

Prediction of Product Distribution in the Delayed Coking of Iranian Vacuum Residue

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ABSTRACT: *The delayed Coker process as an upgrading process has the main impact on the productivity of the Refinery Complexes. To determine the impact of different operating conditions on the product yield distribution of the delayed coking process, several experiments were designed and conducted in a prefabricated pilot plant. The experiments were conducted on different Iranian vacuum residues at temperatures ranging from 420°C to 480°C and at atmospheric pressure. Reaction times were within the range of 5-120 minutes. A four lumps kinetic model has been developed based on the experimental results. The lumps—which included Volatile products, coke, feed, and an intermediate phase between coke and feed—were defined to precisely monitor the yield distribution of products throughout the reaction time. The feedstocks utilized were three different vacuum residues and their blends. The mixtures were produced by using different mixing ratios of the three vacuum residues. The Statistical analysis shows that this model has R-squared, RMSE, SSE, and MRE equal to 0.99, 0.022, 0.08, and 3.537%, respectively. This shows that the developed model is sufficiently accurate. The experimental and modeling results in this research reveal that by increasing the temperature, the yield of coke and gas is abated. However, the yield of the distillate is escalated. This investigation illustrates that the production of an intermediate reaction has the highest amount of activation energy in comparison with the other reactions. Also, the results indicate that the production reaction rate of coke has the highest amount compared to other reactions.*

KEYWORDS: *Delayed coking; Kinetic model; four lumps; Thermal cracking.*

INTRODUCTION

Increasing oil consumption and decreasing oil quality has been forced the oil refinery complex to produce maximum gasoline and minimum fuel oil through the upgrading process. This has happened by converting heavy cuts into lighter ones and improving their quality. This is also done to improve performance, increase profit, and minimize the waste and emissions of the refinery complex. Due to environmental constraints and governmental

restrictions different methods and technologies have been applied in the refinery complexes to conduct the upgrading process. Maximization of Refinery profit has the main impact on the appropriate upgrading processes. The vacuum distillation products including vacuum residue and gas oils are the main nominees to be converted in the upgrading processes. Due to the high impurities together with a high density of the vacuum residue and the necessity

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of minimization of fuel oil which is produced in refinery complexes, the upgrading of vacuum residue has the foremost importance. Some of the products of upgrading processes can be directly sent to pool products. However, the others were sent to the other processes. The delayed coker as one of the upgrading processes can convert a wide variety of feedstocks that have considerable metal (nickel and vanadium), sulfur, resins, and asphaltene content [1,2].

In delayed coking, the feed material is typically the residuum from vacuum distillation towers and frequently includes other heavy oils. Under the operating condition, the cracking process produces different products, the lighter fractions which are produced, are sent to a fractionation tower. A solid residuum of coke is also produced and remains within the drum. When the first drum has reached the maximum level, the feed is diverted to the second coke drum. After that, the drum is cooled by water, then opened, and prepared for decoking. Decoking involves using high-pressure water jets from a rotating cutter to fracture the coke bed and allow it to fall into the receiving area below [3]. Depending on the operating conditions and the kind of feedstock, different coke including sponge coke, needle, and shot coke could be produced in the process. The Coefficient of Thermal Expansion (CTE) is used as an index of the structure of the produced coke. If the value is between 0 to 4 the produced coke will have the needle structure. However, if the index is between 8 to 18 coke has a sponge structure. The shot coke (isotropic) has a CTE greater than twenty [3,4].

Due to the importance of the delayed coker process, many studies have been carried out to clarify different aspects of this process [1-20]. Table 1 provides different aspects of the highlighted history including experimental sections, the operating conditions such as temperature range, Reactor Residence time, reactor pressure, and feedstock.

Many studies have examined the kinetic modeling of the thermal cracking processes of heavy oil cuts. Proposing kinetic models of delayed coking still had two problems: the feedstock residue is tough and inaccurate to detail characterize based on the current analytical procedures and methodologies [6]. Moreover, due to the inaccuracies in the accurate estimation of the intrinsic rate constants. If the investigated feed is assumed as a simple feedstock introducing one discrete lumped, the developed kinetic model will be apparent and strongly depends on the feedstock

structure. In this case, in which feedstock contains several components that cause much complexity, a continuous lumping model may also be applied. By applying this methodology, the reactive mixture is assumed as a continuous lump in the reactor its properties change with the improvement of the reaction network [27,28].

