

# Study on a Kinetic Model of Atmospheric Gas Oil Pyrolysis and Coke Deposition

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The kinetics of pyrolysis and coke deposition of atmospheric gas oil (AGO for short) were studied at atmospheric pressure. The temperature, steam/AGO ratio, and residence time were varied in the range 1063–1208 K, 0.2 mol/mol, and 0.02–1.2 s, respectively. Mathematical models for pyrolysis and coke deposition have been proposed. Ethylene and aromatics are found to be the coke precursors. The study shows that the coking process in AGO pyrolysis is controlled by reaction kinetics.

## 1. Introduction

Ethylene is produced mainly by thermal cracking, i.e., pyrolysis, of hydrocarbons. It is always accompanied by formation of coke. Coke formation is a key factor in determining the run length of industrial cracking furnaces, the service life of cracker coil, and the consumption of feedstock. In the pyrolysis process, AGO cokes faster than naphtha and gaseous hydrocarbons. Therefore, the investigation of coke deposition in AGO pyrolysis is of great commercial importance. Froment (1981) studied the coke deposition in the pyrolysis of ethane and of propane. He pointed out that the coke precursor is propylene in propane pyrolysis and is mainly butadiene and aromatics in ethane pyrolysis. Kumar and Kunzru (1985) studied the coke deposition in naphtha pyrolysis and drew a conclusion that aromatics are coke precursors. They did not mention whether ethylene is a coke precursor or not. The present authors (Lou et al., 1986; Zou et al., 1987) found a different result: that both ethylene and propylene are coke precursors, and ethylene is the more intense precursor.

As a summary, the following conclusions can be drawn (Zou et al., 1991): (i) Coke precursors could be ethylene, propylene, and aromatics. Coke precursors are also dependent on the type of pyrolysis feedstocks used. (ii) The coke deposition of coke precursors is a complex process; however, it can be expressed by an overall reaction in which coke is supposedly formed by one step. At present, only a few studies on the coke deposition in AGO pyrolysis have been reported.

For these reasons, the present work was undertaken to study the influence of various factors, such as temperature, residence time, dilution ratio, etc., on the coke deposition in AGO pyrolysis with steam as diluent, and kinetic models for the corresponding pyrolysis and coke deposition were developed based on these observations.

## 2. Experimental Section

**2.1. Experimental System.** The experimental system used is a tubular reactor system with continuous flow designed and assembled by the authors (Zou et al., 1987). It consists of five units: (i) feedstock-measuring and transporting unit; (ii) temperature-controlling unit; (iii) pyrolysis reactor and continuous coke-measuring unit; (iv) data-recording and processing unit; (v) analysis unit for products. The construction of the pyrolysis reactor and that of the coke depositor are shown in Table I.

Table I. Construction of the Pyrolysis Reactor and Coke Depositor

reactor		coke depositor	
inside diam	19 mm	outside diam	5 mm
length	360 mm	length	20 mm
volume	120 mL	surface area	3.14 cm <sup>2</sup>
material	1Cr18Ni9Ti	material	1Cr18Ni9Ti
		distance from inlet	320 mm

Table II. Characteristics of AGO Used in This Study

$d_4^{20}$	0.7972	av mol wt	170
ASTM distillation	K	composition	wt %
IBP	372	paraffin	60.4
10%	430	naphthene	28.5
30%	487	aromatics	11.1
50%	540	sulfur	410 ppm
70%	577	hydrogen	15
90%	618	carbon	85
95%	632		
EP	641		

The experiments were conducted at atmospheric pressure in the temperature range 1063–1208 K. The inlet steam/AGO ratio was 0.2 mol/mol and the residence time was varied from 0.02 to 1.2 s. The preheating temperature range was 783–793 K. The protective gas in the electronic thermal balance was nitrogen.

The AGO used in the experiment was provided by Chemical Works No. 1 of Beijing Yanshan Petrochemical Corp. The characteristics of AGO are listed in Table II.

