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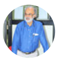

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STUDIES IN COKING OF ARABIAN MIX VACUUM RESIDUE

A. N. Sawarkar, A. B. Pandit and J. B. Joshi*

Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai, India.

Abstract: Batch reaction experiments pertaining to the coking of Arabian mix vacuum residue (AMVR) were carried out in the temperature range of 430–475°C and at a pressure of 0.2 MPa in an autoclave bomb reactor. The reaction time was varied in the range of 5–90 min. An attempt has been made to understand the inception, growth and saturation of coke formation within the range of temperature and reaction time covered in this work. The study revealed that the coke formation starts near the wall and then propagates towards the centre of the reactor and the temperature difference between the reaction mass at the wall and at the centre of the reactor was found to be as low as 0–1°C and as high as 8–12°C depending upon the severity of the reaction and the rate of coke formation. The present investigation also revealed that the coke formation levels off after a certain reaction time and thereafter a slight fall in the coke yield occurs. The reaction mixture was also quantified in terms of gas, distillates and unconverted vacuum residue. A four lump, three rate parameter kinetic model comprising vacuum residue (VR), gas (G), distillates (D) and the coke (C) has been proposed. VR was found to undergo first order decomposition and the apparent activation energy for the reaction pathways involving the formation of gas, distillates and coke from VR was found to be 51, 39 and 63 kcal mol^{-1}, respectively.

Keywords: coking; AMVR; autoclave bomb reactor; coke; residue upgradation; kinetics.

INTRODUCTION

Petroleum residue upgradation is at the zenith of value addition for obtaining the distillates. The high demand for distillates and ever-rising heavy nature of the crude oil has resulted into a renewed interest in the bottom-of-the-barrel processing using various conversion processes. Among the various processes employed, thermal processes *viz.*, visbreaking and delayed coking share a major portion (about 63%) of the petroleum residue upgradation (Shen *et al.*, 1998). In visbreaking process, reactions are arrested so that asphaltenes flocculation does not take place and subsequently a stable fuel oil (visbroken residue) is obtained. This results in low yield of 500°C-material (about 37%) and the remaining material accounts for fuel oil (Zuba, 1998). On the other hand, in delayed coking process, reactions are given sufficient time at relatively high temperatures to proceed to completion resulting in high yield of 500°C-material (about 79%) (Zuba, 1998) along with coke (about 21%). Thus, in delayed coking process, the aim is an economical conversion of residual feedstocks, especially vacuum residues (short residues) to lighter, more value added products while producing a coke material of desired quality (Rahmani *et al.*, 2002). Hence, a refinery with delayed coker is said to be 'zero resid refinery' which clearly brings out the importance of delayed coking process in the refinery set-up. Also, the sheer ability to process virtually any refinery stream has made delayed coking a prime choice for residue upgradation. Furthermore, the growing trend of processing heavy crude oils has brought about a renewed interest in delayed coking (Elliott, 1992; Bansal *et al.*, 1994) and the worldwide coking capacity has reached to about 210 MMTPA (Swaty, 2005).

The upgradation of residual feedstocks obtained by processing heavy crudes leads to higher coke yield because of the higher heteroatom, asphaltenes and Conradson carbon residue (CCR) content in the parent heavy crudes (Trasobares *et al.*, 1999). Coke is defined as a carbonaceous material that is insoluble in an aromatic solvent such as benzene and toluene. Coke formation during the thermal cracking of residual feedstocks indeed is a scientifically intriguing phenomenon. Over the past five decades many researchers worldwide have put in their quality time and efforts to know the intricacies pertaining to coke formation during the cracking of residual feedstocks.

Magaril and Aksenova (1968) have observed that the coke formation begins only after accumulation of considerable

**Correspondence to:*
Professor J.B. Joshi, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai-400 019, India.
E-mail: jbj@udct.org

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amount of asphaltenes. It was also observed that the time for the inception of coke formation coincides with the time of maximum yield of asphaltenes (Magaril *et al*., 1971). Magaril and Aksenova (1968) have reported that the coke formation brings about the formation of a new solid phase and always takes place near the wall. Savage *et al.* (1985) have observed an induction period for the thermolysis of asphaltenes from an off-shore California crude at 400°C that disappeared when the thermolysis temperature was raised to 450°C. Coke formation during heavy oil upgrading has been elucidated by Wiehe (1994) based on the pendant-core model. According to this model, the core, which consists of large aromatics, precipitates when the solubility limit of aromatics in the medium is reached. Further reactions of the aromatic molecules lead to a more organized and stacked arrangement of the aromatic sheets, which eventually form a separate liquid phase known as mesophase. This liquid phase is eventually converted to solid material termed as coke. Similarly, because of the nature of the chemical structure of asphaltene molecules present in heavy oils and bitumen, and their solubility characteristics, asphaltene molecules can form coke rapidly during thermal treatment (Wiehe, 1993).

A systematic analysis of the previous work in this area brings out the following points:

