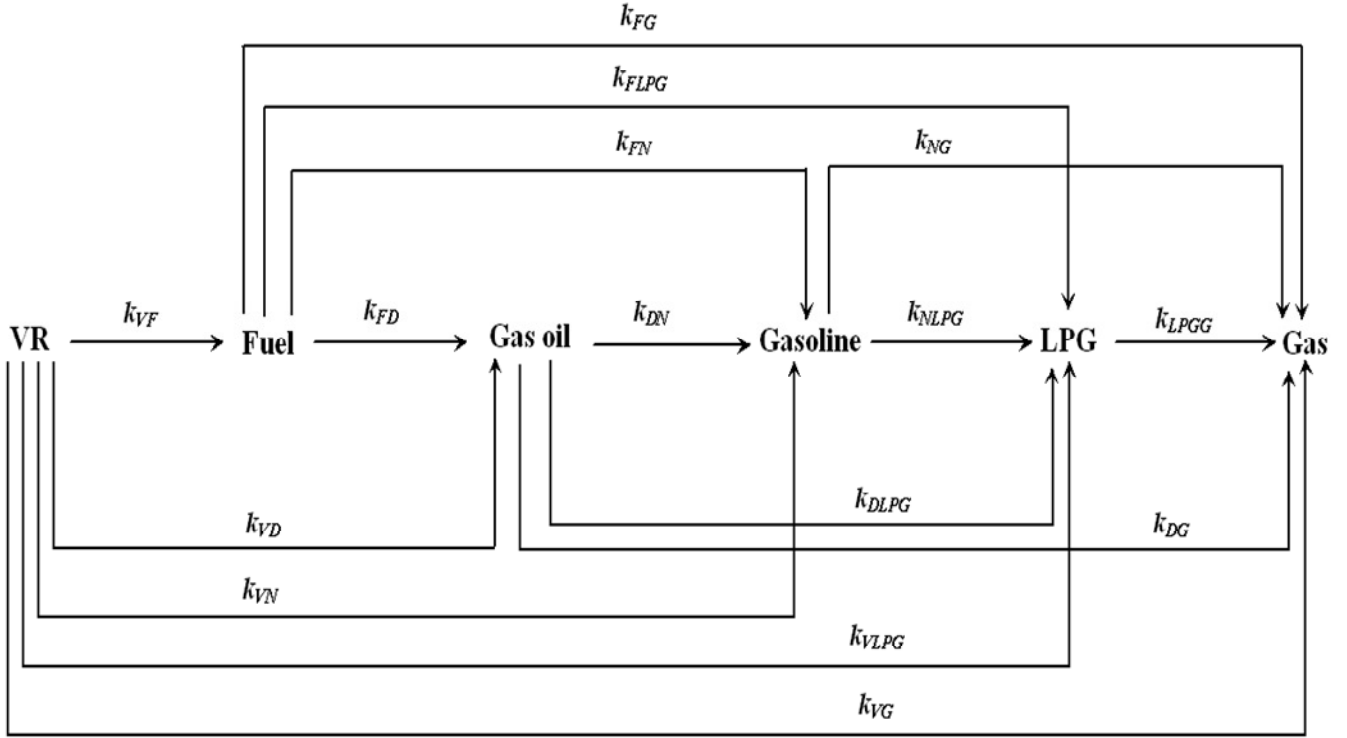$$k_{Dj''} = k_{0Dj''} \exp(\frac{-E_{Dj''}}{RT}) \tag{3}$$

Figure 2. The complete six-lump kinetic model.

where j'' in Equation (3) represents all products lighter than the Gas oil lump;

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

where j''' in Equation (4) represents all products lighter than Gasoline; and

LPG (LPG): $k_{LPGG} = k_{0LPGG} \exp(\dfrac{-E_{LPGG}}{RT})$ (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): $r_V = \sum\limits_{j=V}^{G} k_{Vj} C_V$ (6)

Fuel (r_F): $r_F = k_{VF} C_V - \sum\limits_{j=F}^{G} k_{Fj} C_F$ (7)

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

Gasoline (r_N): $r_N = \sum\limits_{j=V}^{D} k_{jN} C_j - \sum\limits_{j=N}^{G} k_{Nj} C_N$ (9)

LPG (r_{LPG}): $r_{LPG} = \sum\limits_{j=V}^{N} k_{jLPG} C_j - k_{LPGG} C_{LPG}$ (10)

Gas (r_G): $r_G = \sum\limits_{j=V}^{G} k_{jG} C_j$ (11)

MASS BALANCE EQUATIONS

A soaker-visbreaking unit is divided to two reactive parts in series. The first one is the coils of the furnace assumed as an ideal plug-flow reactor (Joshi et al., 2008), and the second one is the soaker drum which is considered as complete mixed reactor. So, the mass balance equations for the coil and soaker drum can be given as follows.