In this research to analyze and optimize the delayed coking process, different experiments were designed and conducted in a prefabricated batch pilot reactor. Moreover, a four-lumps kinetic model was developed to predict the product distribution of the process [5]. The proposed kinetic model is completely applicable for delayed coking processes intended to predict coke and volatile yields. Also, it can be used to predict the coke induction period by an analytical method in these processes. Moreover, it can also be applied for kinetic analyses of the thermal cracking reactions and estimations of the activation energy of the reaction rates. The reaction network contains the reactions between vacuum residue, distillate, and the Intermediate species that form the coke. The existence of the intermediate phase will be approved by the validation of the developed model.

EXPERIMENTAL SECTION

Experimental apparatus and methodology

The Iranian vacuum residue used for conducting the experiments was obtained from three different refineries of vacuum distillation units. Feed was characterized according to standard ASTM / IP methods. Table 2 summarizes the essential physical and chemical specifications of the feedstock.

ASTM International stands for the American Society for Testing and Materials, is an international standards organization that develops and publishes voluntary consensus technical standards for a wide range of materials, products, systems, and services. In this research, ASTM D3289, ASTM D4294, ASTM D5291, ASTM D189, and ASTM D5863 were applied. The first test is the Standard Test Method for the Density of Semi-Solid and Solid Asphalt Materials (Nickel Crucible Method). The second test is the Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry. The third test is the standard Test Method for the Instrumental Determination of Carbon, Hydrogen, and Nitrogen

Table 1: Reported research on the delayed coking kinetic models.