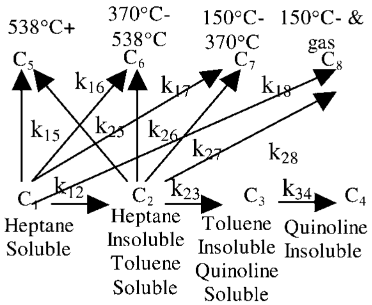
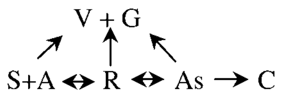
(1) The residue comprises saturates, aromatics, resins and asphaltenes. The coke formation is the consequence of a series of complex reactions and proceeds from saturates to aromatics to resins to asphaltenes and finally to coke.
(2) During thermal cracking, asphaltenes become more aromatic and at a particular stage of conversion they undergo phase separation by breaking of colloidal equilibrium of the whole residue.
(3) In the separated phase, the asphaltenes lack in H-abstraction which otherwise would have undergone radical termination by H-abstraction from maltene components. Thus, they undergo condensation and polymerization reactions resulting into the coke formation.
(4) The model showing the interconversion along with parallel formation of pseudo boiling cuts has been proposed by Takatsuka *et al.* (1989) and has been experimentally validated.
(5) With the help of the structural changes at the molecular level and using solvent-resid phase diagram, it was found that the shift from one class to another such as maltenes (heptane soluble) to asphaltenes (heptane insoluble, toluene soluble) to coke (toluene insoluble) occur via continuous change in the molecular weight and Conradson carbon residue (CCR) within the same class (Wiehe, 1992). This has been observed and corroborated by Yasar *et al.* (2001).
(6) The concept and existence of certain threshold concentration of asphaltenes as solubility limit (S_L) was incorporated in the coke formation model (Wiehe, 1993). Later, using optical microscopy the onset of neophase separation during thermal cracking was also experimentally proved (Li *et al*., 1998).
(7) Song *et al.* (1995) have studied the kinetics of coking of Gudao vacuum residue in the temperature range of 400–440°C and 460–500°C. The thermal cracking reactions were found to follow first order kinetics over the studied temperature range.
(8) The changes in the chemical structure of resins and asphaltenes occurring before and after thermal conversion of the Shengli vacuum residue have been investigated by Wang *et al.* (1998). It was found that during thermal conversion of vacuum residue, the resins bearing shorter alkyl chains and more peri-condensed aromatic units are responsible for asphaltenes formation while asphaltenes bearing shorter alkyl chains and more peri-condensed aromatic units get converted into coke.
(9) The effect of solvent properties (with similar solubility parameter such as maltene, 1-methyl naphthalene and tetralin) on solubility limit and coking kinetics has also been explored (Rahmani *et al*., 2002). It was observed that the hydrogen donating ability of the solvent and the hydrogen accepting ability of the asphaltenes play a major role in determining the ultimate yield of the coke.
(10) The effect of structural properties of asphaltenes on the coking rates and coke yields have also been explored by studying the thermal cracking of asphaltenes obtained from different origins. It was found that the coking rate depends on aliphatic sulphide content of the asphaltene while its aromaticity decides the yield of the coke (Wiehe, 1993).
(11) The above coking kinetic models have been reported to follow first order kinetics with the range of pseudo activation energies (22–83 kcal mol^{-1}) depending upon the feed properties and severity range.

A brief summary comprising the reaction conditions, different feeds studied and the findings of the investigators is given in Table 1. From the foregoing discussion, it can be found that considerable work has been done on coking kinetics with special emphasis on the mechanism of coke formation, inter-conversion of the solubility class components during conversion, role of these components in coke formation, influence of structural properties on coking rate and yields and so on. The proposed models are based on the mechanistic pseudo components, phase separation, pendant core, and so on, which explains the coke formation during thermal conversion.

However, it may be pointed out that the information with regard to the actual coke build up (inception, growth and saturation of coke formation) in the reactor (batch mode or continuous mode) has not been reported in the literature. Qualitative information can be found (Magaril and Aksenova, 1968) with regard to the coke formation. The authors have reported that coke formation first takes place at the wall. However, there is no quantification reported as to how much temperature gradient exists between the wall and the centre of the reactor at different processing severities. Hence, it was thought desirable to undertake a systematic investigation of the coking behaviour of Arabian mix vacuum residue (AMVR) in terms of inception, growth and subsequent saturation of coke formation at different processing severity.

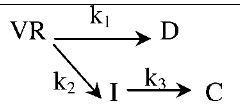
With regard to the kinetic modeling, it was found that most of the models proposed are based on structural changes within the residue and a very few models have been proposed which comprise the lumps of industrial relevance and involve coke as one of the components. After the close scrutiny of the available literature, it was found that the model, which comes close on this account, is proposed by

Table 1. Reported work on the coking kinetics.

Authors	Experimental details		Proposed kinetic model	Conclusions
Magaril (1968)	Feed Reactor Temp. (°C) Reaction time (min)	Resins Quartz test tube 400 160	–	(1) There exists a certain saturation concentration of asphaltenes beyond which they precipitate out from saturate solution. (2) Coke formation is the consequence of precipitation and accumulation of asphaltenes. The coking rate is equal to the rate of asphaltenes precipitated.
Magaril *et al.* (1971)	Feed Solvent Reactor Temp. (°C) Reaction time (min)	Asphaltenes isolated from cracked residue and deasphalted bitumen Transformer oil, anthracene oil. Autoclave without stirring 380–410 5–120	–	(1) The effect of solvent properties on the kinetics of coke formation was studied. (2) Assuming the spherical shapes of asphaltene and solvent molecules and using their molecular wt and density, the asphaltene concentration in the solution was proposed at various conversions. (3) Coking was found to initiate after certain threshold concentration of asphaltene in the solution and this value was found to be higher for solvent with good solvating power. (4) Coke formation was found to occur after a certain severity of cracking has reached.
Takatsuka *et al.* (1989)	Feed Reactor Temp. (°C) Reaction time (min) Pressure (MPa)	Residual oil Flow reactor, semibatch, autoclave 400–450 0–450 0.013–0.45		(1) Atmospheric equivalent temperature and hydrocarbon (HC) partial pressure were used to estimate the Arrhenius rate parameters. (2) Higher HC partial pressure decreases the reaction rate of polycondensation reactions while cracking rate increases with increasing the reactor pressure. (3) The activation energy for the cracking and polycon densation reactions were estimated to be 60 kcal mol^{-1} and 40–50 kcal mol^{-1}, respectively.
Wiehe (1992)	Feed Reactor Temp. (°C) Reaction time (min) Pressure (MPa)	VR and its SARA fractions Batch tubing bomb 400 60 7 MPa (N_2 atm)	 S - saturates; A - aromatics; R - resins; As - asphaltenes; C - coke; V- volatiles; G - gas	(1) The solvent-resid phase diagram (plot of molecular weight–hydrogen content) was proposed to distinguish one pseudocomponent from another and to track the chemical changes that result their movement from one solubility class to another. (2) Elemental analysis and molecular wt. of thermal conversion products of resid and SARA fraction was studied. (3) Thermal cracking of the SARA fractions resulted to reduction in their molecular weight, H-content (slightly in the case of saturate and aromatics) and coke formation.
Wiehe (1993)	Feed Reactor Temp. (°C) Reaction time (min) Pressure (MPa)	Cold Lake VR (3 g) Quartz tube reactor 400 0–180 Open reactor with continuous N_2 flow	–	(1) Inhibition of heptane solubles for coke formation, a maxima for the asphaltenes formation which matches with the coke induction period, parallel decrease in the asphaltenes concentration beyond certain heptane solubles (S_L, solubility limit). (2) A kinetic model was proposed that explains the above observations and estimated the disappearance of asphaltenes by first order with rate constant of 0.026 min^{-1} while S_L, was estimated to be 0.49 wt%.

