Iranian Journal of Oil & Gas Science and Technology, Vol. 7 (2018), No. 3, pp. 53-64
http://ijogst.put.ac.ir

Prediction of the Products Yield of Delayed Coking for Iranian Vacuum Residues

Farshad Torabi Esfahani[1], Javad Ivakpour[2], and Mohammadreza Ehsani[3*]

[1] Ph.D. Student, Department of Chemical Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran
[2] Associate Professor, Upgrading and Optimization Technologies Group, Petroleum Refining Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran
[3] Professor, Department of Chemical Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran

Received: October 24, 2017; *revised*: November 09, 2017; *accepted*: January 17, 2018

Abstract

In this work, new correlations are proposed to predict the products yield of delayed coking as a function of CCR and temperature based on the experimental results. For this purpose, selected Iranian vacuum residues with Conradson carbon residue (CCR) values between 13.40-22.19 wt.% were heated at a 10 °C/min heating rate and thermally cracked in a temperature range of 400-500 °C in a laboratory batch atmospheric delayed coking reactor for 2 hours. The amount of distillate (C_{5+}-500 °C) and coke yield were measured in all the experiments, and the gas (C_1-C_4) product yield was calculated based on mass balance between products and feedstock in each experiment. According to the developed functions, products yield changes with CCR value linearly and is a power function of temperature. The further investigation of the results show that by a 1 wt.% increase in CCR value, the distillate yield decreases by about 2.1 wt.%, but the amount of coke and gas yields rise by 1.2 wt.% and 0.9 wt.% respectively.

Keywords: Product Yield, Delayed Coking, Thermal Cracking

1. Introduction

In recent years, delayed coking processes are the most conventional process to upgrade heavy oils or vacuum residues (VR's) because of its high profitability and well consistency with many feedstocks (Castaneda et al., 2014; Sawarkar et al., 2007; Speight, 2011). The main products of this process are generally gas (C_1-C_4), distillate (C_{5+}-500 °C), and coke (Ancheyta, 2013). The products yield and their purities could be affected by many parameters. The cracking reactions of heavy oils or vacuum residues involve many hydrogenation and dehydrogenation reactions by cracking C-S, C=C, and C≡C bonds in the feedstock and converting them to the products or primary reactants for the secondary reactions (Bayati et al., 2016; Afzal et al., 2014). Therefore, the main parameters affecting the products yield and their qualities are feedstock characteristics and operational severities.

---

* Corresponding Author:
Email: ehsanimr@cc.iut.ac.ir

The important parameters in feedstock characteristics are Conradson carbon residue (CCR), hydrogen to carbon atomic ratio (H/C), SARA fractions, and API gravity. Moreover, the temperature, pressure, heating time schedule, and reflux ratio are dominant parameters in operational conditions (Speight, 2011). Although in delayed coking processes, all feedstock characteristics can affect products yield and their purities, CCR value is the main parameter because it identifies the concentration of components with higher coking ability of a feed in a thermal cracking process. In addition, this parameter has a dependency on other key parameters such as H/C ratio and SARA fractions and has an inherent relation with API gravity. Hence, CCR value is the most important parameter to identify a vacuum residue in a coking process and could be considered as the dominant factor in feedstock selection for delayed coking processes (Wiehe, 2008). CCR value directly depends on SARA fractions, and its corresponding value for each fraction is in the following order: Asphaltene > Resin > Aromatic > Saturate; the concentration of impurities usually follows the same order, too (Al-Saffar et al., 2001; Shishavan et al., 2011; Riazi, 2005; Carrillo et al., 2013). The results showed that coke and gas yields increase by raising CCR value, while a reduction in distillate yield could be seen consequently (Ancheyta et al., 2013; Speight, 2013). It is known that saturates are components with no tendency to produce coke (low CCR value), while asphaltenes have the most propensity for it (Riazi, 2005; Speight, 2007). In one research, Ancheyta et al. (2013) compared the applicable functions to predict the products yield of delayed coking process; they are linearly related to CCR value and operational severities. It is reported that the developed correlation by Volk et al. (2002) had the best consistency to predict coke yields. Volk's correlation to predict coke yield showed that by increasing CCR value by 1 wt.% or the coke drum pressure by 5 psig, the coke yield approximately increases by 1 wt.%; also, for each 15 °F increase in the coke drum temperature, coke yield is reduced by 1 wt.% in a temperature range of 900–950 °F, in a pressure range of 6–40 psig, and in a micro carbon residue (MCR) range of 16-29 wt.%.

In this research, some Iranian VR's were thermally cracked in a laboratory batch atmospheric delayed coking reactor in a temperature range of 400 to 500 °C for 2 hours, and new product functions were correlated to predict products (gas (C_1-C_4), distillate (C_{5+}-500°C), and coke) yield. Furthermore, the correlated functions were validated by the results achieved from delayed coking by a similar feed.

2. Experimental section

2.1. Material

Some Iranian VR's with special CCR values were used as the feedstocks as presented in Table 1. According to the propensity of products yield to the CCR values of feeds, a wide range of VR's was selected based on comparing the values of this special characterization. For example, VR_1 and VR_8 have the smallest and largest CCR values respectively. The other identified VR's are in medium CCR values, applicable to upgrading processes of Iranian refineries.

Table 1

Properties of Iranian vacuum residues.