For the coil: $\dfrac{\partial(\upsilon C_j)}{\partial V_C} \pm r_j = 0$ (12)

For the soaker drum: $\dfrac{\Delta(\upsilon C_j)}{V_D} \pm r_j' = 0$ (13)

In Equations (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; r_j and r'_j are reaction rates; negative sign "-" is used for the feed (or VGO), and a positive sign "+" is used for products.

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

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

$$X_j = \frac{C_j.v}{F_m} \tag{16}$$

$$\frac{1}{\rho} = \sum_{j=V}^{G} \frac{X_j}{\rho_j} \tag{17}$$

In Equations (14) to (17), ρ and V 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; 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, the product yields can be found as the following:

$$Y_j = \frac{C_{j\,out}.v_{out}\,(1-F_R)}{F_m} \tag{18}$$

In Equation (18), F_R is the fraction of recycle of the lumps, which is mixed with the fresh feed.

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:

$$\frac{\partial T}{\partial z} = \frac{F_m\left[(\sum_{j=G}^{V}X_jCp_j.T)_{out} - (\sum_{j=G}^{V}X_jCp_j.T)_{in}\right]}{L_t} \tag{19}$$

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_0 are coil inlet and outlet temperatures, respectively.

Because the difference between the inlet and outlet temperatures of the soaker drum is negligible, it can be modeled similar to an isothermal reactor.

PARAMETER ESTIMATION

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

$$SQE = \sum_{n=1}^{N_t}\sum_{j=V}^{G} (Y_{jn}^{\,meas} - Y_{jn}^{\,pred})^2 \tag{20}$$

In Equation (20), 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 (19) is coded and solved simultaneously using the Aspen Custom Modeler (ACM) programming environment (AspenTech, 2006) to calculate the product yields (Y_{jn}). ACM is an easy-to-use tool for creating, editing and re-using models of process units. ACM uses an object-oriented modeling language to build the simulation applications; then, the entire process can be simulated by combining these applications on a graphical flow sheet.

To estimate kinetic parameters, Equation (20) is minimized by sequential application of the NL2Sol and Nelder-Mead algorithms which are both found in the Aspen Custom Modeler software.

Additionally, to compare the simulated and measured product values, absolute average deviations (*AAD*) are calculated by the following equation (Sadighi et al., 2010a):

$$AAD\% = 100\frac{\sum_{n=1}^{N_t}\sum_{j=F}^{G}\sqrt{\frac{(Y_{jn}^{\,meas} - Y_{jn}^{\,pred})^2}{Y_{jn}^{\,meas\,2}}}}{N_t}\% \tag{21}$$

RESULTS AND DISCUSSION

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 to 320°C), Fuel(320$^+$°C) and Vacuum residue. Hence, the process flow diagram of the visbreaking simulator can be shown as Figure 3.

The thirty kinetic parameters for the assumed model (Figure 1) were estimated, using measured industrial data, reported in Table 5. In this table, the ratio 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 4. Average properties of the visbreaking lumps.

