

# ESTIMATION OF KINETIC PARAMETERS OF COKING REACTION RATE IN PYROLYSIS OF NAPHTHA

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**Abstract** The run length of cracking furnaces is limited by the formation of coke on the internal skin of the reactor tubes. The reaction mechanism of thermal cracking of hydrocarbons is generally accepted as free-radical chain reactions. On the basis of the plant output data and the insight in the mechanisms for coke formation in pyrolysis reactors, a kinetic model describing the coke formation has been developed. It consists of seven reactions for coke formation assuming that the sources of coke formation are ethylene, propylene, butadiene and benzene, toluene, xylene and styrene. The coking model was combined with a rigorous kinetic model for the pyrolysis of naphtha and a reactor model. The parameters for this model were determined using nonlinear Marquardt optimization method. The sum of squares of the deviations between the calculated and plant data was used as the objective function and minimized by the appropriate choice of the portion of each reaction involved in coke formation. Finally the simulated and plant output results agree in a good accuracy.

**Key Words** Thermal Cracking, Coke Formation, Kinetic Parameters

**چکیده** یکی از مهمترین عواملی که زمان کارکرد کوره های شکست حرارتی را محدود می کند، تشکیل و نشست کک روی دیواره داخلی لوله های راکتور در طول عملیات شکست حرارتی خوراک های هیدروکربنی است. در این مقاله با توجه به اطلاعات حاصل از واحدهای صنعتی و با در نظر گرفتن مکانیزم های مختلف تشکیل کک در راکتورهای شکست حرارتی، یک مدل سینتیکی برای تشکیل کک توسعه داده شده است. این مدل شامل هفت واکنش است و در آن منابع اصلی تشکیل کک موادی چون اتیلن، پروپیلن، بوتادین، بنزن، تولوئن، زایلین و استایرین در نظر گرفته شده اند. در نهایت مدل تشکیل کک با مدل سینتیکی شکست حرارتی نفتا و مدل ریاضی راکتور ترکیب گردیده و پارامترهای مدل با استفاده از روش بهینه سازی غیر خطی مارکارد تعیین شده اند. مجموع مربعات انحرافات بین مقادیر محاسبه شده و مقادیر حاصل از واحدهای صنعتی به عنوان یک تابع هدف تعیین شده و با روشهای مناسب به حداقل رسانده می شود.

## 1. INTRODUCTION

The thermal cracking of hydrocarbons ranging from ethane to gas oil is the most important source of olefins and aromatics, the main feedstocks of the petrochemical industries. The hydrocarbon is diluted with steam (e.g. 0.3 kg steam/kg hydrocarbon in ethane cracking, 0.6-0.7 for naphtha) to minimize undesired side reactions and

then preheated to around 600-650°C in the convection section of the furnace.

The thermal cracking of hydrocarbons is always accompanied by coke formation. The coke deposits on the walls of the coil affect the operation of pyrolysis coils with pressure drop increase, heat transfer reduction, hot spot and corrosion by carburization. These phenomena have such penalty as: reduced run length, selectivity reduction,

production losses, high maintenance cost and increased utility cost. Because of the above reasons, the coke has to be periodically removed.

Research has been carried out to understand the mechanisms under which coke formation occurs and to search for solutions to reduce or prediction of coking rate. From the scientific point of view and understanding of the relationship between structure of hydrocarbons and their tendencies to form carbonaceous deposits can be of great help in developing accurate fundamental models for the prediction of the extent of coke formation. During pyrolysis, coke can form both in the gas phase and on the metal surface and possible routes for different types of coke have been suggested. The main mechanisms by which cokes produced in the coil and transfer line exchanger of a cracking furnace were investigated [1,2]. Investigations have shown that coke formation occurs from either reactants and/or products in the reactor. Virk et al. [3] reported that coke is formed from aromatic substances condensation. Froment et al. [4,5] studied the coke deposition in the pyrolysis of ethane and propane. He pointed out that the coke precursor is propylene in propane pyrolysis, and is mainly butadiene and aromatics in ethane pyrolysis. They have been reported the coking rate was correlated with respect to the concentration of a number of products such as C<sub>5</sub>+, olefins, diolefins, butadiene, butene, and aromatics, through a first order rate equation. Dente et al. [6] have reported that coke formation during naphtha pyrolysis involves the continuous transformation of polymeric material into coke through dehydrogenation and dealkylation reactions. In these mechanisms, olefins, diolefins, aromatics, polyaromatics and acetylenic compounds have been postulated as the coke precursors. However, no details of the model have been revealed. Albright et al. [7] developed a general equation and found to correlate the coking rates as a function of run time. Coke deposition in naphtha pyrolysis and drew a conclusion that aromatics are coke precursors by Kumar and Kunzru [8,9]. The rate of coke formation was found to be proportional to the square of the concentration in the cracked products. Lou et al. [10], Zou et al. [11] found a different result that both ethylene and propylene are coke precursors, and ethylene is the more intense precursor.