Property	ASTM method	Iranian VR's							
		VR_1	VR_2	VR_3	VR_4	VR_5	VR_6	VR_7	VR_8
Specific gravity at 25/25°C	**D 3289**	1.013	1.011	1.004	1.011	1.018	1.018	1.025	1.032
CCR (wt.%)	**D 189**	13.40	16.59	16.74	17.07	17.15	18.37	22.03	22.19
Asphaltene (mass %)	**SARA test**	6.3	4.8	3.9	5.3	4.9	9.0	12.1	13.7
Sulfur (mass %)	**D 4294**	3.27	3.62	3.35	3.29	3.23	3.88	3.82	4.42
Vanadium (V) + Nickel (Ni) (ppm)	**D 5863**	94	203	164	267	391	240	344	318

2.2. Experimental setup

Figure 1 shows the schematic diagram of the experimental set-up for the thermal cracking of feedstocks (Safiri et al., 2015). The coking reactor and all the connected tube lines were made of stainless steel 316 which is highly temperature- and corrosion-resistant. The reactor volume was 500 ml.

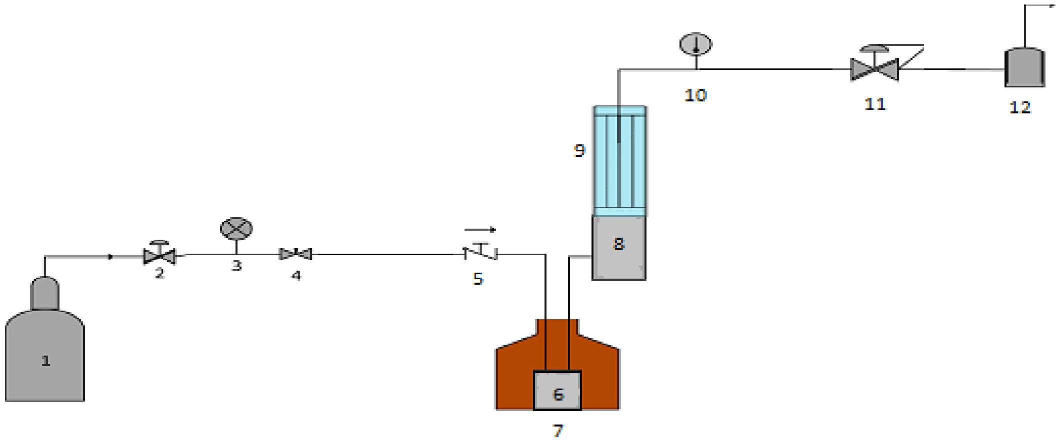


Figure 1
A schematic diagram of the experimental setup: 1) nitrogen source, 2) regulator, 3) pressure gauge, 4) needle valve, 5) check valve, 6) autoclave, 7) furnace, 8) storage tank, 9) condenser, 10) thermometer, 11) back-pressure regulator, and 12) gas scrubber.