**2.2. Gas and Liquid Analysis.** The gaseous effluent was analyzed on-line on a gas chromatograph in which the thermal conductivity detector, methanation reactor, and flame ionization detector are arranged in series.

To analyze its composition, the liquid effluent condensed and collected in each run was separated into three fractions having a boiling range of IBP–473 K, 473 K–EP, and >EP, respectively. The content of unsaturated hydrocarbons in the liquid effluent whose boiling point is from IBP to 473 K was determined by the iodimetry method, and the total content of unsaturated hydrocarbons and aromatics was determined by sulfonation volumetric method. The content of aromatic hydrocarbons in the liquid effluent whose boiling point is from 473 K to EP was determined by ultraviolet spectroscopy. The analytical conditions for the latter were as follows. The ultraviolet spectrometer was Shimadzu UV-3000. The solvent was *n*-heptane. The measured wavelength range was between 240 and 300 nm. The slit width was 2 m. The length of the quartz cell was 100 mm. The liquid distillate higher than EP was taken as high molecular weight condensed aromatics. In addi-

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Table III. Selectivity Coefficients for Primary Reactions in AGO Pyrolysis<sup>a</sup>

component	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>6</sub>
this paper	0.74	1.18	0.34	1.94	0.053	0.87	0.087	0.42	0.36
Hitachi model	0.94	1.59	0.29	2.52	0.04	1.22		0.49	0.20

<sup>a</sup> Average molecular weight of feedstock is 170 for this paper; it is 214.54 for the Hitachi model (Zou, 1990).