(*continued*)

Table 1. Continued

Authors	Experimental details		Proposed kinetic model	Conclusions
Del Bianco *et al.* (1993)	Feed Reactor Temp. (°C) Reaction time (min) Pressure (MPa)	Belaym VR (CCR-20.8 wt%) Batch reactor 410–470 0–120 1 (N_2 atm)	 VR - vacuum residue; D - distillates; I- reaction intermediate; C - coke	(1) The coke formation was proposed to be formed via a reaction intermediate (I) (2) E_1-49.4 kcal mol^{-1}; A_1-31.97 min-1; E2-63.9 kcal mol^{-1}; A_2-40.92 min^{-1}. (3) Structural study shows that thermal cracking of asphaltenes follow dealkylation reactions. (4) Condensation reactions prevail at higher severity levels.
Song *et al.* (1995)	Feed Reactor Temp. (°C) Reaction time (min)	Gudao VR (5 g) Batch tubular reactor 400–500 5–80	–	(1) Assuming the first order kinetics, the Arrhenius parameters were found to vary from $E_{400\text{-}440}$–170.7 kJ mol^{-1}, $A_{400\text{-}440}$–7.853 e^{10} to $E_{460\text{-}500}$–180 kJ mol^{-1}, $A_{460\text{-}500}$–9.24 e^{11}.
Wang *et al.* (1998)	Feed Reactor Temp. (°C) Reaction time (min) Pressure (MPa)	Shengli VR (500+) Autoclave with magnetic stirrer 410 60 0.1	–	(1) Structural parameters were compared between SARA fractions obtained from the feed and after its thermal cracking. (2) Peri-condensed aromatic resins get converted into asphaltenes, which further condense to give coke formation.
Li *et al.* (1998)	Feed Reactor Temp. (°C) Reaction time (min) Pressure (MPa)	Shengli, Daqing, Gudao (300 g) FYX-05A autoclave 370–390 10–70 1.0	–	(1) The variation in the onset of neophase formation, necessary for the coke formation, was studied using optical microscope for three different VR varying largely in their properties. (2) A stability function, based on the SARA composition, was determined to represent the thermodynamic stability of the VR.
Rahmani *et al.* (2002)	Feed Reactor Temp. (°C) Reaction time (min) Pressure (MPa)	Athabasca asphaltenes (nC_7 insol. 3 g) Batch microreactor (15 mL) 430 60 0–4 MPa	$H + \xrightarrow{k_H} bA^+ + (1-b)V$ $A^+ \xrightarrow{k_A} cA^* + (1-c)(H^* + V)$ where, $H^+ =$ fraction of reac. nC_7 sol. $H^* =$ fraction of prod. nC_7 sol. $A^+ =$ fract. of reac. asphaltene $A^* =$ fract. of prod. asphaltene $V =$ cracked distillate prod k_A, $k_H =$ reac. rate const. for the thermolysis of reac. asphaltene and nC7 sol., respectively b, c = stoichiometric coefficients	(1) The solubility limit kinetic model was proposed to study thermal cracking of asphaltenes in maltene, 1-methyl naphthalene and tetralin. (2) Coke formation was found to be strongly influenced by the chemical interactions between the asphaltenes and the solvent medium. (3) The hydrogen donating ability of the solvent and the hydrogen accepting ability of the asphaltenes were found to have a pronounced effect on the coke yield. (4) The model proposed was found to be consistent with the data on coke formation from asphaltenes in studied solvents with low hydrogen donating ability.
Rahmani *et al.* (2003)	Feed Reactor Temp. (°C) Reaction time (min) Pressure (MPa)	Asphaltenes from AL, AH, Maya, GudaoVR Batch microreactor (15 mL) 430 60 9.8 MPa	–	(1) Phase separation model was proposed to study the coking kinetics of asphaltenes having range of structural properties. (2) Structural dependency on coking kinetics showed that sulphide content of asphaltenes correlated with the cracking rate while the aromaticity decided the coke yield.
Schabron *et al.* (2003)	Feed Reactor Temp. (°C) Reaction time (min)	Boscon, Llyodminster, Redwater BC, MaxCL2 (5 g) Tubular reactor 400–450 5–150	–	(1) Coke formation involves a complex set of reactions which fall somewhere between zero-order and first-order kinetic mechanisms. (2) Kinetics followed by coke formation is most likely dependent on the source of the residue. (3) The activation energies of the secondary coke formation reactions of the studied feeds were found to be 2.2 to 2.6 times higher than that for the initial coke formation.

Del Bianco *et al.* (1993). The model proposed by the authors comprises vacuum residue, distillate fraction, reaction intermediate and the coke. A good account of the variation in the rate parameters has been given in the proposed kinetic scheme. However, the proposed kinetic model does not include gas fraction separately. Gas (C_1-C_4) forms one of the major products of delayed coking process with the yield up to 9.5 wt% (Zuba, 1998) depending upon the processing severity. Hence, it was thought desirable to include this fraction in the proposed kinetic scheme so that useful information can be obtained with regard to the rate variations for the paths involving gas fraction, along with rate variations for the paths involving distillates, coke and unconverted vacuum residue (VR). Thus, in the proposed kinetic scheme, all the major products of the delayed coking process have been incorporated and an attempt has been made to investigate the variation in the rate parameters for the possible paths with the help of the generated experimental data.

In the present investigation, the reactor was provided with an additional thermocouple at the wall of the reactor along with the conventional thermocouple at the centre of the reactor. In doing so, the temperature–time profiles at the wall and at the centre were obtained and hence some useful information was obtained with regard to the temperature difference at these two locations in the reactor over the studied temperatures and reaction times. AMVR is a widely produced residue in petroleum refineries and a feed of commercial interest (Schucker, 1983). Hence, AMVR was employed in this investigation for the coking studies.

EXPERIMENTAL SECTION

Arabian mix vacuum residue was obtained from the operational vacuum distillation unit of HPCL refinery located in Mumbai. The feed was characterized as per the standard ASTM/IP methods. Table 2 summarizes the important physico-chemical properties of the feedstock studied.

Table 2. Physico-chemical characteristics[a] of Arabian mix vacuum residue (AMVR).