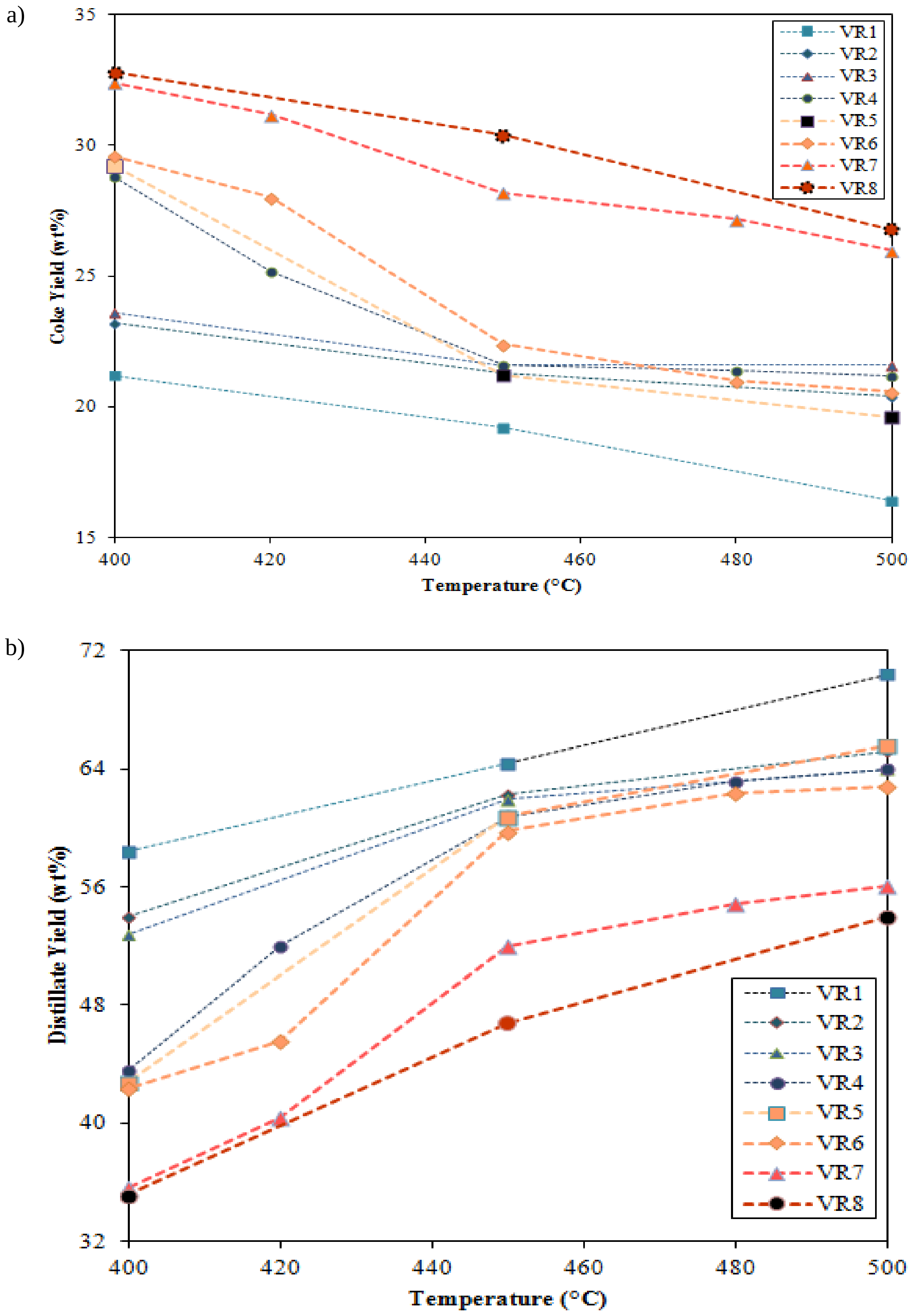
2.3. Experimental procedure

In each test, 25 grams of feed was used in a batch atmospheric reactor, and nitrogen flow was used at atmospheric pressure during each test. The reactor was located inside a furnace that provided the required heating in two steps. First, the heating rate was set at a rate of 10 °C/min until the reactor temperature reached its desired value; it was then remained at this temperature for 2 hours. After that, the furnace is turned off and the reactor is cooled to ambient temperature. The coke and distillate yields were measured and gas yield was calculated based on the mass balance between the products and feedstock; by measuring the weight of the reactor before and after the coking process, the coke yield could also be calculated. Moreover, the amount of distillate yield was calculated based on the accumulated distillate in the storage tank. Weight measurements have been performed by using a one-digit balance. Hence, because of 25 grams of feed used in each test, the products yield has an error of ±0.4 wt.%.

3. Result and discussions

3.1. Measurement of products yield

In the delayed coking process, the conventional industrial temperature in different instruments of the coking sections is usually in the range of 380 to 500 °C (Speight, 2011; Ancheyta et al., 2013; Wiehe, 2008). In this study, the cracking of Iranian VR's with special CCR values in the range of 13.4 to 22.19 wt.% at 400-500 °C was examined in an atmospheric delayed coking reactor, and their products yield was measured. According to the influence of CCR value on the products yield, a wide range of CCR values were selected for Iranian VR's. Figure 2 shows the results of products yield in the performed tests.


a)
35
30
25
20
15
Coke Yield (wt%)
400
420
440
460
480
500
Temperature (°C)
VR1
VR2
VR3
VR4
VR5
VR6
VR7
VR8
b)
72
64
56
48
40
32
Distillate Yield (wt%)
400
420
440
460
480
500
Temperature (°C)
VR1
VR2
VR3
VR4
VR5
VR6
VR7
VR8

c)

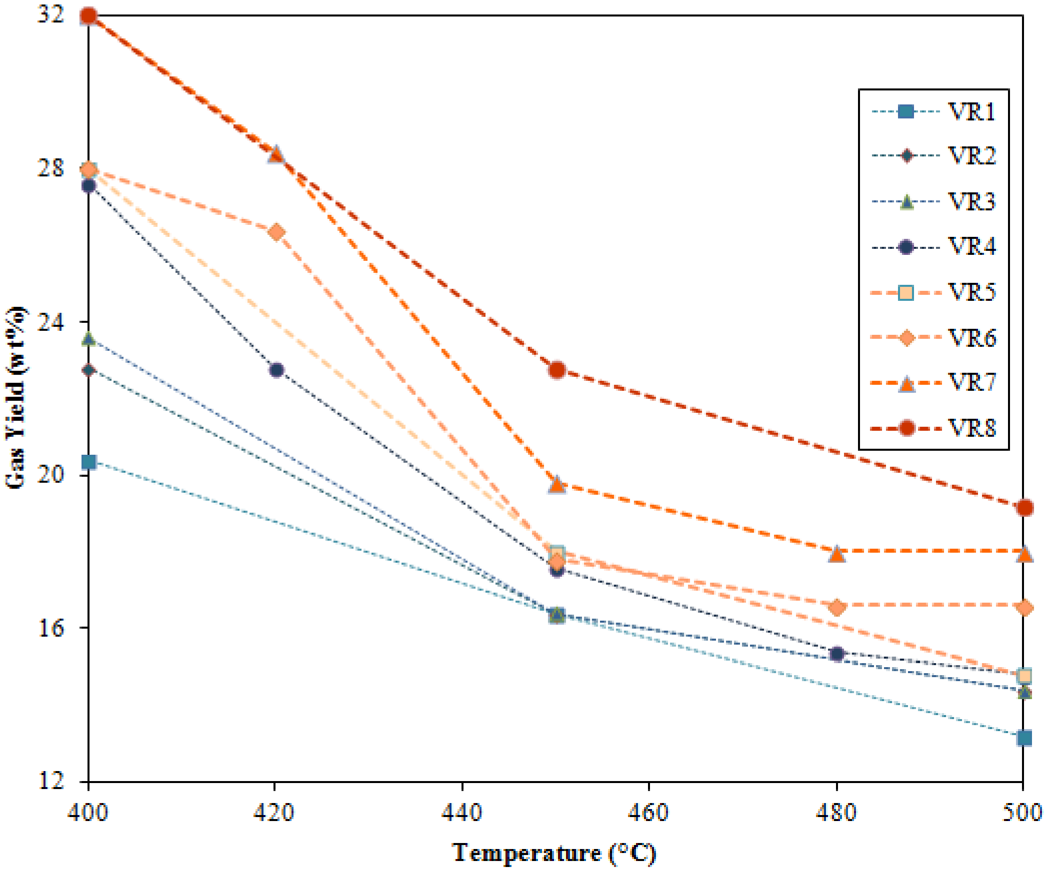


Figure 2

Experimental product yields.