## 2. PYROLYSIS KINETIC MODEL

The reaction mechanism of thermal cracking of hydrocarbons is generally accepted as free-radical chain reactions. A complete reaction network, using a rigorous kinetic model, for the decomposition of the naphtha feed, which was developed by Towfighi et al. [12-14], is used for the simulation of a naphtha cracker. The dimensions and complexity of the detailed kinetic models of hydrocarbon pyrolysis imposed and justifies the adoption of a proper simplification level, coherent with the final aim of the model itself. These simplifications and/or lumping procedures reduce the total number of equivalent chemical species and equivalent reactions.

The very detailed mechanistic kinetic scheme in this simulation network, developed during the last decades, involves over hundreds of reactions and 91 molecular and radical species. As usual this chain radical mechanism consists of several radical and molecular elementary reactions, which can be briefly summarized as follows. Some kinetic extensions were made and the kinetic parameters were verified and tuned with a large amount of pilot plant data and industrial data. Some of the experiments are shown and compared with those obtained from model. The summary of the model for thermal cracking of naphtha is given in Table 1.

The governing mass, energy, and momentum balance equations for the cracking coil which has a significant stiffness in the numerical simulation due to the large differences in concentration gradient between radicals and molecules. This problem can be tackled through the application of the Gear method.

## 3. EXPERIMENTAL SECTION

**3.1 Experimental Setup** The pyrolysis experiments were conducted in a tubular pilot plant system, which is designed and assembled by the ORG, for studying of the pyrolysis reaction kinetics. The setup, used for the experiments of the naphtha thermal cracking is a computer controlled pilot plant unit, shown schematically in Figure 1. The hydrocarbon and diluent water are pumped into the preheaters. Liquid hydrocarbons and water

**TABLE 1. Typical Samples of Radical and Molecular Reactions in Thermal Cracking of Naphtha.**

Reactions	Log (A) (1/s, 1/mol,s)	E (kcal/mol)
<b>Radical Reactions</b>		
<b>Initiation</b>		
$n-C_6H_{14} \rightarrow C_2H_5 \cdot + 1-C_4H_9 \cdot$	16.8	82
$C_3H_8 \rightarrow H \cdot + 1-C_3H_7 \cdot$	17.3	92
<b>H Abstraction</b>		
$H \cdot + C_2H_6 \rightarrow H_2 + C_2H_5 \cdot$	11.1	9.7
$CH_3 \cdot + C_3H_8 \rightarrow CH_4 + 2C_3H_7 \cdot$	8.8	10.5
<b>Radical Decomposition</b>		
$i-C_4H_9 \rightarrow CH_3 + C_3H_6$	14.2	32.7
$n-C_4H_9 \rightarrow H + C_4H_8$	12.7	37.9
<b>Radical Addition</b>		
$CH_3 \cdot + C_3H_6 \rightarrow 1,n-C_4H_9$	8.5	7.4
$CH_3 \cdot + C_2H_4 \rightarrow 1C_3H_7$	8.1	7.7
<b>Termination Reaction</b>		
$C_2H_5 \cdot + C_2H_5 \cdot \rightarrow n-C_4H_{10}$	12.3	0.0
$CH_3 \cdot + \alpha-C_3H_5 \cdot \rightarrow 1-C_4H_8$	12.9	0.0
<b>Molecular Reactions</b>		
<b>Olefin Isomerization</b>		
$1-C_4H_8 \rightarrow 2-C_4H_8$	12.4	14.3
$2-C_4H_8 \rightarrow 1-C_4H_8$	12.3	14.8
<b>Olefin Dehydrogenation</b>		
$1-C_4H_8 \rightarrow 1,3-C_4H_6 + H_2$	4.0	18.1
<b>Olefin Decomposition</b>		
$1,3-C_4H_6 + C_2H_2 \rightarrow C_6H_6 + H_2$	11.2	5.38
$1,3-C_4H_6 + C_2H_4 \rightarrow Cyclo C_6H_{10}$	10.5	6.33

as dilution steam are fed by means of dowsing and pulsation-free pumps. The hydrocarbon and steam are mixed and preheated up to 600°C. The furnace consists of two electrical preheaters for the water and hydrocarbon feeds. An additional electrical heater is used for the reactor section. The preheaters are single zones and the reaction section heater is divided into eight zones, which can be heated independently to set any type of temperature profile. Each heating zone can be controlled on the process computer. The reactor is a 1 m long, 10 mm internal diameter tube, made of Inconel 600. There are eighteen thermocouples along the reactor, 8 inside the furnace, 8 on the external tube skin and additional 2 for measuring of XOT (Cross over temperature) and COT (Coil outlet temperature). The reactor is heated electrically and placed vertically in a cylindrical