Sr No	Property	Feedstock AMVR
1	Density, gm cc^{-1}	1.023
2	Kinematic viscosity, cSt	
	at 100°C	1084.10
	at 135°C	168.49
3	S, wt%	4.43
4	CCR, wt%	21.10
5	C/H ratio	6.59
6	Mol. Wt.	800.2
7	nC5 insol. wt%	18.72
8	Pour point, °C	+42
9	Metal content, ppm	
	V	89.00
	Ni	31.65
	Fe	32.00
10	H-C type analysis, wt%	
	Saturates	15.00
	Aromatics	66.28
	Resins	7.6
	Asphaltenes	11.12

[a]All the tests were performed as per the ASTM/IP methods.

Experimental Set-Up and Procedure

Figure 1 shows the schematic representation of the experimental set-up employed for investigating the coking behaviour of AMVR and subsequently generating the batch kinetic data of residue cracking under coking conditions. The reactor used was SS-316 autoclave (80 mm i.d. and 94 mm o.d.) having 600 mL capacity with a provision of simultaneously measuring the temperature of the reaction mass near the wall and at the centre of the reactor and the vapour temperature. Molten tin bath was used as the heating medium. A cold trap was used for the separation of the lighter products from the gaseous components formed during cracking. A gas meter (wet type) was used to quantify the gas formed during the course of the reaction. The molten tin bath was heated electrically and the temperature was controlled within ±2°C using a PID controller.

About 300 g of the feed was charged to the reactor and it was initially flushed with nitrogen and then pressurized to 0.2 MPa. The pressure was maintained throughout the reaction period using needle valve. The molten tin bath was kept approximately 50–60°C higher than the desired reaction temperature so as to maintain the temperature gradient and provide the heat required for the various thermal cracking reactions. The reactor was placed just above the molten tin bath for preheating up to 350°C. This preheating reduced the time period required to attain the experimental temperature. As soon as the reaction mass attained the preheating temperature, the reactor was dipped in the bath with constant manual rocking of the reactor for temperature uniformity. The desired temperature was achieved within 1.5–2 min. Once the desired reaction temperature was attained, the stopwatch was reset at zero time i.e., $t = 0$. Thus, the reaction time reported in this work is the time period after the reaction mixture attains the desired reaction temperature. Since the coking process starts near the wall, the wall temperature has been reported as the temperature of reaction. The temperatures of the reaction mass and bath were measured at the interval of every 30 s. The cracked lighters and gas fractions were allowed to escape the reactor using needle valve

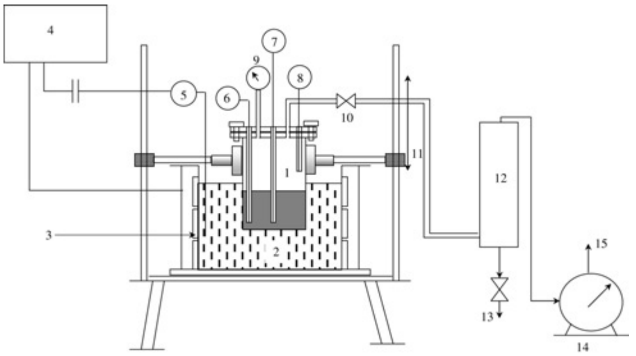


Figure 1. Schematic diagram for experimental set-up: (1) SS-316 reactor (600 mL capacity); (2) molten tin bath; (3) electric heaters for furnace; (4) furnace temperature control; (5) thermocouple for the tin bath; (6) thermocouple for the reaction mass near the wall; (7) thermocouple for the reaction mass at the centre; (8) thermocouple for the vapours of the reaction mass; (9) pressure indicator; (10) pressure release needle valve; (11) vertical moveable stand; (12) cold trap for liquid product; (13) liquid product collector; (14) gas meter; (15) gas outlet.

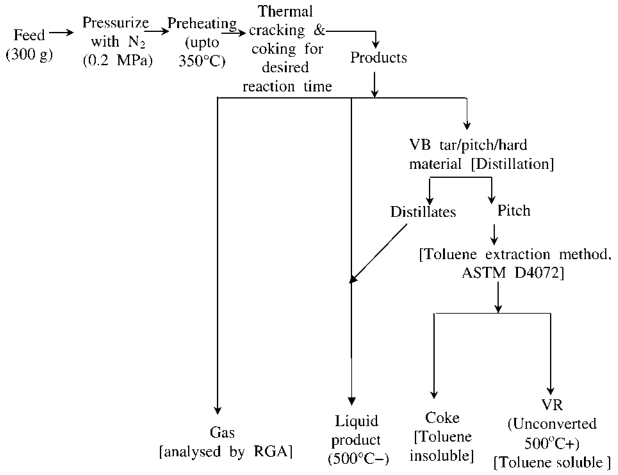


Figure 2. Schematic representation of experimental procedure and analysis.

maintaining the desired pressure. The lighter fractions were separated using cold-trap kept at 0–3°C while the volume of the gas fraction formed after passing through the cold-trap was measured using a gas meter. The gas sample was collected for its compositional analysis. The desired reaction temperature was maintained throughout the run by adjusting the position (lowering or raising) of the reactor in the tin bath. After the desired reaction time, the reactor was removed from the tin bath and was immediately quenched using water bath (~25°C). The quenching period was approximately 1 min. The reactor was then slowly depressurized to atmospheric pressure and the entrained vapours and gaseous products were collected and quantified separately. The volume of nitrogen was subtracted from the measured cumulative volume of the gaseous products so as to obtain the volume of the formed gaseous products during the reaction. The leftover (visbroken tar/hard material depending upon the severity of the reaction) in the preweighed reactor was collected and weighed in a flask for further analysis. The reactor was again weighed so as to account for the uncollected material. The material balance was accounted in terms of gaseous products, liquid product and visbroken tar/hard material and was always within 98–99%.

Separation Scheme and Analysis

The reaction was based on the conversion of the VR (500°C+) to the components boiling below 500°C and coke (defined as toluene insoluble material). Figure 2 shows the complete reaction scheme and analysis of the reaction products. The feed was thermally cracked for the desired reaction temperature and residence time. The gas was analysed by refinery gas analyser (RGA) for its compositional analysis. In the case of low severity experiments, the tar/pitch material was distilled so as to separate the distillate fraction (500°C−). The coke content was determined as toluene insoluble fraction using ASTM D-4072 from the remaining 500°C+ material. Similarly, the coke content was determined from the hard material (obtained in case of high severity runs).