Parameter	IBP-FBP (°C)	Sp. g	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
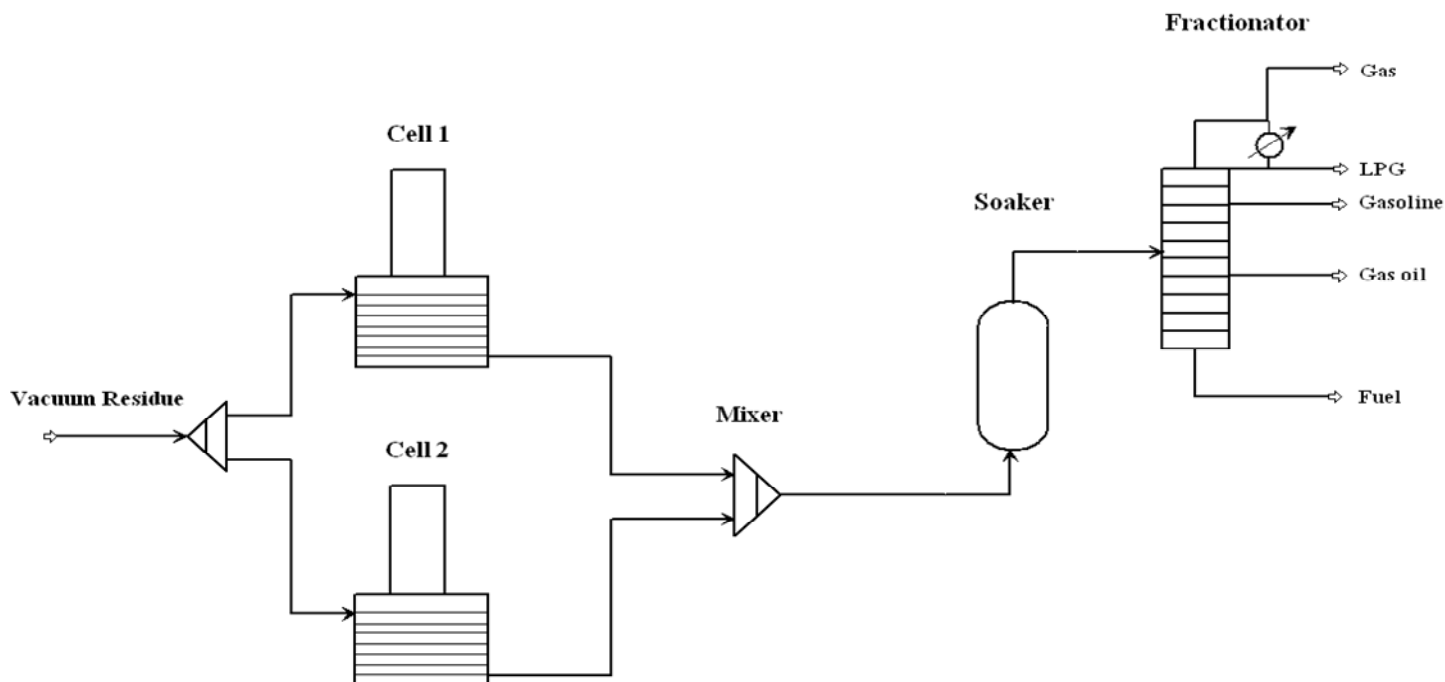
Figure 3. The scheme of the process flow diagram of visbreaking simulator.

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
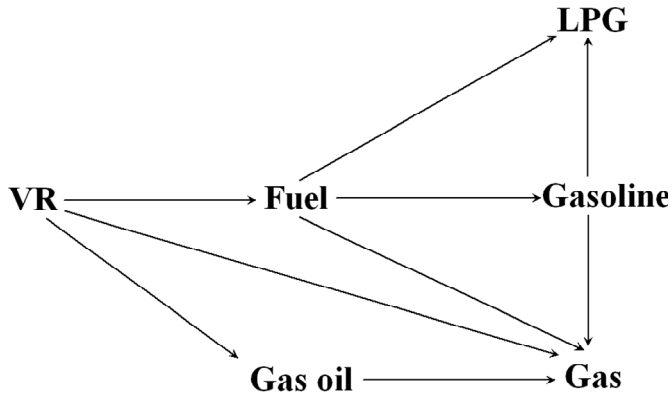
Figure 4. The complete six-lump kinetic model.

From Table 5 it can be concluded that I) the selectivity of the process to convert vacuum residue to fuel is the highest. 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 gas and LPG of the visbreaking unit are produced from the 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 re-predicting the yields, the *AAD%* of reduced model were found to be still 4.75%. This deviation is acceptable thus justifying the removal of the less important reactions.

The simplified reaction-path network for the six-lump visbreaking model is shown in the Figure 4 named as the reduced model.

Figures 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 supposed that the observed deviation was caused by assuming the average density for the VGO feed and visbreaking products (Equation 17) reported in Table 4, and also some fluctuations in the property of the feed (such as sulfur, nitrogen and aromatic contents) and also reactor pressure which were not included in the model. Furthermore, we cannot neglect the possibility of error measurements in gathering data obtained with some faults such as signal transmission, calibration and power fluctuation.

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%*.

Conclusions

In this research, a six-lump kinetic model for a commercial vacuum residue visbreaker was proposed. The model consists of vacuum residue, fuel oil, gas oil, gasoline, LPG and light gas as the discrete lumps. 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 satisfy 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 reason for higher deviation of gas and LPG was probably difficulties in measuring these gaseous flows.

Nomenclature

V , Vacuum residue lump.

F , Fuel lump.

D , Gas oil lump.

N , Gasoline lump.

LPG , LPG lump.

G , Light gas lump.

k , Rate constant (m^3 h^{-1} $m^{-3}_{cat.}$).

k_0 , Frequency factor (m^3 h^{-1} $m^{-3}_{cat.}$).