**TABLE 2. Specification of Analysis System.**

Chromatograph			
1. Varian Chrompack CP3800			
		Detector	Product analysis
Column A	Capillary CP-CIL 5CB	FID	$C_2H_4, C_3H_6, C_4H_6, \dots$
Column B	Packed column	Methanizer and FID in series	$CO, CO_2$
2. Varian Chrompack CP3800			
Column A	Capillary CP - CIL-PONA	FID With split/splitless	$C_5+$ , Aromatics
Column B	Packed column	TCD	$H_2, CH_4$

furnace. The temperature reading is also visualized on a color digital thermometer display.

The reactor effluent is cooled in a double pipe heat exchanger by circulating ice water. Liquid products, tars and any possible solid particles cooled and separated by means of three glass condensers and cyclones. A fraction of the product gas is then withdrawn for the on-line analysis on gas chromatograph, while the rest is sent directly to the flare. The on-line analysis of the reactor effluent is performed by means of two computerized gas chromatographs for analysis of the non-condensable gases and heavy components (PIONA) including  $C_5+$  and aromatics, whose specifications are mentioned in Table 2.

**3.2 Experimental Analysis** Developing a coking model requires a suitable model of thermal cracking reactor based on a reliable kinetic model. To obtain reliable results these models shall be solved simultaneously. Therefore, the ORG complete reaction network was used. Then it was verified and tuned by pilot plant data. For this purpose, a series of experiments were carried out, using naphtha as the feed of pilot plant reactor. In the experiments, the pyrolysis of naphtha was studied under different operating conditions. The composition of product mixtures of thermal cracking process is influenced by the variation of