RESULTS AND DISCUSSION

The coking behaviour of Arabian mix vacuum residue (AMVR) has been investigated over the temperature range of 430–475°C. Figure 3 shows the temperature profiles of the reaction mass near the wall and at the centre of the reactor at different severities which represent no coke formation [Figure 3(a)], inception of coke formation [Figure (3b)], growth of coke [Figure (3c)] and the final limiting coke formation [Figure (3d)] conditions. T_W represents the temperature of the hydrocarbon mixture at the wall of the reactor and T_C represents the temperature of the hydrocarbon mixture at the centre of the reactor.

Figure 3(a) shows the temperature profile during the mild reaction condition, i.e., 430°C and for 5 min reaction time. From Figure 3(a), it can be observed that there is no change in the temperatures of the reaction mass at the wall (T_w) and at the centre (T_C) as the coke formation does not take place at that reaction conditions (time and temperature) which was also corroborated by performing the standard merit number test (IFP-3024-82, severity test for thermal reactions by spot method and residue stability determination) wherein the 500°C+ was found to be stable. Figure 3(b) shows the temperature profile at a temperature of 445°C and for 10 min reaction time. From Figure 3(b), it can be observed that there is no change in the temperatures of the reaction mass at the wall and at the centre for the entire reaction time of 10 min except for last couple of minutes or so wherein a difference of about 2–3°C was found between the wall and centre temperatures, which indicates the inception of coke. The inception of coke was corroborated by performing the standard merit number test, wherein the 500°C+ material was found to be unstable. The coke content was determined as toluene insoluble fraction using ASTM D-4072 from the remaining 500°C+ material and from the hard material (in the case of high severity runs). Figure 3(c) shows the temperature profile at a temperature of 460°C and for 15 min reaction time. From Figure 3(c), a temperature difference of about 4–6°C could be seen after a reaction time of 12 min. An incremental temperature difference at the wall and at the centre of the reactor at these conditions indicates the rise of coke forming tendencies. Figure 3(d) shows the temperature profile at a temperature of 475°C and for 20 min reaction time. A further increase in the temperature difference (8–12°C) at the wall and at the centre of the reactor can be attributed to the pronounced effect of polymerization and polycondensation reactions at such a high temperature. Table 3 shows the yield of coke when the feed was thermally cracked at different temperatures and reaction times.

Product Distribution

The product lumping procedure has been adopted by many researchers to describe the kinetic behaviour of components undergoing various types of reactions that include cracking, polymerization, condensation, H-abstraction, and so on. Though such lumping approach has certain pitfalls (Weekman, 1979), it explains the kinetic behaviour to a satisfactory level and can be readily used by the refiners. In the present case, a four lump parallel reaction model, consisting of VR, G, D and C has been proposed to describe the kinetic behavior of the AMVR (Figure 4).

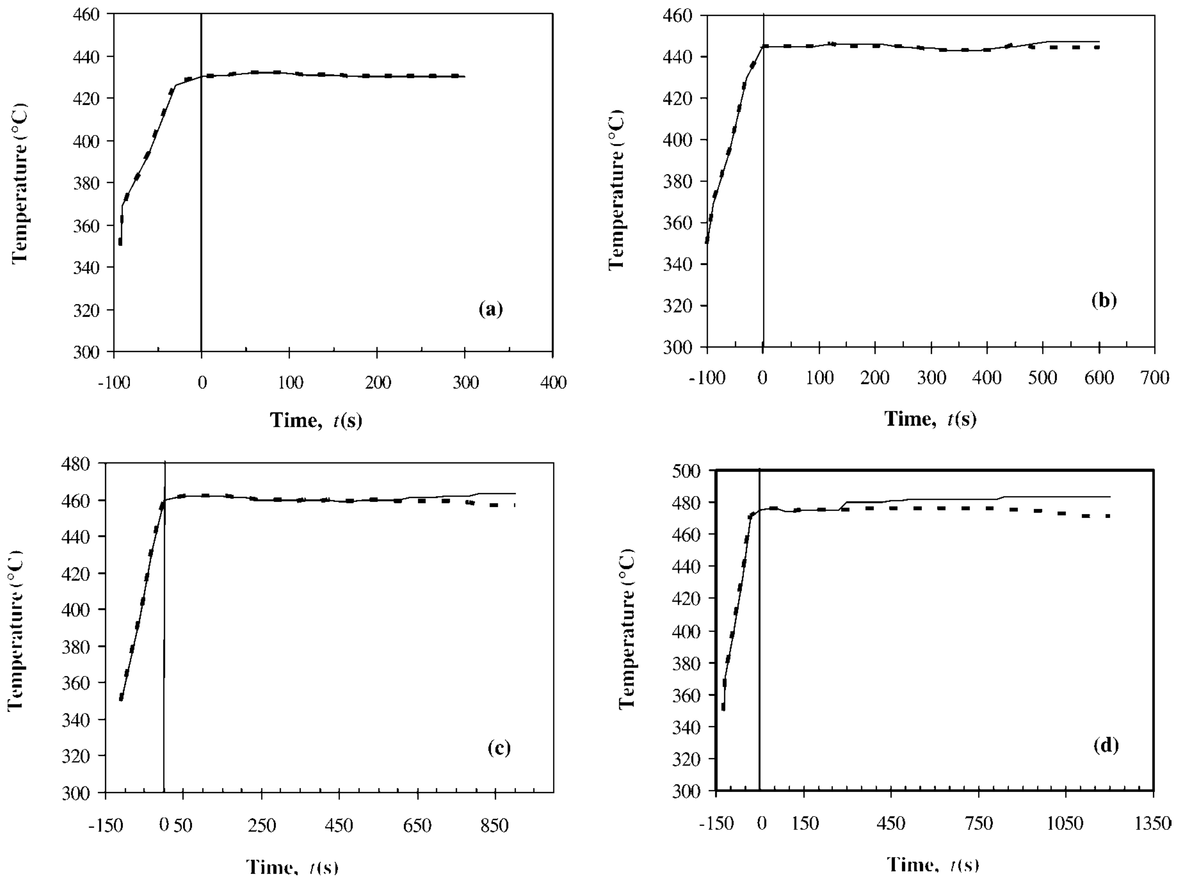


Figure 3. Temperature–time profiles at different severities: (a) 430°C, 5 min; (b) 445°C, 10 min; (c) 460°C, 15 min; (d) 475°C, 20 min (— T_w; — T_c).

Table 3. Yield of coke at different severities.