E , Activation energy (kcal/mol).

T , Absolute temperature (K).

R , Ideal gas constant (kcal $kmol^{-1}K^{-1}$).

j , All products lighter than the vacuum residue lump.

j' , All products lighter than the fuel lump.

j'' , All products lighter than the gas oil lump.

j''' , All products lighter than gasoline lump.

r , Reaction rate (kg $h^{-1}m^{-3}$).

C , Lump mass concentration (kgm^{-3}).

V_C , Coil volume (m^3).

V_D , Drum volume (m^3).

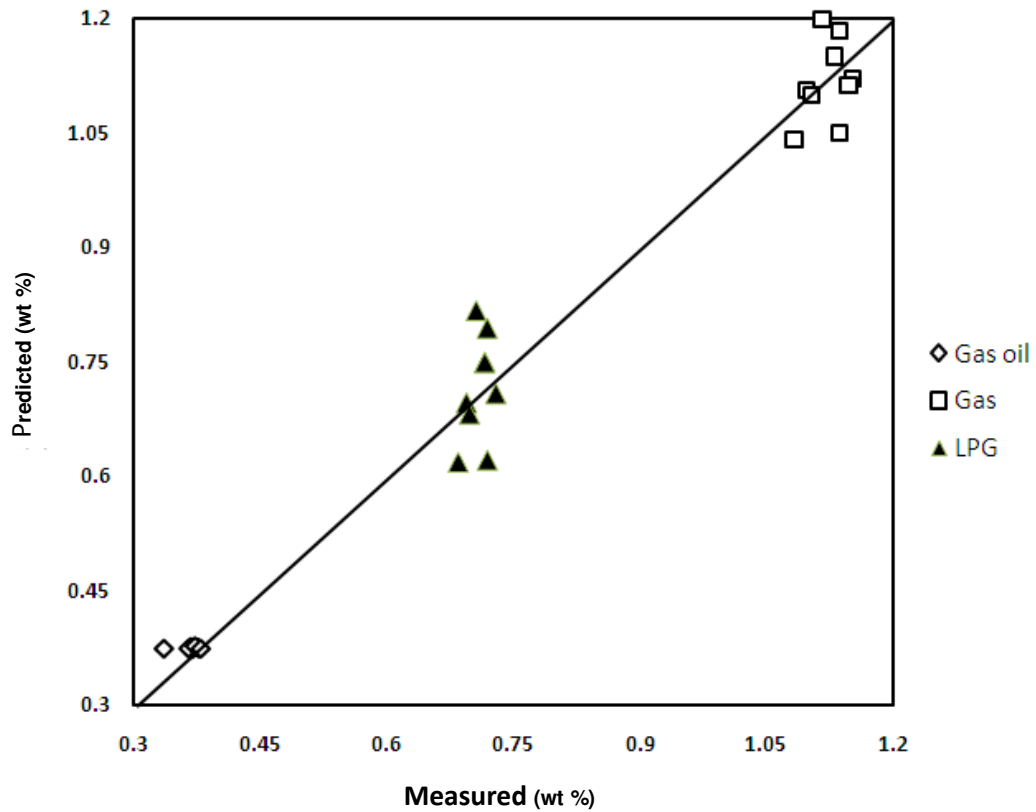ρ , Stream density (kg m^{-3}).