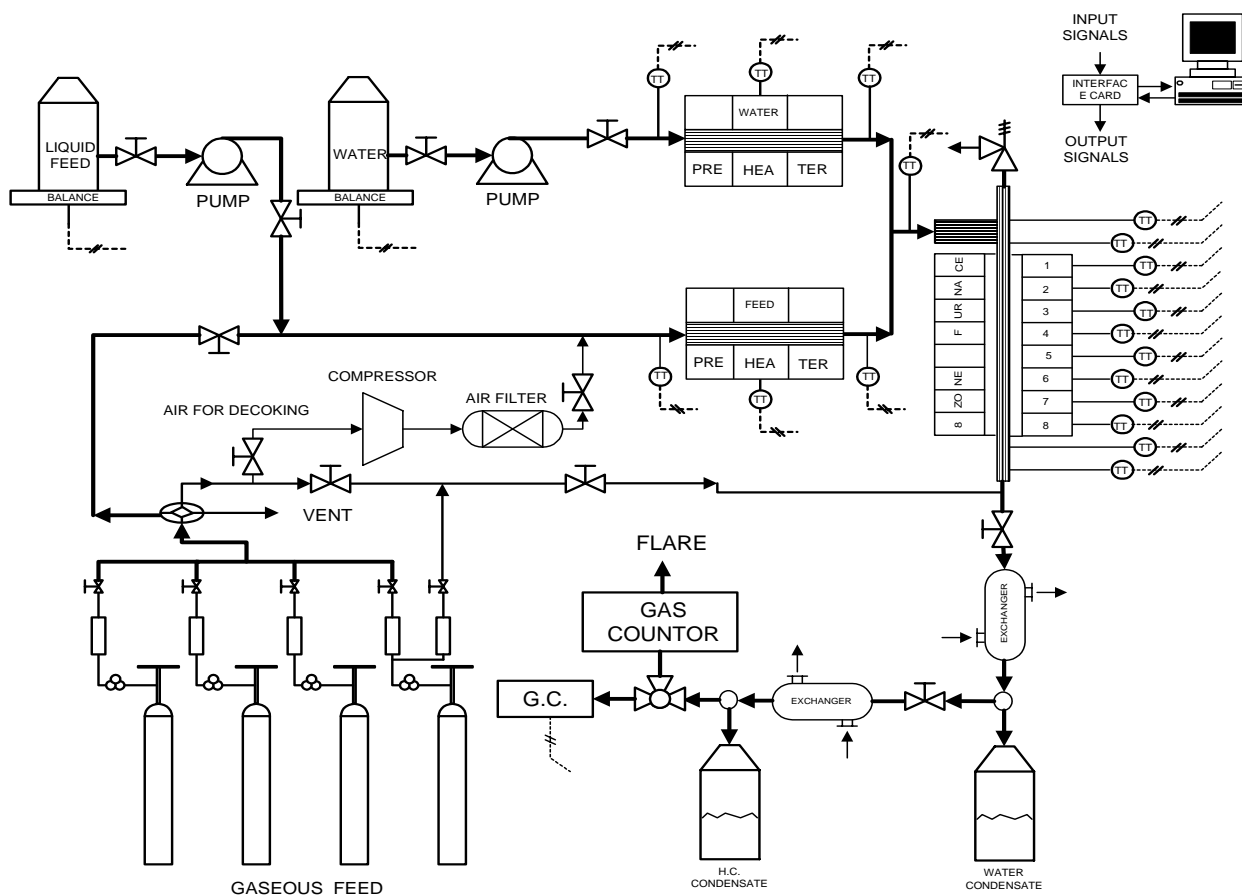


Figure 1. Flow diagram of thermal cracking pilot plant.

operating conditions such as temperature, partial pressure and space-time. Process gas temperature profile along the cracking coil is the most important factor that affects the product selectivity. In order to study the effect of operating conditions on product yields following changes were considered:

- Variation of temperature profile along the coil
- Variation of space-time in the coil by changing the hydrocarbon feed flow rate at constant steam ratio values.

The feedstock was straight run naphtha from ARPC with the composition as shown in Table 3. The reaction conditions were similar to industrial reactors ( $T=800-920\text{ }^{\circ}\text{C}$ ; space time = 0.1-0.5 sec; total pressure = 1 bar; dilution ratio  $\text{H}_2\text{O}$  /naphtha

= 0.5 - 0.8). The preheating temperature range was  $580-600\text{ }^{\circ}\text{C}$ .

#### 4. COKE MODEL DEVELOPMENT

Coke formation in the pyrolysis of hydrocarbons is a complex phenomenon due to the various possible coke forming free radical reactions and the exact mechanism is still not clear. Taking into account all the possible reaction pathways would lead to an unrealistically high number of kinetic parameters, and their estimation would not be possible or at least inaccurate. The number of reactions can be decreased by restricting the number of coke precursors. Paraffins are the main components in a naphtha feedstock. These components do not

**TABLE 3. Specification of Naphtha Feed (%wt).**

Naphtha Composition (wt%)			
n-Butane	4.53	2,2,3triMethylButane	7.20
iso-Butane	0.12	Benzene	2.17
n-Pentane	22.52	Toluene	0.37
iso-Pentane	16.48	P&m-Xylene	0.44
2,2diMethylButane	0.30	Cyclo-Hexane	7.112
2,3diMethylButane	1.18	n-Heptane	1.69
Cyclo-Pentane	7.38	2,3diMethylPentane	1.10
2 Methyl-Pentane	12.17	n-Octane	0.63
n-Hexane	12.02	iso-Octane	0.20
2,4diMethylPentane	2.30	n-Nonane	0.07

disappear through addition reactions so that their direct contribution to coke formation is low. Moreover, the coking rate is highest in the high temperature section of the reactor. In this section the paraffin content in the reacting mixture has decreased to a large extent. For the same reasons, naphthenes can also be neglected as direct precursors to coke.

Unsaturates are a very important class of coke precursors. They are reaction products of the pyrolysis reactions so that their concentration in the high- temperature zone of the reactor is high (ethylene about 35%, propylene 14%, butadiene 4 - 5 %wt). Furthermore, unsaturates are reactive and are good candidates for radical addition. C4 components, which are present in high concentration, are important coke precursors. Longer chain unsaturated components decompose rapidly to smaller components.

Aromatics form a second class of important coke precursors. The aromatic ring structure is close to the structure of the coke matrix. Further, (branched) aromatics are reactive components, especially at the high temperatures prevailing in thermal cracking coils (their concentration in the high- temperature zone of the reactor is about 10-12 wt% depends on the nature of feedstocks). Due to these uncertainties, only simple models involving either the reactant and/or products were postulated. Important factors can be considered, as coke precursors are reactivity and local

concentration of coke precursors along the coil. The proposed model assumes that coke can be formed either from the reactant, ethylene, propylene, butadiene and aromatic as coke precursors. Coke models consist of seven parallel reactions as follows:

- 1) Ethylene →Coke
- 2) Propylene →Coke
- 3) Butadiene →Coke
- 4) Benzene →Coke
- 5) Toluene →Coke
- 6) Xylene →Coke
- 7) Styrene →Coke

For each reaction, the following expression can be written for the rate of coking:

$$r_{ci} = C_{H_2} C_{CH_4} k_i C_i \quad (1)$$

To reduce the number of independent variables, coke precursors are classified into groups depending upon their characteristic (olefins, diene and aromatic ring). The coking rate with precursors which belongs to the same group is considered to have the same activation energy ( $E_i$ ). A reference component is chosen in each group. The reference for the coke formation out of the other members of the group are related to that of the other members of the group and relative reactivity for coke