Authors	Experimental Details	Conclusion
Magaril (1968)	Temperature range: 400°C. Residence time: 0 – 160 minutes Pressure: 1 MPa Reactor: Quartz test tube Feed: Resins	1- Coke formation is the result of the sedimentation and cumulation of asphaltenes. The rate of the coking is equivalent to the rate of asphaltenes precipitated.
Krishna et al. (1987)	Temperature range: 427-500°C. Pressure: 1.7 MPa Reactor: Bench-scale unit Feed: Aghajari long residue	1- E = 53.4 kcal/mol 2- A = 2.17× 10 ¹² 1/s 3- The yield of the kerosene fraction shows a relatively sharp increase after the 7wt% conversion level.
Takatsuka et al. (1988)	Temperature range: 400-450°C. Residence time: 0-450 minutes Pressure: 0.013-0.45 MPa Reactor: Flow reactor, semi-batch, autoclave Feed: Residual oil	1- E = 60 kcal/mol
Di Carlo and Janis (1992)	Temperature range: 455-500°C. Reactor: Pilot plant Feed : Rospo dimare , Balayam, Es sider atm.Residue	1- Activation energy for Rospo di mare = 31.3 kcal/mol 2- Activation energy for belayem = 68 kcal/mol 3- Activation energy for Es Sider = 78.8 kcal/mol 4- Thermal cracking follows a first-order equation.
Del Bianco et al. (1993)	Temperature range: 410-470°C. Residence time :0 – 120 minutes Pressure: 1 MPa Reactor: Batch Reactor Feed : Belaym vacuum residue(CCR-20.8 wt.%)	1- E ₁ = 49.4 kcal/mol 2- A ₁ = 31.973× 10 ⁻² 1/min 3- E ₂ = 41.4 kcal/mol 4- A ₂ = 25.808× 10 ⁻² 1/min 5- E ₃ = 63.9 kcal/mol 6- A ₃ = 40.× 10 ⁻² 1/min
Wiehe (1993)	Temperature range: 400°C. Residence time: 0 – 180 minutes Pressure: 1 MPa Reactor: Quartz tube reactor Feed: Cold lake VR & Arabian Heavy & Hondo & Canada & off-shore California	1- The pendant-core building block model has proved to be an excellent approximation considering its simplicity.
Benito et al. (1995)	Temperature range: 425-475°C. Residence time:5 –40 minutes Reactor: steel tubular Feed: Asphatenic Coal Residue (Spanish coal)	1- First-order thermal cracking. 2- E ₁ = 14.6 kcal/mol
Song et al. (1995)	Temperature range: 400-500°C. Residence time: 5 –80 minutes Reactor: batch tubular reactor Feed: Guadao VR	1- The first-order reaction at the temperature range of 400_500 C 2- E ₄₀₀₋₄₄₀ = 170.7 KJ/mol 3- A ₄₀₀₋₄₄₀ = 7.853×10 ¹⁰ 1/min 4- E ₄₆₀₋₅₀₀ = 179.9 KJ/mol 5- A ₄₆₀₋₅₀₀ = 9.241×10 ¹¹ 1/min
Wang et al. (1998)	Temperature range: 410°C. Residence time: 60 minutes Pressure:0.1 MPa Reactor: Autoclave Reactor Feed: Shengli vacuum residue	1- Structural parameters have been estimated among SARA fractions obtained from the feed and subsequent its thermal cracking.
Al-soufi et al. (1998)	Temperature range: 435-480 °C. Residence time: Coil 0.72-1.81 minutes Soaker 2.5-6.3 minutes Pressure: 0.7 MPa Reactor: Pilot plant Coil-Soaker type Feed: heavy Iraqi residue	1- First-order thermal cracking. 2- E = 23.7 kcal/mol
Zhou et al. (1999)	Temperature range: 400-460 °C. Residence time: 0-90 minutes Feed: Daqing, Guanshu and Liaohe short residue	1- Three different residues were separated into six pseudo components of saturating, light and heavy aromatics, light, and heavy asphaltenes based on their solubility in different solvents.
Xiao et al. (2002)	Temperature range: 400-500°C Reactor: Micro-reactor Feed: Heavy oil	1- E = 65.79 kcal/mol 2- The suggested model was based on the pseudo-elements based on their boiling cuts.
N. Sawarkar, A. B. Pandit and J. B. Joshi (2007)	Temperature range: 430- 475°C. Residence time: 5– 90 minutes Pressure: 0.2 MPa Reactor: autoclave bomb reactor. Feed: Arabian mix vacuum residue (AMVR)	1- the temperature within the core of the reactor and near the wall of the reactor was different. this difference was found in the range of 0-12 C. 2- Maximum coke formation (about 30.83 wt% for Arabian mix vacuum residue was found at the temperature of 475 C and at a reaction time of 30 minutes.

Table 2: Feedstock analysis.

Property	Standard Test	Feedstock Iranian vacuum residue
Density, gm cm ³	ASTM D3289	1.018
S, wt%	ASTM D4294	3.67
C (mass%)	ASTM D5291	85.8
H (mass%)		10.2
C/H ratio (mole %)		1.43
CCR, (wt%)	ASTM D189	18.46
V (ppm)	ASTM D5863	220
Ni (ppm)		65
Fe (ppm)		2
Saturates	SARA Test	23.2
Aromatics		48.0
Resins		21.3
Asphaltenes		7.5

in Petroleum Products and Lubricants. the fourth test is the Standard Test Method for Conradson Carbon Residue of Petroleum Products and the last one is the Standard Test Method for the Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by using Flame Atomic Absorption Spectrometry. [29-33]

Experimental Set-Up and Process

A Schematic configuration of the prefabricated batch pilot plant is introduced in figure 1. Different experiments were designed and conducted to investigate Iranian Mix Vacuum Residue (IMVR) coking behavior and, subsequently, to generate residual batch cracking kinetic data under coke conditions. The system consists of the reactor as the main part, the molten salt bath for the rapid heating of the reactor, and the cold oil bath for its rapid cooling. The system is used to obtain data for kinetic investigation.