According to Figure 2, it seems that the products yield can be considered as a linear function of CCR value. They have a significant deviation from the experimental results regarding temperature, especially at temperatures higher than 450 °C. In addition, it is concluded that the highest gas yield and coke yield is achieved in VR_8 with the highest CCR value (at 400 °C), which means the lowest distillate yield. Moreover, the highest distillate yield belongs to VR_1 with the lowest CCR value at the highest temperature (500 °C). The results confirm that CCR value directly depends on the concentration of the components with a higher coking ability in a VR that has a higher tendency to form coke. In addition, by increasing the temperature, hydrocarbons with higher initial boiling points can leave the coking reaction condition earlier. Therefore, as the temperature rises, the distillate yields increases. It is expected that the average boiling point of distillate increases in this condition. On the other hand, higher temperature could result in the cracking of the hydrocarbon branches from the coking components. Hence, by increasing temperature, the coke yield drops, but distillate yield will increase consequently. Furthermore, by increasing CCR value, the amount of asphaltene meso-phase (a special separated phase of asphaltene produced during delayed coking process) increases (Speight, 1998; Wiehe et al., 1993; Wang et al., 2009). The researchers showed that the asphaltene meso-phase could be converted to coke and gas products (Wiehe et al., 1993; Wang et al., 2009). Increasing the amount of CCR value of the feedstock could increase the coke yield and gas yield in the process simultaneously. Furthermore, by increasing the temperature of the process, the rate of reactions between free radicals could increase exponentially (Sawarkar et al., 2007; Ancheyta, 2013; Speight, 2013), whereas the needed time to produce gas (C_1-C_4) components is limited. Therefore, the gas yield falls by increasing temperature, but liquid yield increments consequently. From the above discussion, it can be concluded that the similar trend could be seen for the yields of both coke and gas products by changing temperature and CCR value in delayed coking processes (Jia et al., 2009; Schaborn et al., 2001).

3.2. Developed products yield prediction

In one research, Ancheyta et al. (2013) developed the applicable correlations to predict products yield from delayed coking processes in different conditions for a number of vacuum residues. The results showed that a linear function of CCR values of feedstocks and operational conditions could be efficiently applicable to predicting products yield. Therefore, in the first step Equations 1-3 were developed from the experimental results of Figure 2 to estimate coke, distillate, and gas yields for Iranian vacuum residues with optimized parameters:

$$Coke(wt.\%) = 31.2783 + 1.2317CCR - 0.0650T \qquad R^2=0.88 \tag{1}$$

$$Distillate(wt.\%) = 10.9604 - 2.1042CCR + 0.1832T \qquad R^2=0.89 \tag{2}$$

$$Gas(wt.\%) = 100 - Coke(wt.\%) - Distillate(wt.\%) \qquad R^2=0.87 \tag{3}$$

In Equation 1-3, CCR and temperature (*T*) are in weight percentage (wt.%) and degree of Celsius (°C) respectively. Also, these equations are developed for atmospheric pressure, for temperature range of 400 to 500 °C, for a CCR value between 13.4 and 22.19 wt.%, and for the heating scenario mentioned in section 2.2. According to Equations 1-3, for a defined feedstock, the amount of distillate yield increases by about 1.8 wt.% for a 10 °C increment in temperature, whereas coke yield and gas yield decrease by about 0.6 wt.% and 1.2 wt.% respectively. Also, it can be seen that by increasing CCR value of a feedstock by 1 wt.% at a constant reactor temperature, the coke yield and gas yield rise by about 1.2 wt.% and 0.9 wt.% respectively, while the distillate yield drops by up to 2.1 wt.% consequently.

However, regarding the results of Figure 2 for the trends of the products yield, it can be seen that products yield trends are not properly defined by a linear function for Iranian vacuum residues. Therefore, a power function could be considered for products yield estimation as follows:

$$yield = A + B \times CCR + C \times T + D \times (T - TR)^{e} \tag{4}$$

where, A, B, C, D, TR, and *e* are the constants defined by curve-fitting based on the experimental results. According to this point and after optimizing the parameters, Equations 5-7 were developed to estimate coke, distillate, and gas yields as follows:

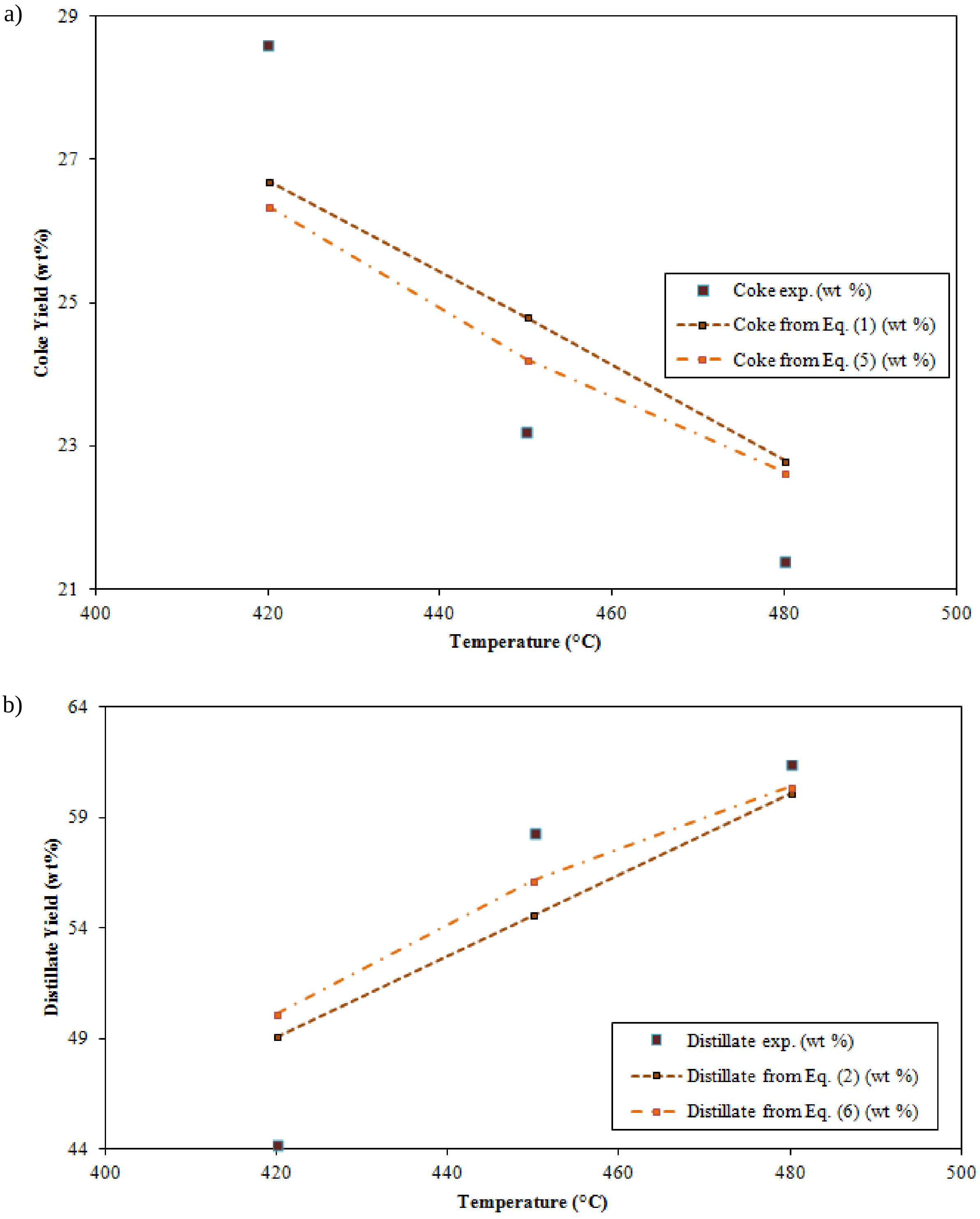
$$Coke(wt.\%) = 289 + 1.2410CCR - 262.6(T - 353.9)^{0.0200} \qquad R^2=0.90 \tag{5}$$

$$Distillate(wt.\%) = -2.1350CCR + 52.51(T - 370.4)^{0.1367} \qquad R^2=0.91 \tag{6}$$

$$Gas(wt.\%) = 100 - Coke(wt.\%) - Distillate(wt.\%) \qquad R^2=0.91 \tag{7}$$

Comparing the precisions of Equations 1-3 and Equations 5-7, it can be concluded that power functions could predict the results precisely. It is also shown that the distillate yield shows more dependency to temperature comparing the coke yield. The power functions are also consistent with the power function proposed by researchers for the kinetic models of the coking process (Sawarkar et al., 2007; Speight, 2011; Ancheyta, 2013; Wiehe, 2008).

For validation, the experimental products yield from the delayed coking of a similar VR is compared with the results of Equations 1-3 and Equations 5-7. Therefore, an Iranian VR sample with a CCR value of 18.46 was thermally cracked in the reactor at different temperatures. The products yield is measured by the procedure mentioned in section 3.1. Figure 3 shows the experimental and predicted results of products yield from a selected VR in a temperature range of 420 to 480 ºC.