**TABLE 4. Kinetic Parameters of Coking Model.**

Group	$k_0$ [Kg coke/((m <sup>2</sup> )(hr)(kmol/m <sup>3</sup> ) <sup>3</sup> )]	E (J/mole.K)
Olefins	7.8589e+8	7.4164e+4
Butadiene	2.099e+12	1.2794e+5
Aromatics	4.1865e+8	2.9977e+4

**TABLE 5. Basic Information of Cracking Furnace.**

Furnace characteristics	
Height (m)	11.473
Length (m)	10.488
Depth (m)	2.1
No. of Burners	108
Reactor configuration	
Total length (m)	45
Total length pass 1: (m)	22.5
Internal/External dia.(mm)	85 / 92
Total length pass 2: (m)	22.5
Internal/External dia. (mm)	121 / 130
Material properties	
Tube thermal conductivity	-1.257 + 0.0432 T
Coke thermal conductivity	6.46
Coke specific gravity (kg/m <sup>3</sup> )	1680

formation derived by Kopinke et al. [15,16]. Coking rate for these groups is:

$$R_{olefin} = k_{01} e^{(-E_1/RT)} (k_{C_2H_4} \cdot C_{C_2H_4} + k_{C_3H_6} \cdot C_{C_3H_6}) \quad (2a)$$

$$R_{diene} = k_{02} e^{(-E_2/RT)} \cdot C_{C_4H_6} \quad (2b)$$

$$R_{aromatic} = k_{03} e^{(-E_3/RT)} (k_B C_B + k_T C_T + k_X C_X + k_S C_S) \quad (2c)$$

$$R_{total} = (C_{H_2} \cdot C_{CH_4}) \sum_{i=1}^3 R_i \quad (2d)$$

where  $R_i$  is the rate of coke formation because of coke precursors, (e.g.  $R_1$  is the rate of coke formation because of ethylene and propylene coke precursors,  $R_2$  is the rate of coke formation

**TABLE 6. Feed and Operating Conditions.**

HC flow rate (kg/hr/furnace)	11600
Steam dilution (kg steam/kg HC)	0.7
Coil inlet temp. (°C)	600
Coil inlet pressure (bar)	2.15
Feed stokes characterization	
Specific gravity d (15/15)	0.67
PIONA analyses	
n-paraffins	41.46
Iso-paraffins	41.05
Naphthenes	14.51
Aromatics	2.98

because of butadiene coke precursor,  $R_3$  is the rate of coke formation out of aromatic coke precursors.),  $k_{0i}$  is the pre exponential factor for coking rate,  $E_i$  is the activation energy for coking rate, and  $k_i$  is the relative coking rate coefficients of coke precursors (e.g.  $k_{C_2H_4}$ ,  $k_{C_3H_6}$ , are relative coking rate coefficients for  $C_2H_4$  and  $C_3H_6$  respectively).

The parameters for this model are given in Table 4. The parameters for this model were determined using nonlinear Marquardt optimization method. The sum of squares of the deviations between the calculated and plant data for coking reaction rates was used as the objective function and minimized by the appropriate choice of the order of reactions contributed to coke precursors.

## 5. SIMULATION OF INDUSTRIAL OPERATION

To study the coke formation during naphtha pyrolysis, investigations have been made at Arak petrochemical complex. Thermal cracking, an endothermic process is carried out in long coils, vertically inserted in large, rectangular gas fired furnaces. These consist of convection and a radiant section. The coking model must be combined with exact kinetic model for the pyrolysis of naphtha, which generates the local concentrations of products and coke precursors along the coil. The details of the spilt coil reactors and operating conditions are given in Tables 5 and 6.