The stainless steel reactor has a capacity of 1 liter. Also, the molten salt bath contains NaNO₃ and KNO₃ salts with a weight ratio of 50:50 had a melting temperature range of 300°C to 350°C and is being controlled by a digital temperature control system. Furthermore, the cold oil bath contains a type of synthetic oil that is kept

at room temperature. Products include light gases (C1-C4), liquid products (C5 + 500°C), coke (residue in the reactor and insoluble in toluene), and unconventional feed (residue in the reactor and soluble in toluene) are obtained after completion of the process.

100 g of the feed is used to carry out each test. The accuracy of weighing scales for feed and products is 0.1 g. Therefore, the percentage of weight error in the initial feedstock is 1.0%, but the percentage of error of returning products depends on their values. After filling the reactor with the feeds, it is preheated to 300°C, the height of the reactive mixture is slightly above the surface of the molten salt bath. This procedure causes the reactor to save time as it reaches the reaction temperature after immersion inside the reactor.

The reactions start at the moment the reactor is immersed in the molten salt bath. It then takes about 1-1.5 minutes for the reactor to reach the reaction temperature. The end of the reaction time happens when the reactor is taken out of them the molten salt bath and immersed in the cold oil bath, it also takes approximately 1 to 1.5 minutes to drop the reactor temperature below 300°C, which is suspended in the reactions. So, the loss of reaction time is largely neutralized.

After each test, the liquid and coke products are collected and weighed, and their efficiency is measured based on the values obtained. Moreover, the efficiency of light gases is calculated based on the mass balance between the products and the feed. To determine the amount of feed converted and the amount of coke in each reaction, after each test, the reagent is washed with toluene and passed through a previously weighed 42 mesh filter paper. The unconverted feed is soluted in toluene and passes through the filter paper, while the coke particles remain on the filter paper. To find the amount of unconverted feed, the toluene solvent is then recycled using a rotary dryer, and the weight percent is calculated from the unconverted feed weight.

After removing the unconverted feed from the reactor, the coke yield is measured by immersing the reactor with the coke in an oven for 30 minutes at 100°C, the temperature at which the solvent is completely dried out. The reactor is then weighed and subtracted from its initial weight to obtain the amount of the coke sedimented in the reactor. However, some coke particles remain on the filter paper when the reactor is washed with toluene.