Figure 5. Comparison between the measured yields and the predicted yields of Gas, LPG and Gas oil.
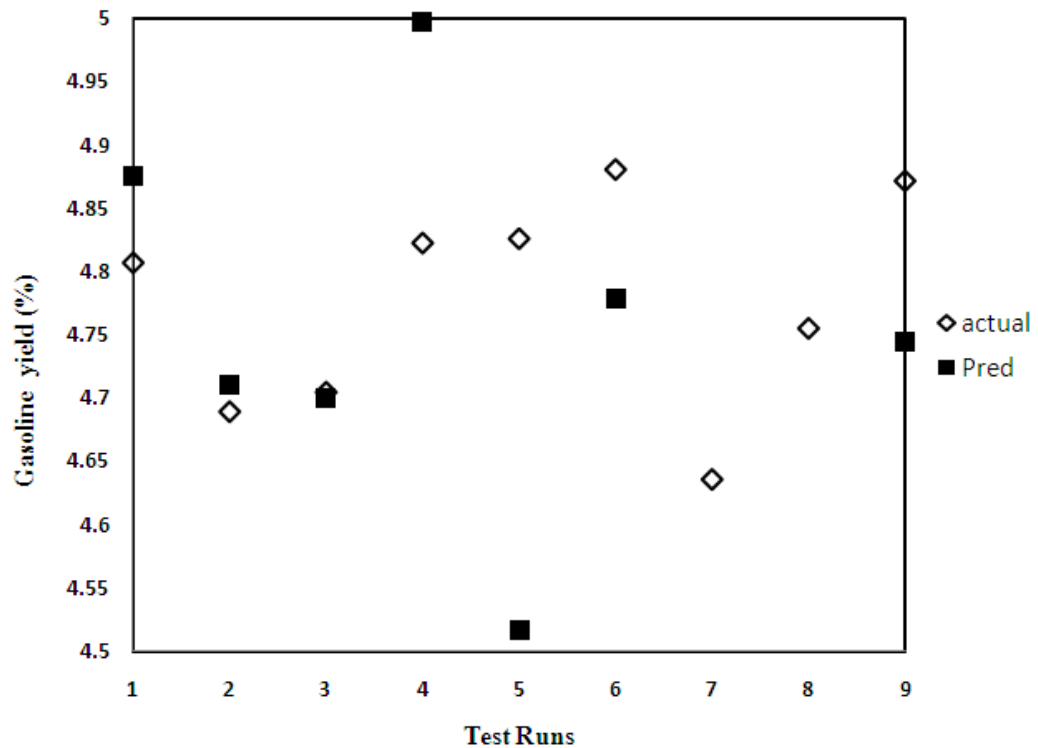

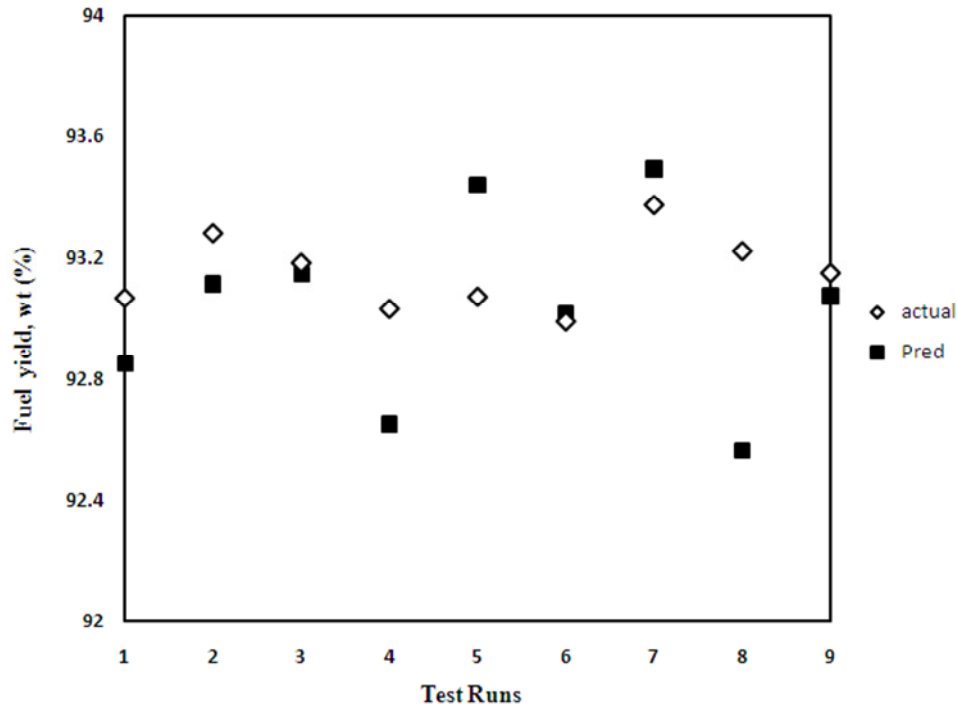**Figure 6.** Comparison between the measured yields and the predicted yield of Gasoline.

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

N_t, Number of test runs.

Y_{jn}^{meas}, Measured product yield (wt %).

Y_{jn}^{pred}, Yield predicted by the model (wt %).

$AAD\%$, Absolute average deviations.

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v, Volumetric flow rate (m^3 h^{-1}).

F_m, Mass flow rate of the stream passing through the coil (kg h^{-1}).

X_j, Mass fraction of lump.

ρ_j, Density of lump (kgm^{-3}).

F_R, Fraction of recycle of the lumps.

L_t, Total length of the tubes (m).

Cp_j, Heat capacity of lump (kJ/kg.°C).

z, Furnace tubes Length (m).

SQE, Summation of squared errors.

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