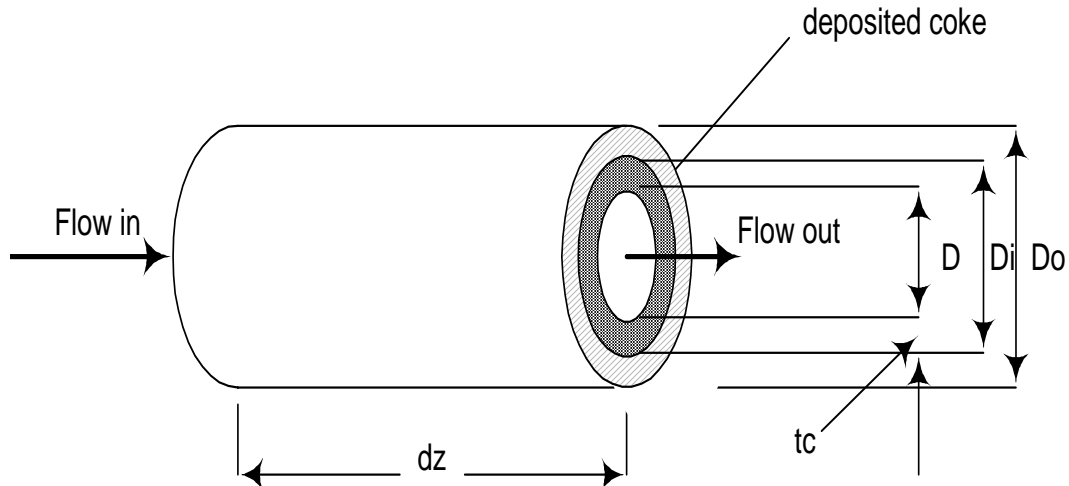


Figure 2. Differential element of a cracking coil.

## 6. PROCESS MODEL

The set of continuity equations for the various species, the energy and pressure drop and the coking rate equations required for this simulation was found in Heynderick & Froment [17]. The geometry of the reactor model configuration is shown in Figure 2.

Let's make the following assumptions:

1. One dimensional system,
2. Plug flow,
3. Negligible radial concentration gradients and axial dispersion,
4. Ideal gas behavior,
5. Inertness of the steam diluent in feed and
6. No hydrodynamic or thermal entrance region effects.

With the above assumptions, the following design equation can be written. Since the coking rate is slow, quasi steady state conditions may be assumed so that the continuity equations reduce to ordinary differential equations.

$$\frac{dF_j}{dz} = \left( \sum_i n_{ij} r_{ri} \right) \frac{\pi d_t^2}{4} \quad (3)$$

$$\sum_j F_j c_{pj} \frac{dT}{dz} \equiv Q(z) \pi d_t + \frac{\pi d_t^2}{4} \sum_i r_{ri} (-\Delta H)_i \quad (4)$$

$$\left( \frac{1}{M_m P_t} - \frac{P_t}{\eta \cdot G^2 RT} \right) \frac{dp_t}{dz} = \frac{d}{dz} \left( \frac{1}{M_m} \right) + \frac{1}{M_m} \left( \frac{1}{T} \frac{dT}{dz} + Fr \right) \quad (5)$$

With the friction factor

$$Fr = 0.092 \frac{Re^{-0.2}}{d_t} \quad (6)$$

For the straight parts of the reactor coils and

$$Fr = 0.092 \frac{Re^{-0.2}}{d_t} + \frac{\zeta}{\pi R_b} \quad (7)$$

For the tube bends, with

$$\zeta = \left( 0.7 + 0.35 \frac{\Lambda}{90^\circ} \right) \left( 0.051 + 0.19 \frac{d_t}{R_b} \right) \quad (8)$$

We can write the rate of coke formation:

$$\frac{\partial C}{\partial t} = (D - 2t_c) \frac{\alpha M_c r_c}{4\rho_c} \quad (9)$$

Using a mathematical process model, the amount of coke deposited on the internal wall of the reactor tubes has been calculated. The limiting

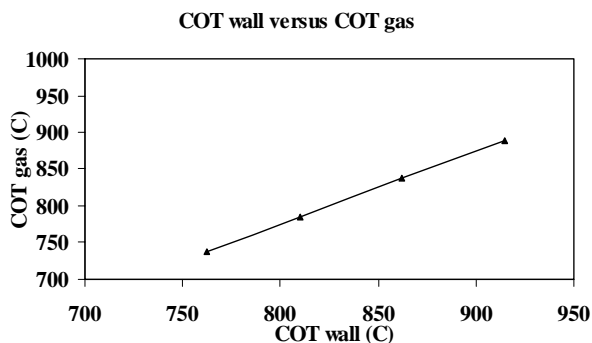


Figure 3. Evolution of COTwall versus COT gas.

value for tube skin temperature is 1100°C. The result obtained by this model has been compared with plant data and confirmed approximately. In the following, the effect of the coke thickness on the yield of the products and the operating parameters has been demonstrated in three stages: 0 hr, 800 hr, 1700 hr.

## 7. RESULTS AND DISCUSSION

In the experimental results, the product yields are shown versus coil outlet temperature. The process gas temperature profile along the cracking coil or coil outlet temperature is the most important factor that affects the product selectivity. In other means, coil outlet temperature indication of severity or conversion of the cracking process. Figure 3 shows the approximate relationship of process gas coil outlet temperature and COT<sub>wall</sub> temperature in the pilot plant. Figures 4 and 5 show the typical variations of the main product yields such as methane, 1,3 butadiene, C5+ yields and total condensed yields with respect COT<sub>wall</sub> temperature. The yields of ethylene and methane increase monotonically with temperature, 1,3 butadiene yield increased slightly at all the space times investigated. Also, propylene yield tended to go through a maximum at temperatures greater than 760 C, while 1-butene yields generally passed through a broad maximum. Also, selectivity of ethylene and methane increased with space-time, while those of 1-butene, 1-pentane and 1-hexane decreased. On the other hand, propylene selectivity