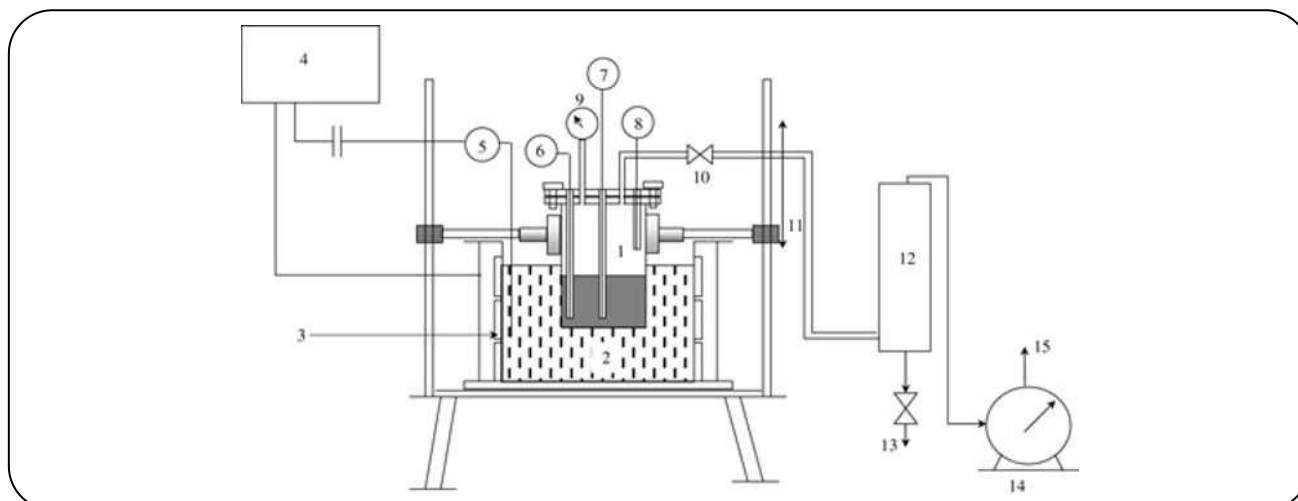


Fig. 1: The experimental set-up: (1) reactor (1 lit. capacity); (2) molten tin bath; (3) electrical heaters for kiln; (4) kiln's temperature controller; (5) thermocouple for the tin bath; (6) thermocouple for the reaction mass near the wall; (7) thermocouple for the reaction mass at the center; (8) thermocouple for the vapors of the reaction mass; (9) pressure indicator; (10) pressure release needle valve; (11) vertical moveable stand; (12) cold trap for the liquid product; (13) liquid product collector; (14) gas meter; (15) gas outlet.

The number of accumulated coke particles on the filter paper can be calculated from the difference between the dry weight of the filter paper and the filter paper including the coke particles. To determine the total amount of coke, the weight of particles is added to the weight of the coke accumulated in the reactor.

Liquid products are collected and weighed after the end of each test and the yields of the liquid products are also determined. The efficiency of light gases is also calculated based on the mass balance between the products and feed. It should be noted that the toluene and acetone solvents used in all experiments have an industrial grade and 95% purity. Also to prevent material leakage from the reactor during the reaction period carbon gaskets on the reactor are used. These gaskets have enough flexibility and resistance to work at temperatures below 500°C. These gaskets should be replaced after every five tests performed within the temperature range of 400 to 500°C.

Moreover, statistics which are collected from our prototype shown in Table 3.

RESULTS AND DISCUSSION

The experiments conducted were carried out at three temperatures (420, 450, and 480°C), and the residence time was 140 minutes. All information about product yield and the reaction conditions are provided in Table 4.

When a reaction takes place, all converted components of the feedstock are split to produce coke and volatile products. The kinetics of the reaction network was developed based on three pseudo components. The pseudo components were considered and defined based on physical and chemical properties. The concentration of VR diminishes over time (Fig. 5). Figs. 3 and 4 show the time courses of coke production and distillate, respectively, at different temperatures. For the various temperatures, distillate production climbs over time, peaking at about $t=40$ minutes. Therefore, it has a constant trend. So, the formation of distillate follows first-order kinetics at various temperatures.

The coke formation process (Fig. 3) demonstrates an induction period that diminishes as temperature rises, which arises to be consideration of the reaction of intermediates. The related reactions were demonstrated in Fig. 2.

In this model, (I) is the reaction intermediate in the coke generation and VR is the fraction of vacuum residue not converted at time t . We cannot experimentally determine the concentration of I at any given time. At any moment, we can find VR from $VR_{exp} = VR + I$, where VR represents the experimental data. Only the first-order reactions are considered when determining the kinetic parameters of this reaction scheme.

Table 3: Collected data from the pilot in detail.

Temp (°C)	time(min)	Coke	Distillate	Vacuum Residue
420	0	0	0	100
	5	0	3.2	96.8
	10	0	8	92
	15	2.9	16.8	80.3
	20	7.5	31.2	61.3
	30	14.7	49.3	36
	40	21.9	58.7	19.4
	50	23.6	64.8	11.6
	60	25.3	68	6.7
	90	27.4	71.4	1.2
	120	28.6	71.4	0
450	0	0	0	100
	5	1.6	8.6	89.8
	10	4.1	17.4	78.5
	15	8.2	35.4	56.4
	20	12.6	50.1	37.3
	30	15.2	59.3	25.5
	40	18	68.2	13.8
	50	21.4	74.1	4.5
	60	22.1	76.5	1.4
	90	22.8	76.8	0.4
	120	23.2	76.8	0
480	0	0	0	100
	5	3.5	15.6	80.9
	10	5.8	27	67.2
	15	9.1	48.3	42.6
	20	13.5	64.2	22.3
	30	16.8	70.7	12.5
	40	19.3	73.6	7.1
	50	20.8	74.2	5
	60	21	78.6	0.4
	90	21.4	78.6	0
	120	21.4	78.6	0

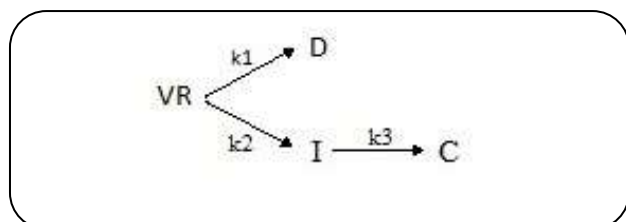


Fig. 2: Proposed four-lump kinetic model with three rate parameters.