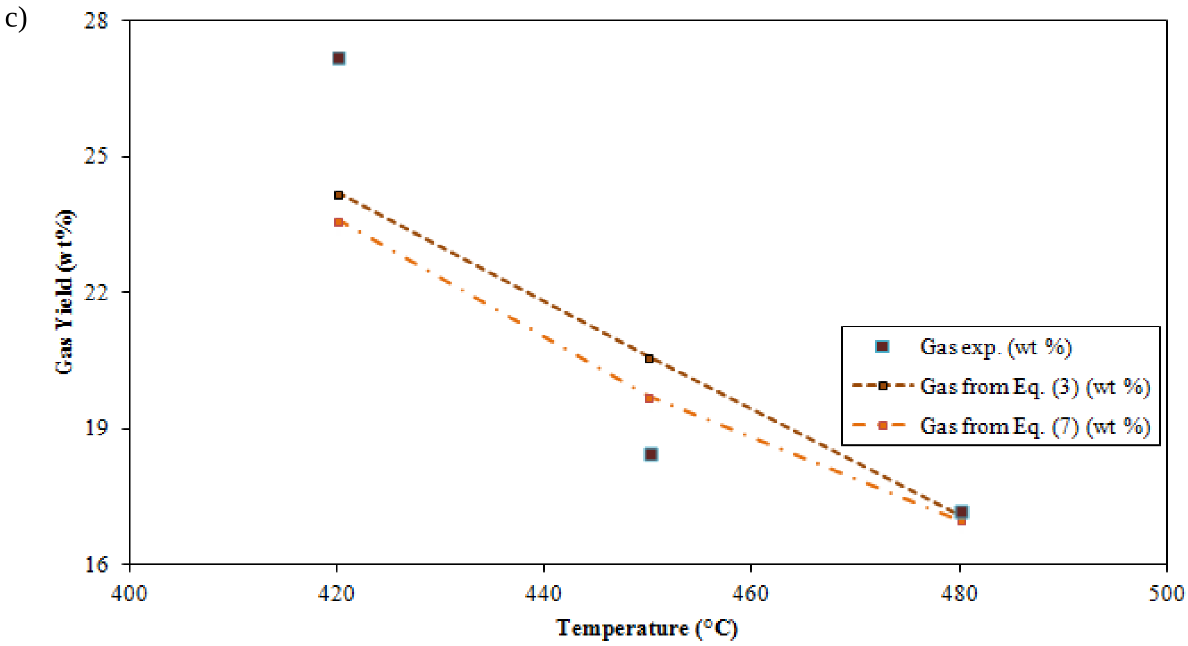


Figure 3
Experimental and predicted product yields: a) coke yield, b) distillate yield, and c) gas yield; (CCR=18.46) wt. %).

To compare the precisions of Equations 1-3 with those of Equations 5-7, the amount of absolute average error (wt. %) (AAE) can be calculated by Equation 8 (Tharanivasan et al., 2009):

$$E_f = \frac{1}{n}\sum_{i=1}^{n}\frac{\left|Y_i^{\exp.} - Y_i^{pred.}\right|}{Y_i^{\exp.}}\times 100 \qquad (8)$$

Where, $Y_i^{\exp.}$ is the experimental value and $Y_i^{pred.}$ is the predicted one from the related equation.

The AAE (wt. %) values of the predicted production yields from equations 1-3 and 5-7 would be 6.9 wt. % and 6.3 wt. %, respectively. Therefore, Equations 5-7 show greater consistency with the experimental results compared to Equations 1-3 for the Iranian residues in the mentioned test conditions. For a better comparison of the proposed functions, the Parity plots of the products yield for Equations 1-3 and for Equations 5-7 are illustrated in Figures 4 and 5 respectively. These figures also confirm the better prediction of the products yield by using Equations 5-7.

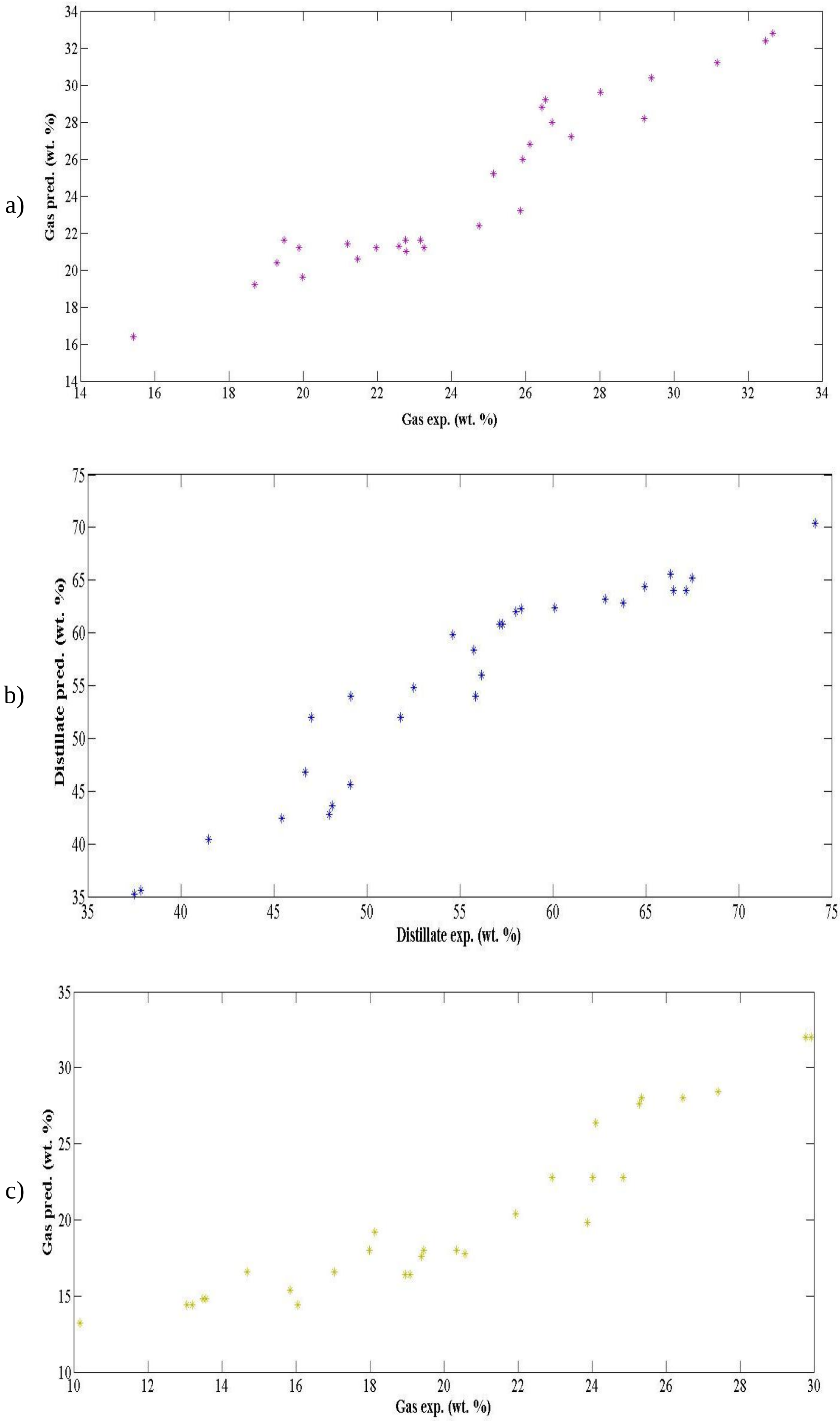


Figure 4
Parity plots of the products yield for Equations 1-3: a) coke yield (wt.%), b) distillate yield (wt.%), and c) gas yield (wt.%).