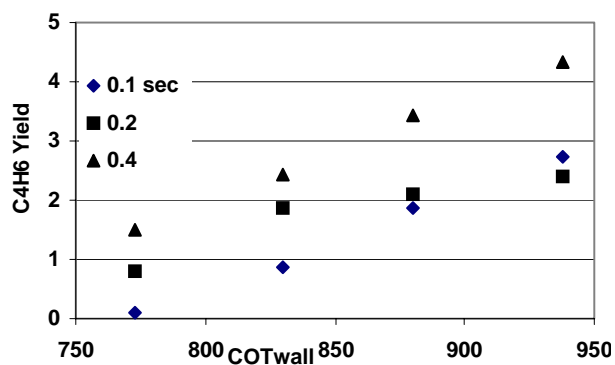
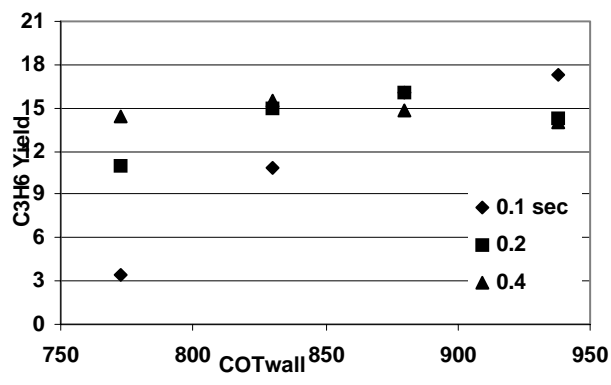
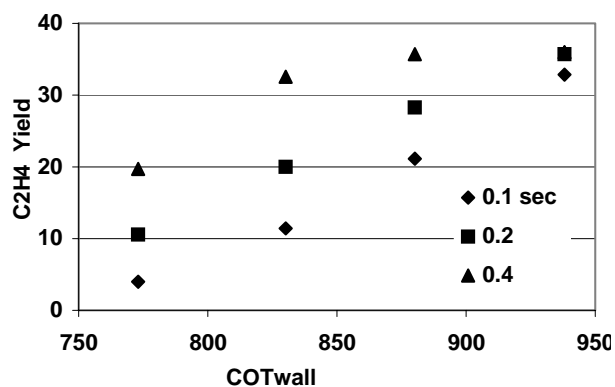
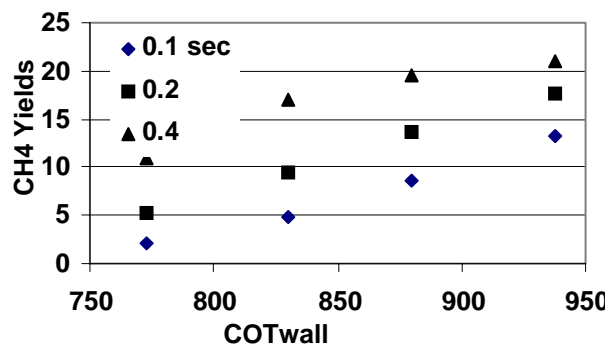


Figure 4. Main Product yields of pyrolysis of naphtha in COT wall and space time.



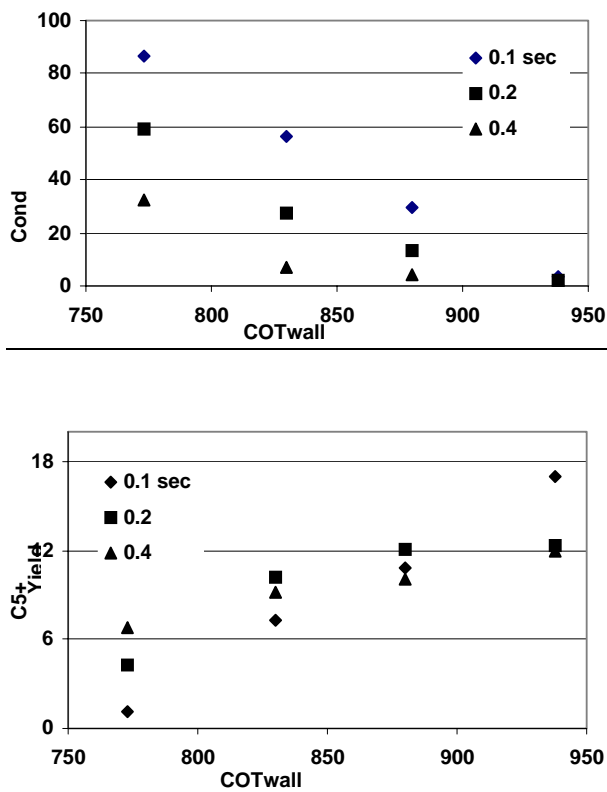
passed through a broad maximum with increasing space-time. Similar trends were observed in cracking of straight run naphtha by Bajus et al. [18].