The equations of reaction rate are demonstrated as follows:

$$\frac{dVR}{dt} = -(k_1 + k_2) \times VR \quad (1)$$

$$\frac{dI}{dt} = k_2 VR - k_3 I \quad (2)$$

$$\frac{dC}{dt} = k_3 I \quad (3)$$

$$\frac{dD}{dt} = k_1 VR \quad (4)$$

Solving the above differential equations determines the concentration of the pseudo components:

$$VR = VR_0 e^{-kt} \quad (5)$$

$$I = \frac{VR_0 k_2}{k_3 - k} \times [e^{-kt} - e^{-k_3 t}] \quad (6)$$

$$C = \frac{k_2 k_3 VR_0}{k_3 - k} \times [k_3 e^{k_3 t} - k e^{-kt}] \quad (7)$$

$$k_1 + k_2 = k \quad (8)$$

VR_0 is the initial value. The amount of distillate (D) can be calculated by this equation:

$$D = VR_0 - VR - I \quad (9)$$

Since the first-order reaction was selected, the rate constants including activation energy and frequency factors can be calculated by applying the equation which is formed by logarithms of the ratio of two different reaction rates and the least square methodology:

$$\ln \frac{k_1}{k_2} = \ln \left(\frac{A_1}{A_2} \right) - \frac{(E - E_2)}{RT} \quad (11)$$

A_1 , A_2 , A_3 as the frequency factors, and the activation energy E_3 were calculated using MATLAB program based on the optimization with a genetic algorithm.

Indeed, the reaction rate constants were determined by minimization of the difference of concentration values obtained by the experiments and calculations:

$$F = \sum_{i=1}^n |C_i^{\text{exp}} - C_i^{\text{calc}}|^2 \quad (12)$$

Where C_i^{exp} and C_i^{calc} describe the experimental and the estimated quantities of the components, respectively, at different reaction times and temperatures.

Product yields were calculated using the following equation:

$$\text{yield (wt\%)} = \frac{w_i}{w_{VR}} \times 100 \quad (13)$$

Where W_i ($i=C, D$, and I) is the fraction weight of the product species.

$$K = k_0 \times \left(\frac{T}{T_r} \right)^m \times e^{\left(\frac{-E}{RT} \right)} \quad (14)$$

In the above equations, m must be between 0 and 1. For the overall reaction, m is 0.309.

According to the optimization, the best value for $T_r = 315^\circ\text{C}$ is considered. Depending on previous studies [1-30] the cracking reactions are performed for the reactive mixture with more than 315°C . The rate constants including Frequency factors and Activation Energy are respectively demonstrated in Table 4 and Table 5.

The accuracy of the recommended kinetic model with data from Iranian crude oil was estimated using statistical parameters, such as the coefficient of determination (R^2), the root means square error (RMSE), and the mean relative error (MRE). The R^2 , RMSE, and MRE are calculated by the following equations:

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_{\text{exp}i} - y_{\text{cal}i})^2}{\sum_{i=1}^n (y_{\text{exp}i} - y_{\text{exp}})^2} \quad (15)$$

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_{\text{exp}i} - y_{\text{cal}i})^2} \quad (16)$$

$$\text{MRE} = 1 - \sum_{i=1}^n \left| \frac{y_{\text{exp}i} - y_{\text{cal}i}}{y_{\text{exp}i}} \right| \times 100 \quad (17)$$

$$\text{SSE} = 1 - \sum_{i=1}^n \sum_{j=1}^m (y_{\text{exp}ij} - y_{\text{cal}ij})^2 \quad (18)$$

Where y_{exp} and y_{cal} are the experimental and calculated values, respectively, y_{exp} is the mean of the experimental values and n is the total number of data points. The optimal values of R^2 , RMSE, and MRE are 1.0, 0.0, and 0.0, respectively. Table 6 introduces the results of the statistical tests.