Table IV. Kinetic Models for AGO Pyrolysis<sup>a</sup>

reaction no.	reaction	A (s <sup>-1</sup> )	E (kJ mol <sup>-1</sup> )
1	F → 0.74H <sub>2</sub> + 1.18CH <sub>4</sub> + 0.34C <sub>2</sub> H <sub>6</sub> + 1.94C <sub>2</sub> H <sub>4</sub> + 0.053C <sub>3</sub> H <sub>8</sub> + 0.87C <sub>3</sub> H <sub>6</sub> + 0.087C <sub>4</sub> H <sub>10</sub> + 0.42C <sub>4</sub> H <sub>8</sub> + 0.36C <sub>4</sub> H <sub>6</sub>	4.52 × 10 <sup>11</sup>	2.134 × 10 <sup>2</sup>
2	C <sub>2</sub> H <sub>6</sub> = C <sub>2</sub> H <sub>4</sub> + H <sub>2</sub>	4.65 × 10 <sup>13</sup>	2.730 × 10 <sup>2</sup>
3	2C <sub>2</sub> H <sub>6</sub> → C <sub>3</sub> H <sub>8</sub> + CH <sub>4</sub>	1.2 × 10 <sup>12</sup>	2.754 × 10 <sup>2</sup>
4	C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>6</sub> → C <sub>3</sub> H <sub>6</sub> + CH <sub>4</sub>	7.08 × 10 <sup>10b</sup>	2.530 × 10 <sup>2</sup>
5	C <sub>3</sub> H <sub>8</sub> = C <sub>3</sub> H <sub>6</sub> + H <sub>2</sub>	5.89 × 10 <sup>10</sup>	2.147 × 10 <sup>2</sup>
6	C <sub>3</sub> H <sub>8</sub> → C <sub>2</sub> H <sub>4</sub> + CH <sub>4</sub>	4.69 × 10 <sup>10</sup>	2.118 × 10 <sup>2</sup>
7	C <sub>3</sub> H <sub>8</sub> + C <sub>2</sub> H <sub>4</sub> → C <sub>2</sub> H <sub>6</sub> + C <sub>3</sub> H <sub>6</sub>	2.54 × 10 <sup>10b</sup>	2.472 × 10 <sup>2</sup>
8	2C <sub>3</sub> H <sub>6</sub> → 3C <sub>2</sub> H <sub>4</sub>	1.2 × 10 <sup>11</sup>	2.687 × 10 <sup>2</sup>
9	2C <sub>3</sub> H <sub>6</sub> → 0.3C <sub>6.5</sub> H <sub>7</sub> + 0.14L + 3CH <sub>4</sub>	1.24 × 10 <sup>9</sup>	2.080 × 10 <sup>2</sup>
10	C <sub>4</sub> H <sub>10</sub> = 2C <sub>2</sub> H <sub>4</sub> + H <sub>2</sub>	7.2 × 10 <sup>14</sup>	2.959 × 10 <sup>2</sup>
11	C <sub>4</sub> H <sub>10</sub> → C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>6</sub>	4.1 × 10 <sup>12</sup>	2.566 × 10 <sup>2</sup>
12	C <sub>4</sub> H <sub>10</sub> = C <sub>4</sub> H <sub>8</sub> + H <sub>2</sub>	1.64 × 10 <sup>12</sup>	2.610 × 10 <sup>2</sup>
13	C <sub>4</sub> H <sub>8</sub> → 0.41C <sub>6.5</sub> H <sub>7</sub> + 0.19L	1.03 × 10 <sup>9</sup>	2.124 × 10 <sup>2</sup>
14	C <sub>4</sub> H <sub>8</sub> → C <sub>4</sub> H <sub>6</sub> + H <sub>2</sub>	1.0 × 10 <sup>10</sup>	2.093 × 10 <sup>2</sup>
15	C <sub>2</sub> H <sub>4</sub> + C <sub>4</sub> H <sub>6</sub> → B + 2H <sub>2</sub>	1.46 × 10 <sup>2b</sup>	1.032 × 10 <sup>2</sup>
16	C <sub>4</sub> H <sub>6</sub> + C <sub>3</sub> H <sub>6</sub> → T + 2H <sub>2</sub>	1.38 × 10 <sup>b</sup>	1.404 × 10 <sup>2</sup>
17	C <sub>4</sub> H <sub>6</sub> + C <sub>4</sub> H <sub>8</sub> → EB + 2H <sub>2</sub>	1.40 × 10 <sup>11b</sup>	2.461 × 10 <sup>2</sup>
18	2C <sub>4</sub> H <sub>6</sub> → ST + 2H <sub>2</sub>	1.94 × 10 <sup>12b</sup>	2.634 × 10 <sup>2</sup>
19	C <sub>2</sub> H <sub>4</sub> → 0.15C <sub>2</sub> H <sub>6</sub> + 0.233C <sub>3</sub> H <sub>6</sub> + 0.1C <sub>4</sub> H <sub>8</sub>	1.06 × 10 <sup>13</sup>	3.038 × 10 <sup>2</sup>
20	C <sub>3</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>6</sub> → C <sub>4</sub> H <sub>8</sub> + CH <sub>4</sub>	1.18 × 10 <sup>12b</sup>	2.911 × 10 <sup>2</sup>

<sup>a</sup> F, raw material (N + P); B, benzene; T, toluene; EB, ethylbenzene; ST, styrene; L, C<sub>5</sub><sup>+</sup>, average carbon number 7.5, average molecular weight 91. <sup>b</sup> Unit: m<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

tion, average molecular weight, specific gravity, etc. for liquid effluent were also measured.

### 3. Pyrolysis Reaction Model

In order to establish a coking model for AGO pyrolysis, the concentration of coke precursors at the coke depositor must be determined in advance. Therefore, it is necessary, first, to establish a pyrolysis reaction model which could be used to predict the major product yields including the aromatics.