Product (wt%)	Reaction time (s)	Temperature (°C) 430	445	460	475
	300	0.00	0.20	0.66	13.89
	600	0.00	1.09	12.89	21.16
	900	0.85	6.54	16.74	27.80
Coke	1200	1.19	13.65	21.09	30.39
	1800	3.40	19.22	28.22	30.83
	3600	12.41	27.99	30.42	30.13
	5400	24.14	29.83	29.74	29.83

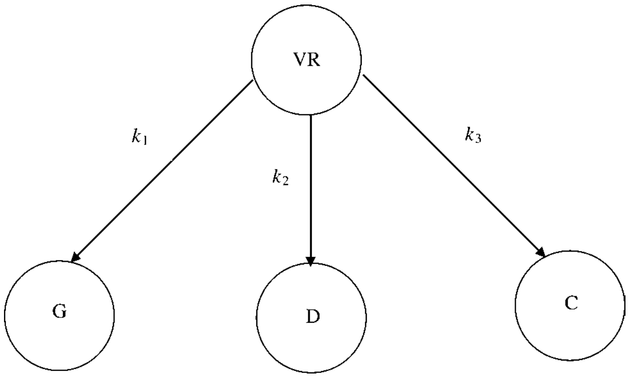


Figure 4. Proposed four lump kinetic model with three rate parameters: VR—vacuum residue (500°C+); G—gas (C_1–C_4); D—distillates (IBP-500°C); C—coke.

The maltene phase has certain solubility limit beyond which the asphaltenes precipitate out and exist as a separate phase. In this phase, the high rate of condensation of the asphaltene radicals which are thus lean by H-abstraction (from the maltene phase) leads to the toluene insoluble material (coke). The above theory of coke formation has been used by different authors (Wiehe, 1993; Rahmani *et al.*, 2002, 2003) to explain the kinetic behaviour of different feeds for the range of coking operation severities. From Figure 5, it can be observed that the coke formation does not start at 430°C unless a reaction time of 15 min is attained. At 445°C, the inception of coke formation was found to start at 10 min. At 460°C, coke formation was found to be high (about 13 wt%) even for the reaction time of 10 min. It was also observed that after a reaction time of 60 min at 460°C, coke formation levels off. At 475°C, markedly high yield of coke (about 14 wt%) was obtained even at a reaction time of 5 min because of the high rate of polymerization and polycondensation reactions prevailing at this temperature. In fact, the coke formation was found to level off as early as at 20 min of reaction time, thus indicating that coke formation rapidly proceeds to completion at higher temperature. This observation is in agreement with the results of Schabron *et al.* (2003). The second and important observation was that, once the coke

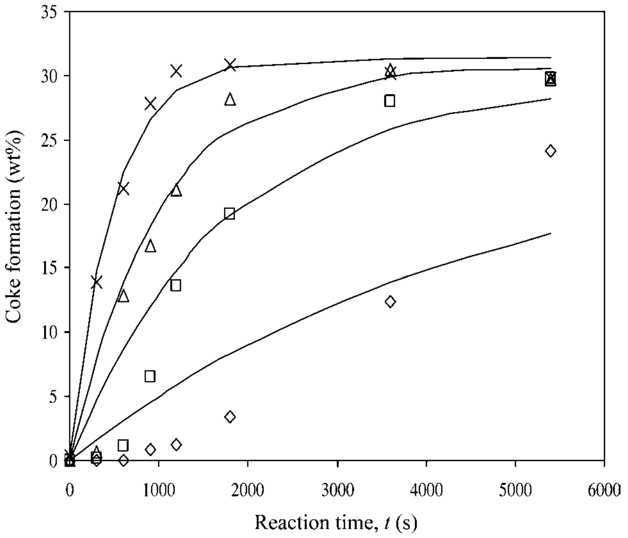


Figure 5. Comparison between experimental and predicted values of coke at different temperatures: ◇, 430°C; □, 445°C; △, 460°C; ×, 475°C (—predicted curves).

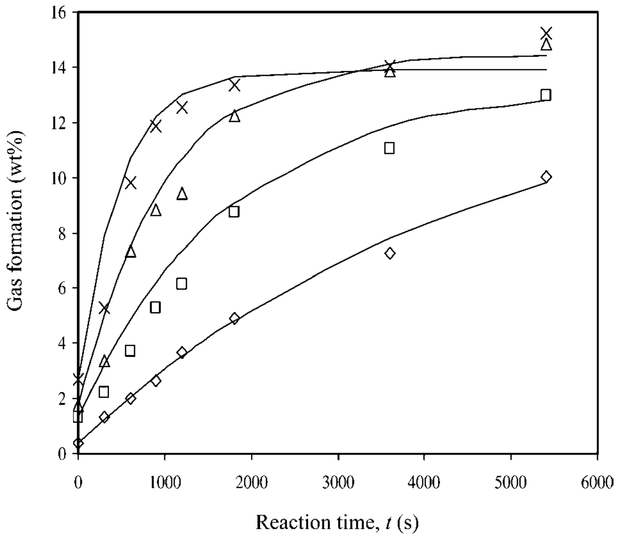


Figure 6. Comparison between experimental and predicted values of gas at different temperatures: ◇, 430°C; □, 445°C; △, 460°C; ×, 475°C (—predicted curves).

has reached saturation and if the reaction time is still raised, a slight fall in the coke yield was found to occur at 460°C, 90 min and at 475°C, 60 and 90 min. The marginal reduction in the coke formation, over extended time can be attributed to the enhanced devolatilization of the volatiles trapped in the coke matrix at higher temperatures. This observation is in agreement with Gray *et al.* (2004). Maximum coke yield (30.83 wt%) was found to be at 475°C and for reaction time of 30 min. The coke near the wall was found to be hard and had to be removed with the aid of a chisel and hammer thus corroborating the notion that polymerization reaction starts progressing from the wall to the centre of the reactor.

Along with coke, the reaction mixture was also quantified in terms of gas (G), distillates (D) and unconverted vacuum residue (VR) and the variation of each of these fractions with time within the studied temperature range was also investigated. The yield of the products was calculated using the following equation:

$$\text{yield (wt\%)} = \frac{W_i}{W_{VR}} \times 100 \qquad (1)$$

where W_i ($i = G$, D and C) is the fractional weight of the product specie.

Table 4. Gas composition at various severities.