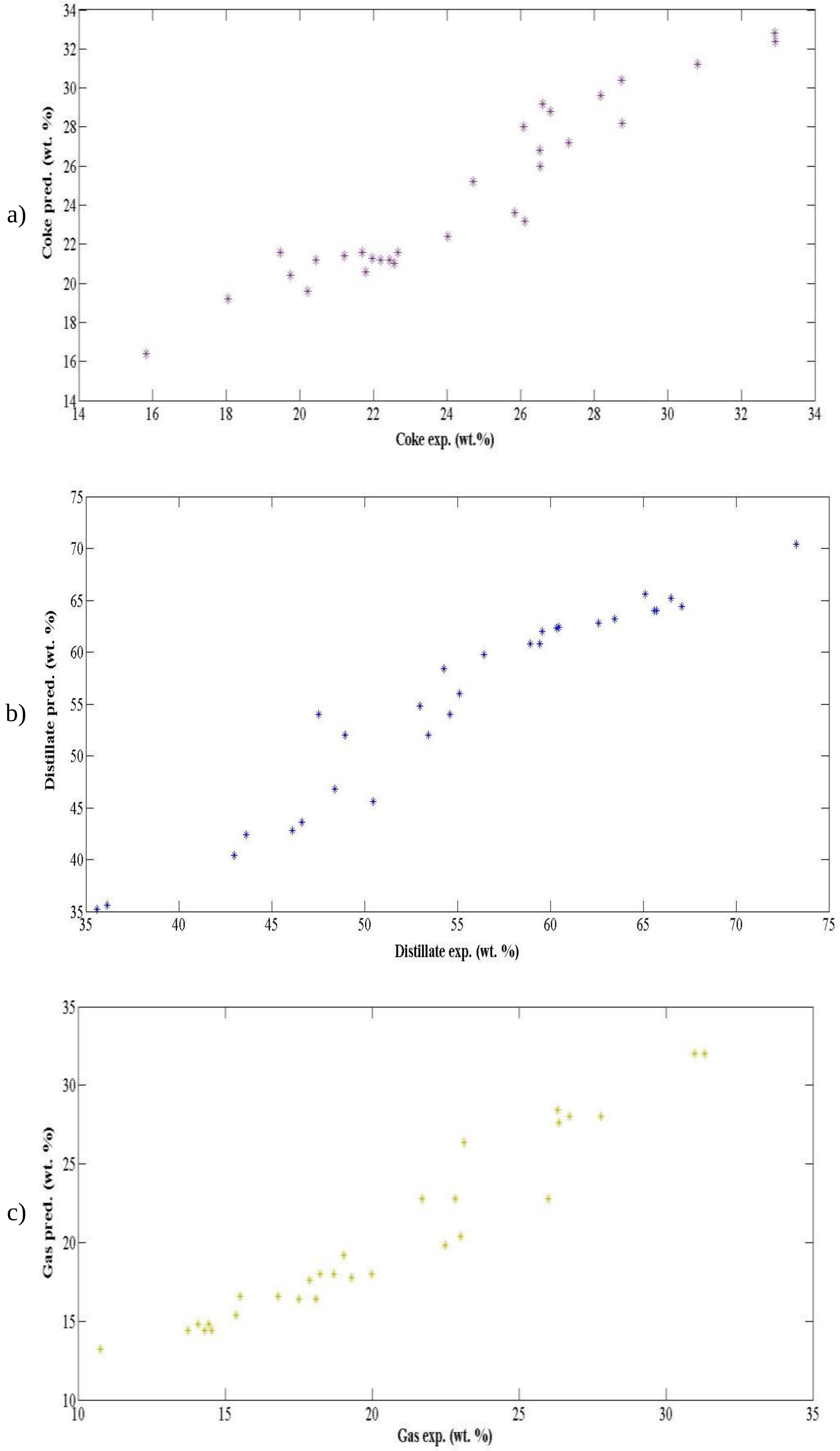


Figure 5

Parity plots of products yield for Equations 4-7: a) coke yield (wt. %), b) distillate yield (wt.%), and c) gas yield (wt.%).

4. Conclusions

Some Iranian vacuum residues are tested in a laboratory scale atmospheric batch delayed coking reactor in a temperature range of 400 to 500 °C with defined heating scenarios. The yields of distillate and coke were measured, and the gas (C_1-C_4) yield was calculated based on mass balance between the initial vacuum residue and the final products in each experiment. For the experimental results in the mentioned condition, the products yield dependency on CCR value and the temperature of the reaction was studied using two types of functions. In the first type, the developed functions were considered to linearly depend on CCR value and reaction temperature. In the second one, a combined power function of temperature and linear function of CCR value was proposed for the product yield estimation. Finally, the precision of the proposed functions in both methods was compared with the results of delayed coking for a different Iranian vacuum residue; it was confirmed that the function using a power relationship with temperature has greater consistency with the experimental results. Both types of the predicting functions showed that by increasing CCR value and reducing temperature, the coke yield and gas yield rise simultaneously, but consequently reverse effects could be seen for the distillate yield.