AGO is a complicated mixture of hydrocarbons; therefore, it is very necessary to define the AGO conversion. In the present study, it is calculated by the following expression:

$$X = W_G + W_{C_5^+} + A_L - A_F \quad (1)$$

and residence time is calculated by the following expression:

$$\theta_e = V_e / V_{out} \quad (2)$$

The pyrolysis reaction is a complex process which is composed of concurrent and consecutive reactions. The selectivity coefficients for primary reaction products vary with conversion  $X$ . In general, with increase of conversion,  $X$ , the selectivity coefficients of H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>4</sub>H<sub>8</sub> will be slightly increased, while those of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub> will be slightly decreased. In our experiment process, the above-mentioned trend has been also observed; however, the variation was very small. Therefore, the arithmetic average value of the selectivity coefficients for each product is acceptable. In order to determine the selectivity coefficients for primary reaction in AGO pyrolysis, a set of experiments of low conversion were carried out as part of our study. The selectivity coefficients obtained from the experimental results are shown in Table III. The selectivity coefficients for AGO pyrolysis in the Hitachi model (Zou, 1990) are also listed in the table for

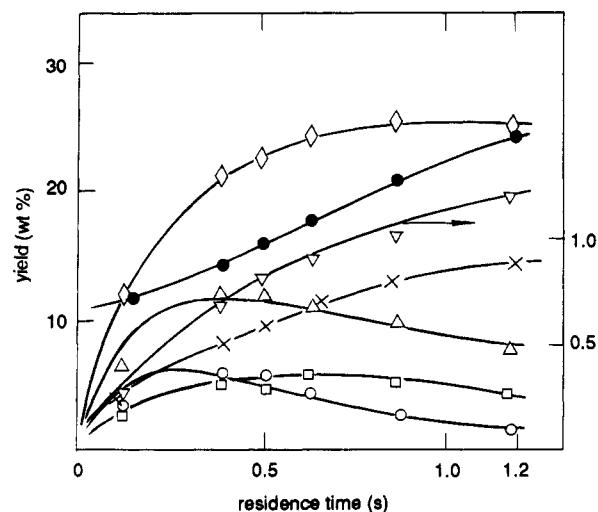


Figure 1. Comparison between experimental product yields and calculated values (solid curves denote calculated values; symbols denote experimental values). (▽) Hydrogen; (×) methane; (◇) ethylene; (Δ) propylene; (○) butylenes; (□) butadiene; (●) aromatics.  $T = 1121$  K.

comparison. It can be seen from the table that the selectivity coefficients vary greatly with molecular weight of feedstock.

The experimental results show that AGO pyrolysis is retarded by self-inhibition action; that is, the rate constant for the primary reaction decreases with increase of conversion. Especially at high conversion, this effect must be taken into account. The variation of rate constant  $k_F$  for the primary reaction with conversion,  $X$ , can be expressed in the formula with hyperbolic form

$$k_F = \frac{k_0}{1 + \alpha X} \quad (3)$$

where

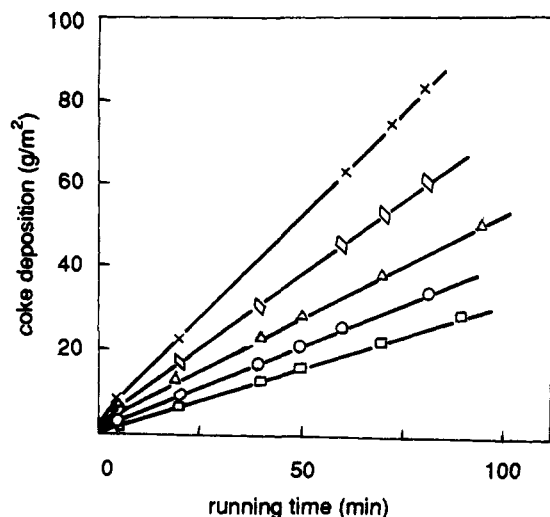


Figure 2. Coke deposition vs running time. (□) Residence time 0.337 s; (O) residence time 0.498 s; (Δ) residence time 0.543 s; (◇) residence time 0.775 s; (X) residence time 1.136 s.  $T = 1151$  K.