	Gas composition (wt%)			
Component	430°C, 600 s	445°C, 600 s	460°C, 900 s	475°C, 1200 s
C_1	45.71	44.08	43.72	44.70
C_2	22.47	22.17	21.87	22.91
C_2'	2.85	2.82	3.21	2.98
$C_3 + C_3'$	21.71	21.37	22.55	20.17
nC_4	5.52	6.04	6.43	5.60
iC_4	0.19	0	0.12	0
C_4'	1.52	3.49	2.05	3.61

Gas concentration

The analysis of gas by refinery gas analyser (RGA) showed that methane is the major component (about 42 wt%) followed by ethane (about 22 wt%) (Table 4). Furthermore, processing severity was found to have negligible effect on overall gas composition. The gas formation was found to increase with an increase in the processing temperature. Maximum gas yield was found to be 15.23 wt% at 475°C and for 90 min of reaction time (Figure 6).

Distillate concentration

Distillate yield was found to increase with increasing processing severity. At 460 and 475°C, the distillate yield was found to level off and showed asymptotic behaviour

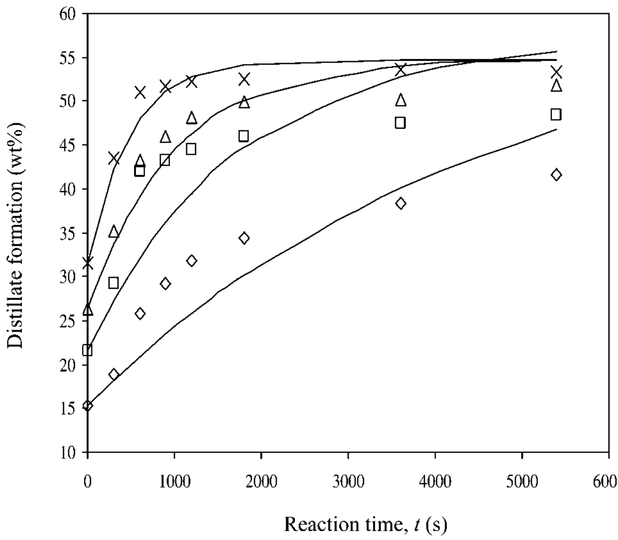


Figure 7. Comparison between experimental and predicted values of distillate at different temperatures: ◇, 430°C; □, 445°C; △, 460°C; ×, 475°C (—predicted curves).

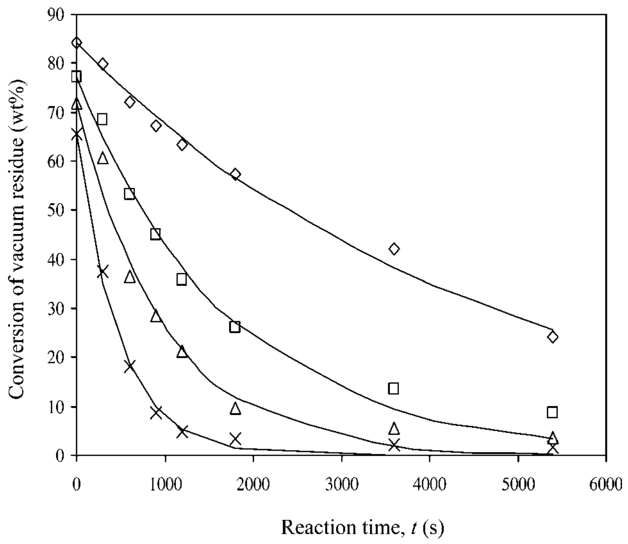


Figure 8. Comparison between experimental and predicted values of VR at different temperatures: ◇, 430°C; □, 445°C; △, 460°C; ×, 475°C (— predicted curves).

(Figure 7) at higher reaction times (60 and 90 min). Maximum distillate yield (53.59 wt%) was found to be at 475°C and for the reaction time of 60 min.

VR concentration

The 500°C+ was found to decrease with increasing severity. At higher temperatures (460 and 475°C), the conversion of VR was found to be pronounced and the maximum conversion of vacuum residue was found to be 99.38% at 475°C and for the reaction time of 90 min (Figure 8).

Reaction Kinetics

Schabron *et al.* (2002) have reported that coke formation involves a complex set of reactions and may fall somewhere between zero order and first order kinetics. For the present kinetic scheme (which involves formation of gas and distillate along with formation of coke), attempt was made to investigate the order for three reactions as shown in Figure 4. The correlation coefficients of the parity plots for the 0th, 0.5th and 1st order reaction are given in Table 5. It can be seen that the best fit for the kinetic scheme proposed is obtained with first order kinetics for all the reactions. Hence, the different reaction pathways possible from the proposed kinetic scheme i.e., formation of gas, distillates, coke and conversion of vacuum residue have been modelled with first order kinetics.

Table 5. Correlation coefficient (C.C.) of the parity plots for different orders of reaction. Temperature range: 430–475°C.

	Correlation coefficient for			
Order of reaction	Vacuum residue concentration	Gas concentration	Distillate concentration	Coke concentration
0th order	0.9326	0.9678	0.7857	0.6659
0.5th order	0.7636	0.9021	0.5239	0.4584
1st order	0.9857	0.975	0.8855	0.921

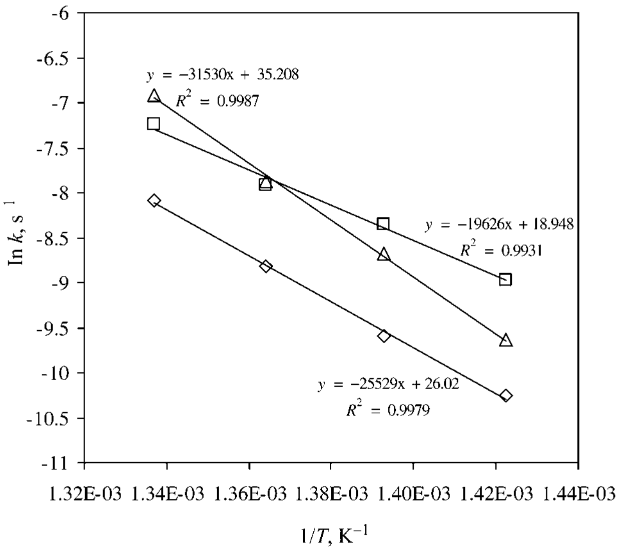


Figure 9. Arrhenius plot for four lump, three parameter model (◇, VR → G; □, VR → D; △, VR → C).

The rate equations for different species considered in the proposed kinetic model (Figure 4) based on first order kinetics can be given by the following set of differential equations:

$$\frac{dVR}{dt} = -kVR \tag{2}$$

$$\frac{dG}{dt} = k_1 VR \tag{3}$$

$$\frac{dD}{dt} = k_2 VR \tag{4}$$

$$\frac{dC}{dt} = k_3 VR \tag{5}$$

where $k = k_1 + k_2 + k_3$.