It is generally accepted that the production of coke mainly depends on asphaltene cracking. The curves in Fig. 3 indicate that the yield of coke formation depends on the temperature. For various temperatures, the maximum coke production occurs at different residences time. From Fig. 3, it can be observed that coke formation does not start at 420°C unless a reaction time of 10 minutes is attained. At 450°C , coke formation starts at 5 minutes.

Table 4: Rate constants for different reactions at different operating temperatures.

RATE CONSTANT ($10^{-2} \times 1/\text{MIN}$)			
TEMPERATURE ($^{\circ}\text{C}$)	T=420	T=450	T=480
K ₁	1.580	3.733	7.979
K ₂	0.551	1.227	2.479
K ₃	87.400	129.383	182.396
K	2.845	5.692	10.459

Table 5: Activation energy and frequency factor for different reactions proposed in the reaction network.

	Activation energy (kcal 1/mol)	Frequency factor, (1/min)
E ₁	9.3	4.58E+02
E ₂	9.2	2.82E+02
E ₃	4.9	2.99E+02
E	8.4	6.49E+02

Table 6: The Results of Statistical tests

SSE=0.080
RMSE=0.022
MRE=3.537
R ² _{VR} =0.992
R ² _{k₁} =0.999
R ² _{k₂} =0.990
R ² _{k₃} =0.943

Distillate yield increased as process severity increased. Fig. 4 shows the progressive compositional variations of distillates as a function of severity. For the various temperatures, the maximum distillate production occurs at different residence times. At 420°C, the maximum distillate yield occurs after 140 min. Meanwhile, at 450°C, it occurs near 90 min. At 480°C, it happens before one hour has elapsed.

As the graph illustrates the conversion of vacuum residue is higher in high temperatures. At higher temperatures (450°C and 480°C), the conversion of VR was enunciated; the maximum amount of conversion of Iranian vacuum residue was near 99% at 480°C for the reaction time of 80 min (Fig. 5).

In the delayed Coker process, the Coke induction period is the main parameter. Indeed, in this process when the reaction reaches a certain extent, the Coker rate is significantly accelerated to reach the Coke induction period. Definitely, feedstock properties have an enormous

impact on the characteristics of coke formation during thermal conversion. The coke induction period has highly affected by the reaction temperature. Consequently, the higher the reaction temperature the lower the coke induction period. The reduction does not have a linear trend. So, the reduction has a higher rate at higher temperatures [37]. To Calculate, the coke induction period the Intermediate rate of formation is set to zero:

$$\frac{dI}{dt} = k_2 VR - k_3 \times \left[\frac{VR_0 \times k_2}{k_3 - k} \times (e^{-kt} - e^{-k_3 t}) \right] = 0 \quad (19)$$

So, the coke induction period is estimated by applying the following equation:

$$t = \frac{\ln(k_3) - \ln(k)}{k_3 - k} \quad (20)$$

Fig. 6 provides coke induction periods with different reaction temperatures. Based on experimental data, the coke induction periods for 420°C, 450°C and 480°C, are 4.051, 2.525 and 1.663 minutes respectively.

CONCLUSIONS

A blend sample of Iranian vacuum residues was prepared for a process of delayed coking in a batch pilot set-up. Four lumps kinetic model was developed to predict coke and volatile yield components in a delayed coking process at atmospheric pressure and temperatures within the range of 420-480°C.

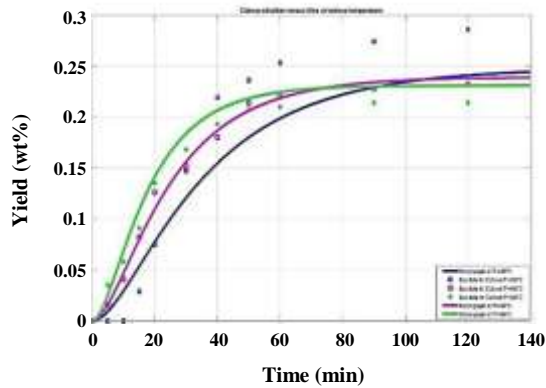


Fig. 3: Deduction between experimental and predicted values of coke at different temperatures.