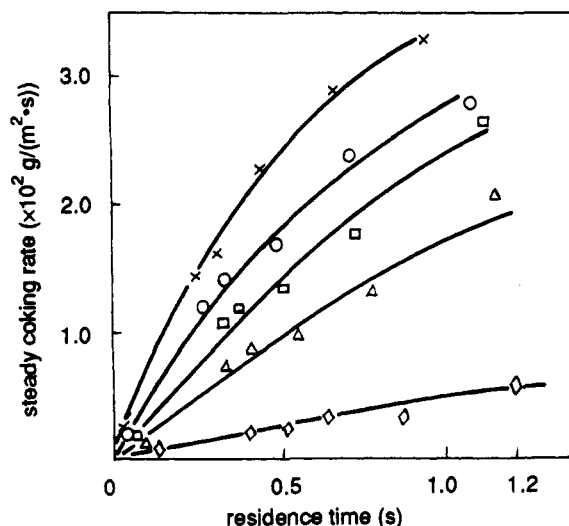


Figure 3. Steady coking rate vs residence time. (◇) Equivalent temperature 1121 K; (Δ) equivalent temperature 1151 K; (□) equivalent temperature 1173 K; (O) equivalent temperature 1191 K; (X) equivalent temperature 1207 K.

$$k_0 = A \exp(-E/RT) \quad (4)$$

$$\alpha = 3.50 \times 10^5 \exp(-10367/T) \quad (5)$$

The pyrolysis reaction model established in the present paper is shown in Table IV. The calculated value of each product yield in AGO pyrolysis is in good agreement with the experimental one as shown in Figure 1.

#### 4. Coke Deposition Reaction Model

The coke deposition process in AGO pyrolysis can be divided into two stages, i.e., the initial coke deposition stage and the steady-state coke deposition stage. In the initial stage, the coking rate is increased, but as reaction proceeds, the coke depositor surface is gradually covered and passivated with the deposited coke. At this point, the coking rate gradually decreases and finally tends to a steady-state value; this coking rate is called the steady-state coking rate. Typical plots for the variation of coking amount with running time are shown in Figure 2. From the experimental results, the conclusion can be drawn that, in the initial stage, the exposed metal surface catalyzes

Table V. Some Possible Kinetic Models for Coke Deposition in AGO Pyrolysis

model no.	model
1	$F \xrightarrow{k_F} \text{products}$
	$C_2H_4 \xrightarrow{k_{12}^*} \text{coke}$
2	$F \xrightarrow{k_F} \text{products}$
	$\text{aromatics} \xrightarrow{k_{15}^*} \text{coke}$
3	$F \xrightarrow{k_F} \text{products}$
	$C_2H_4 \xrightarrow{k_{12}^*} \text{coke}$
	$\text{aromatics} \xrightarrow{k_{15}^*} \text{coke}$
4	$F \xrightarrow{k_F} \text{products}$
	$C_3H_6 \xrightarrow{k_{16}^*} \text{coke}$
	$\text{aromatics} \xrightarrow{k_{15}^*} \text{coke}$
5	$F \xrightarrow{k_F} \text{products}$
	$C_4H_8 \xrightarrow{k_{22}^*} \text{coke}$
	$\text{aromatics} \xrightarrow{k_{21}^*} \text{coke}$
6	$F \xrightarrow{k_F} \text{products}$
	$C_4H_6 \xrightarrow{k_{24}^*} \text{coke}$
	$\text{aromatics} \xrightarrow{k_{25}^*} \text{coke}$

<sup>a</sup> F: (N + P) of AGO.

the coke-forming reactions. The initial coke deposition stage is a surface reaction controlled process.

It is found from experiments that the steady-state coking rate is not influenced by the surface area of the coke depositor. Moreover, as residence time is increased, the steady-state coking rate monotonically increases, as shown in Figure 3. In the meantime, as the residence time is increased, the conversion increases while the mass-transfer coefficient decreases; therefore, the steady-state coke deposition stage is also a surface reaction controlled process.