The analytical solutions for the above equations (2)–(5) are as follows;

$$VR = VR_o e^{-kt} \tag{6}$$

$$G = G_0 + \frac{k_1 VR_0}{k}(1 - e^{-kt}) \tag{7}$$

$$D = D_0 + \frac{k_2 VR_0}{k}(1 - e^{-kt}) \tag{8}$$

$$C = C_0 + \frac{k_3 VR_0}{k}(1 - e^{-kt}) \tag{9}$$

where $k = k_1 + k_2 + k_3$ and VR_0, G_0, D_0 and C_0 are zero time concentrations of VR, G, D and C, respectively.

The estimation of the rate constants was achieved by non-linear regression (Kataria *et al.*, 2004), which involves minimization of the sum of square of error (SSE) objective function given as follows:

$$SSE = \sum_{i=1}^{m}\sum_{j=1}^{n}\left(y_{\exp_{ij}} - Y_{\mathrm{pred}_{ij}}\right)^2$$

The rate constants were estimated by Simplex method using the MS-EXCEL spreadsheet programme. The guess values

Table 6. Variation in rate constants for different pathways at different temperatures.

Rate constants, s^{-1} (1×10^{-4})	$T = 430°C$	$T = 445°C$	$T = 460°C$	$T = 475°C$
k_1 (VR → G)	0.35	0.68	1.47	3.09
k_2 (VR → D)	1.27	2.36	3.65	7.13
k_3 (VR → C)	0.65	1.69	3.82	9.96

Table 7. Activation energy and frequency factor for different pathways.

	Activation energy, cal mol^{-1}	Frequency factor, s^{-1}
E_1 (VR → G)	50 726 (±7013)	1.997E + 11 (±130)
E_2 (VR → D)	38 997 (±9864)	1.694E + 08 (±942)
E_3 (VR → C)	62 650 (±6981)	1.953E + 15 (±127)

were selected using the methodology given by Mosby *et al.* (1986) and Ayasse *et al.* (1997). Figures 5, 6, 7 and 8 shows the comparison between the experimental and predicted values for coke, gas, distillate and VR, respectively in the proposed kinetic scheme. Figure 9 shows the Arrhenius plot for the proposed four lump, three parameter model. The estimated rate constants and the apparent activation energy for various product lumps for different reaction pathways are given in Table 6 and Table 7, respectively. From Table 6, it can be seen that the value of k_3 (reaction pathway involving formation of coke from VR) at 475°C is about 2.5 times higher than corresponding value at 460°C indicating that coking reactions are predominantly favorable at 475°C. This has been corroborated by the experimental data (Table 3) wherein it can be seen that at 475°C, about 14 wt% of coke yield was obtained for the reaction time of 5 min whereas for the same reaction time at 430°C, 445°C and 460°C, the yield of coke was only about 1 wt%. In the present work, the activation energy of the coke formation reaction (63 kcal mol^{-1}) was found to be higher than that of activation energy of the distillate formation reaction (39 kcal mol^{-1}). With regard to the confidence estimate of the kinetic parameters, 95% confidence interval was estimated. The values in bracket (Table 7) indicate 95% confidence interval. As can be seen from confidence intervals in Table 7, the activation energy of the path pertaining to coke formation is significantly higher than the activation energy of the path pertaining to distillate formation. It can also be seen that the activation energy of the path pertaining to coke formation is comparable to the activation energy of the path pertaining to the gas formation. The activation energy for the reaction pertaining to the formation of coke is in line with the activation energy (63.9 kcal mol^{-1}) reported by Del Bianco *et al.* (1993). The higher activation energy pertaining to the coke formation vis-à-vis distillate formation imply that the reactions responsible for the coke formation become relatively more important with the increase in temperature and coke formation proceed to completion rapidly.

CONCLUSIONS

(1) A new experimental set-up presented in this work was able to give the insight of inception, growth and subsequent saturation of coke formation within the severity range studied.

(2) The temperature difference of the reaction mass at the wall and at the centre of the reactor was found to be as low as 0–1°C and as high as 8–12°C depending upon the severity of the reaction.

(3) The coke formation levels off after a certain severity of the reaction and thereafter there is a slight fall in the coke yield as the volatiles trapped in the coke matrix are cracked when the reaction time is further increased.

(4) 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 min.

(5) Severity was found to have negligible effect on overall gas composition and methane (about 42 wt%) was found to be the major component.

(6) A four lump, three rate parameter model has been proposed to explain the mechanism of cracking and coking reactions. A very good agreement between the experimental yield and predicted yield of different pseudocuts was obtained.

(7) The value of k_3 (rate constant representing formation of coke from VR) at 475°C was found to be about 2.5 times higher than its corresponding value at 460°C indicating that coking reactions are predominantly favourable at 475°C.

(8) Over the temperature range studied, VR was found to undergo first order decomposition and the apparent activation energy for the reaction pathway involving the formation of coke from VR was found to be about 24 kcal mol^{-1} higher than the activation energy of formation of distillates from VR.

(9) Over the temperature range studied, the apparent activation energy pertaining to the reaction involving the formation of gas from VR was found to be 51 kcal mol^{-1}.

NOMENCLATURE

AMVR	Arabian mix vacuum residue
C	coke (defined as toluene insoluble), wt%
C_0	concentration of coke at zero reaction time, wt%
CCR	Conradson carbon residue, wt%
D	distillates (IBP-500°C), wt%
D_0	concentration of distillates at zero reaction time, wt%
E_1, E_2, E_3	activation energy, kcal mol^{-1}
G	gas (C_1–C_4), wt%
G_0	concentration of gas at zero reaction time, wt%
k_1, k_2, k_3	rate constants, s^{-1}
k	$k_1 + k_2 + k_3$, s^{-1}
SARA	saturates, aromatics, resins, asphaltenes
S_L	solubility limit of solvent for asphaltenes, wt%
SSE	sum of square of errors
t	time, s
T_C	temperature of the reaction mass at the centre of the reactor, °C
T_W	temperature of the reaction mass near the wall, °C
VR	vacuum residue (500°C+), wt%
VR_0	concentration of vacuum residue at zero reaction time, wt%
W_i	weight fraction of product specie obtained, g
W_{VR}	weight fraction of VR charged, g
y_i	variable

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