Acknowledgments

The authors would like to appreciate the financial support from Research Institute of Petroleum Industry of Iran (RIPI) and the Iranian Mines and Mining Industries Development and Renovation Organization (IMIDRO) for this work.

Nomenclature

AAE : Absolute average error (wt.%)
C : Carbon
CCR : Conradson carbon residue (wt.%)
H : Hydrogen
H/C : Hydrogen to carbon atomic (mole ratio)
MCR : Micro carbon residue (wt.%)
Ni : Nickel (ppm)
S : Sulfur (mass%)
SARA : Saturate, aromatic, resin, asphaltene
V : Vanadium (ppm)
VR : Vacuum residue

References

Afzal, S., Nikookar, M., Ehsani, M. R., and Roayaei, E., An Experimental Investigation of the Catalytic Effect of Fe_2O_3 Nanoparticle on Steam Injection Process of an Iranian Reservoir, Iranian Journal of Oil and Gas Science and Technology, Vol. 3, No. 2, p. 27-36, 2014.

Al-Saffar, H. B., Hasanin, H., Price, D., and Hughes, R., Oxidation Reactions of a Light Crude Oil and its SARA Fractions in Consolidated Cores, Energy and Fuels, Vol. 15, No. 1, p. 182-188, 2001.

Ancheyta, J., Modeling of Processes and Reactors for Upgrading of Heavy Petroleum, CRC Press, 2013.

Bayati, B., Ejtemaei, M., Charchi Aghdam, N., Babaluo, A. A., Haghighi, M., and Sharafi, A., Hydroisomerization of n-Pentane over Pt/Mordenite Catalyst: Effect of Feed Composition and Process Conditions, Iranian Journal of Oil and Gas Science and Technology, Vol. 5, No. 2, p. 84-99, 2016.

Carrillo, J. A. and Corredor, L. M., Upgrading of heavy crude oils: Castilla, Fuel Processing Technology, Vol. 109, p. 156-162, 2013.

Castaneda, L. C., Munoz, J. A., and Ancheyta, J., Current Situation of Emerging Technologies for Upgrading of Heavy Oils, Catalysis Today, Vol. 220, p. 248-273, 2014.

Jia, N., Moore, R. G., Mehta, S. A., and Ursenbach, M. G., Kinetic Modeling of Thermal Cracking Reactions, Fuel, Vol. 88, No. 8, p. 1376-1382, 2009.

Muñoz, J. A. D., Aguilar, R. Castañeda, L. C., and Ancheyta. J., Comparison of Correlations for Estimating Product Yields from Delayed Coking, Energy and Fuels, Vol. 27, No. 11, p. 7179-7190, 2013.

Riazi, M. R., Characterization and Properties of Petroleum Fractions, ASTM international, 2005.

Safiri, A., Ivakpour, J., and Khorasheh, F., Effect of Operating Conditions and Additives on the Product Yield and Sulfur Content in Thermal Cracking of a Vacuum Residue from the Abadan Refinery, Energy and Fuels, Vol. 29, No. 8, p. 5452-5457, 2015.

Sawarkar, A. N., Pandit, A. B., Samant, S. D., and Joshi, J. B., Petroleum Residue Upgrading via Delayed Coking: A Review, The Canadian Journal of Chemical Engineering, Vol. 85, No. 1, p. 1-24, 2007.

Schabron, J. F., Pauli, A. T., Rovani, J. F., and Miknis, F. P., Predicting Coke Formation Tendencies, Fuel, Vol. 80, No. 10, p. 1435-1446, 2001.

Shishavan, R. A., Ghashghaee, M., and Karimzadeh, R., Investigation of Kinetics and Cracked Oil Structural Changes in Thermal Cracking of Iranian Vacuum Residues, Fuel Processing Technology, Vol. 92, No. 12, p. 2226-2234, 2011.

Speight, J. G., The Chemistry and Physics of Coking. Korean Journal of Chemical Engineering, Vol. 15, No. 1, p. 1-8, 1998.

Speight, J. G., The Chemistry and Technology of Petroleum, CRC Press, 2007.

Speight, J. G., The Refinery of the Future, Gulf Professional Publishing, 2011.

Speight, J. G., Heavy and Extra-heavy oil upgrading technologies, Gulf Professional Publishing, 2013.

Tharanivasan, A. K., Svrcek, W. Y., Yarranton, H. W., Taylor, S. D., Merino-Garcia, D., and Rahimi, M., Measurement and Modeling of Asphaltene Precipitation from Crude Oil Blends, Energy and Fuels, Vol. 23, No. 8, p. 3971-3980, 2009.

Volk, M., Wisecarver, K., and Sheppard, C., Fundamentals of Delayed Coking Joint Industry Project, Department of Chemical Engineering, University of Tulsa, Tulsa, Oklahoma, USA, 2002.

Wang, J., Li, C., Zhang, L., Deng, W. and Que, G., Phase Separation and Colloidal Stability Change of Karamay Residue Oil during Thermal Reaction, Energy and Fuels, Vol. 23, No. 6, p. 3002-3007, 2009.

Wiehe I. A., A Phase-separation Kinetic Model for Coke Formation, Industrial Engineering and Chemical Research, Vol. 32, No. 11, p. 2447–2454, 1993.

Wiehe, I. A., Process Chemistry of Petroleum Macromolecules, CRC Press, 2008.