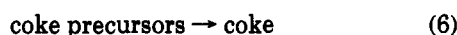
In the experiment, the coke deposited on the reactor surface was burned up with air. This process is called the decoking process. It was observed by measuring the decrease in the amount of coke remaining on the reactor surface as decoking time is prolonged. It was found that the coke deposited during AGO pyrolysis has a two-layer structure. It was observed in the experiment that the outer layer is filamentous and has a nonuniform distribution, while the inner layer is thick and has a uniform distribution.

Coke deposition carried out in AGO pyrolysis is a complex process. The exact mechanism is still not clear. From coke precursor to final coke, many reaction and mass-transfer steps will occur. Due to these uncertainties, only simplified models were postulated. In various authors' models, the coke deposition reactions are always expressed as an overall reaction during which coke is formed through one step, that is

Table VI. Result of the Screened Coking Models<sup>a</sup>

model no.	$k^*$	$A^*$	$E^*$	$n$	RSS
1	$k_1^*$	$(1.47 \pm 2.42) \times 10^{14}$	$(2.21 \pm 0.86) \times 10^2$	$0.87 \pm 1.3$	$2.75 \times 10^{-2}$
2	$k_5^*$	$(1.13 \pm 0.61) \times 10^{11}$	$(1.40 \pm 0.22) \times 10^2$	$1.01 \pm 0.52$	$3.84 \times 10^{-4}$
3	$k_{12}^*$	$(5.00 \pm 0.05) \times 10^{14}$	$(2.24 \pm 0.06) \times 10^2$	$1.34 \pm 0.10$	$3.14 \times 10^{-5}$
	$k_{13}^*$	$(1.39 \pm 0.04) \times 10^{12}$	$(1.41 \pm 0.07) \times 10^2$	$1.37 \pm 0.05$	
4	$k_{18}^*$	$(2.77 \pm 6.81) \times 10^9$	$(1.16 \pm 0.18) \times 10^2$	$2.89 \pm 0.50$	$5.37 \times 10^{-3}$
	$k_{19}^*$	$(5.36 \pm 2.05) \times 10^{10}$	$(1.24 \pm 0.10) \times 10^2$	$1.12 \pm 0.28$	
5	$k_{22}^*$	$(6.17 \pm 6.97) \times 10^{13}$	$(1.82 \pm 0.44) \times 10^2$	$1.28 \pm 2.47$	$6.86 \times 10^{-4}$
	$k_{23}^*$	$(5.19 \pm 0.38) \times 10^{10}$	$(1.06 \pm 0.16) \times 10^2$	$1.41 \pm 0.21$	
6	$k_{24}^*$	$(5.61 \pm 8.67) \times 10^{18}$	$(2.74 \pm 0.54) \times 10^2$	$2.17 \pm 1.35$	$8.84 \times 10^{-4}$
	$k_{25}^*$	$(1.13 \pm 0.22) \times 10^{11}$	$(1.40 \pm 0.20) \times 10^2$	$1.01 \pm 0.32$	

<sup>a</sup>  $k^*$ , reaction rate constant;  $A^*$ , frequency factor;  $E^*$ , activation energy;  $n$ , reaction order; RSS, residual sum of squares.



considering that both the coke depositor and the reactor of our experimental system are in an identical reaction atmosphere, the asymptotic coking rate at the coke depositor can be expressed by

$$r_c = k^*(C^*)^n \quad (7)$$

From the Arrhenius equation

$$k^* = A^* \exp(-E^*/RT) \quad (8)$$

and the equation of state

$$C^* = \frac{F^*P}{FRT} \quad (9)$$

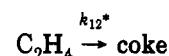
eq 7 can be arranged into

$$r_c = A^*[\exp(-E^*/RT)](F^*P/FRT) \quad (10)$$

On the basis of the above-mentioned possible coke precursors, 30 simplified coking models were proposed by permutation and combinations. Six examples are listed in Table V.