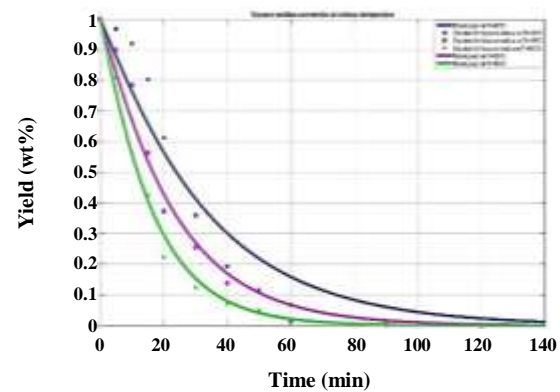


Fig. 5: Deduction between experimental and prediction of the model of VR at different temperatures.

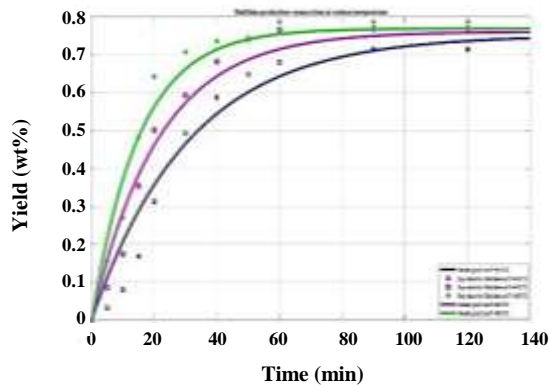


Fig. 4: Deduction between experimental and prediction of the model of distillate at different temperatures.

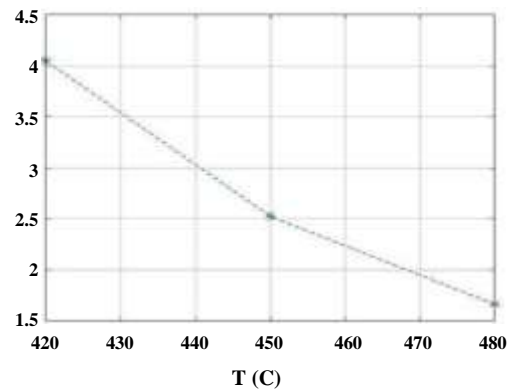


Fig. 6: The Coke induction period at 420°C, 450°C, and 480°C.

The results showed that the activation energy of the coke production from the intermediate phase has the highest value in comparison with the other activation energies. The rate of coke production from the intermediate phase is also the highest. The intermediate phase was converted into coke as soon as it reached its maximum value in the network reaction.

Moreover, the results showed that the energy needed for activation of the coke reaction is the lowest (Table 4). Furthermore, the rate of intermediate reaction is the lowest in the network reaction.

So, the kinetic model is completely applicable to predict coke and volatile yields at atmospheric pressure and conventional temperatures in delayed coking processes. Additionally, the model is applied to predict the incipient of coke production in delayed coking processes. It is shown that by increasing the reaction temperature,

the coke induction period is also decreased.

Nomenclature

°C	Degree of centigrade
Cal.	Calculated result
E	Activation energy
exp.	Experimental result
I	Intermediate component
K	Kinetic rate
K_{0i}	Frequency factor
N	Number of specially selected data
Temp.	Temperature
Y.	Production yield
°	Degree
/	Divided into
Σ	Summation
IMVR	Iranian mix vacuum residue

C	Coke, wt%
D	Distillates, wt%
SARA	Saturates, aromatics, resins, asphaltenes
SSE	The sum of the square of errors
VR	Vacuum residue, wt%
VR ₀	The concentration of vacuum residue at zero reaction time, wt%
W _i	The weight fraction of product species obtained, g
W _{VR}	The weight fraction of VR charged, g

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