In the present paper, the residual sum of squares between the calculated value and experimental asymptotic coking rate was used as the objective function and minimized by the appropriate choice of frequency factor, activation energy, and reaction order. The unified parameter estimation of parameters  $A^*$ ,  $E^*$ , and  $n$  was made by using the modified random-search algorithm (Lou, 1985) combined with the Marquardt algorithm. In order to make the iteration converge, reparametrization was necessary because of the strong correlation between  $A^*$  and  $E^*$  and the great difference in order of magnitude among  $A^*$ ,  $E^*$ , and  $n$ . The concentration of coke precursors can be calculated by using the models shown in Table IV combined with eq 3. The 30 possible kinetic models for coke deposition have been screened by discarding the models in which the value(s) of  $E^*$ ,  $A^*$ , or (and)  $n$  is (are) negative and the models whose kinetic parameters are much beyond the range of the ordinary kinetic parameter value for coke deposition. For the sake of reliability, the  $t$ -test has also been made; the screened models are just the models given in Table V. The result of the screened coking models and the interval estimation of various parameters at the 95% confidence level are listed in Table VI.

From Table VI, it can be seen that model 3 was preferred over the other models because the residual sum of squares (RSS) was significantly lower. Therefore, it is clear that the coke precursors in AGO pyrolysis are ethylene and aromatics. The coking model is



The calculated results show that aromatics are more intense coke precursors during the coking process in AGO pyrolysis.

## Conclusions

On the basis of the studies on the coke deposition process in AGO pyrolysis, the following conclusions can be drawn:

(i) Coke deposition in AGO pyrolysis is a complicated physical and chemical process and is controlled by surface chemical reaction.

(ii) Coke precursors in AGO pyrolysis are aromatics and ethylene, but coking from aromatics is predominant.

(iii) The coking rate can be expressed as a function of temperature and concentrations of two components, aromatics and ethylene, as follows:

$$r_c = 5.00 \times 10^{14} [\exp(-2.24 \times 10^2/RT)] C_{C_2H_4}^{1.34} + 1.39 \times 10^{12} [\exp(-1.41 \times 10^2/RT)] C_{Ar}^{1.37} \quad (12)$$

It is expected that the model proposed in the present paper can be used to predict coking profiles in commercial cracker coil.

## Acknowledgment

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## Nomenclature

$A$  = frequency factor  
 $A_F$  = total content of aromatics in feedstock (wt %)  
 $A_L$  = total content of aromatics in liquid effluent (wt %)  
 $C$  = concentration (mol m<sup>-3</sup>)  
 $E$  = activation energy (kJ mol<sup>-1</sup>)  
 $F$  = total molar flow rate (mol s<sup>-1</sup>)  
 $k$  = reaction rate constant  
 $n$  = reaction order  
 $P$  = pressure (N m<sup>-2</sup>)  
 $r_c$  = coking rate (mg m<sup>-2</sup> s<sup>-1</sup>)  
 $R$  = gas constant (kJ mol<sup>-1</sup> K<sup>-1</sup>)  
 $S$  = surface area of coil (m<sup>2</sup>)  
 $T$  = temperature (K)  
 $V$  = volume of coil (m<sup>3</sup>)  
 $V_e$  = equivalent reactor volume (m<sup>3</sup>)  
 $V_{out}$  = volumetric flow rate in the outlet of reactor (m<sup>3</sup> s<sup>-1</sup>)  
 $X$  = conversion

$W_G$  = gaseous product yield (wt %)

$W_{C_5^+}$  = yield of  $C_5^+$  distillate in liquid effluent (wt %)

#### Greek Symbols

$\alpha$  = self-inhibition coefficient of pyrolysis reaction

$\theta_e$  = equivalent apparent residence time (s)

#### Superscripts and Subscripts

\* = coke deposition or coke precursor

Ar = aromatics

0 = zero conversion

**Registry No.** The following registry numbers were provided by the authors. C, 7440-44-0; ethylene, 74-85-1; propylene, 115-07-1.

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