In general, with increase of coil outlet temperature, the yield of propylene increases and attains a maximum value and thermally stable methane, ethylene and aromatic yields will be increased. Methane and benzene are thermally quite stable. Aromatics also formed by reaction between the cracking products of olefins and diolefins. In our experimental process, the above-mentioned trend has been also observed. The calculated values from the kinetic reaction network, which has been developed in ORG for each product yield in naphtha pyrolysis is in good agreement with the experimental data. Table 7 compares the simulated results with the pilot plant data. The calculated product yields; coil outlet temperature and pressure match the pilot plant data exactly. The accuracy of kinetic reaction scheme is tested by the experimental results of pilot plant. For different operating conditions the calculated results are in good agreement with and experimental data, as typically presented in this table.

By using the developed coking model, the predicted results for evolution with time of coking thickness, external tube wall temperature and heat flux, also the distribution of main cracking products, have been shown in Figures 6 to 7. Figure 6 shows the comparison between the simulated coke thickness and the plant design data (predicted by designer) at the end of run. During the first 10 meters of the coil, the coke thickness is negligible. Because the absorbed heat flux mainly increases the temperature of process gas and cracking reaction have not initiated yet. In 22 meters where the diameter of the coil increases and absorbed heat flux is low (As shown in Figure 8), coke thickness undergoes a sharp reduce. Since the coke formation occurs at the gas/coke interface temperature, coke thickness profile very similar to tube skin temperature profile. The concentration of coke precursors in the high temperature zone is high so that the coking rate is high in the second part of the reactor. As a consequence, the coke layer grows fast there and creates an additional resistance to heat transfer and causes a decrease in the cross sectional area of coil, so to keep the temperature profile of the gas stable, more heat flux should be applied. This reduction also is

TABLE 7. Comparison of Simulation Results with Pilot Plant Data.

Yields(%)	Pilot Plant	Simulation	Pilot Plant	Simulation	Pilot Plant	Simulation
<i>COT</i> , °C	820		840		860	
H <sub>2</sub>	0.48	0.52	0.64	0.68	0.87	0.9
CH <sub>4</sub>	14.12	14.3	15.23	15.6	17.11	17.53
C <sub>2</sub> H <sub>2</sub>	0.53	0.40	0.79	0.68	1.18	1.08
C <sub>2</sub> H <sub>4</sub>	25.73	25.79	31.6	31.9	35.14	35.2
C <sub>2</sub> H <sub>6</sub>	7.58	8.0	6.84	7.3	5.05	5.5
C <sub>3</sub> H <sub>6</sub>	15.8	15.7	14.9	14.77	12.8	12.63
C <sub>3</sub> H <sub>8</sub>	0.58	0.68	0.54	0.74	0.43	0.63
C <sub>4</sub> H <sub>6</sub>	2.81	2.79	3.01	3.5	3.45	4.0
C <sub>4</sub> H <sub>8</sub>	3.47	3.01	3.11	2.8	2.53	2.03
C5+ (gaseous product)	8.6	9.82	10.5	11.9	11.2	12.93
<b>Operating condition</b>						
<i>H.C. flow rate</i> , kg/h	0.4	0.4	0.4	0.4	0.4	0.4
<i>COT</i> , °C	820	820	840	840	860	860
<i>Coil outlet Pressure</i>	1	1	1	1	1	1
<i>Steam Ratio</i>	0.7	0.7	0.7	0.7	0.7	0.7
<i>Residence time</i> , sec	0.4	0.42	0.4	0.42	0.4	0.42



**Figure 5.** Condensed Liquid and C5+ yields of pyrolysis of naphtha in COT wall and space time.

related to decrease in heat flux and consequently outside tube wall temperature, which shown in Figures 7 and 8, respectively. Heat flux profile for each furnace is directly related to the designed parameters of that furnace such as the configuration of the coils and the number of burners. All of these reduce the total conversion along running period and reduce the yield of the ethylene and aromatics which shown in Figures 9 to 11. The coils of the simulated furnace are made of HP-modified alloy whose maximum allowable temperature is 1100 °C. This upper limit is reached after 1700 hr running period, which is in good agreement with plant run length.

## 8. CONCLUSIONS

Developing a coking model requires a suitable model of thermal cracking reactor based on a

reliable kinetic model. Therefore, some kinetic extensions were made and the kinetic parameters were verified and tuned with a large amount of pilot plant data and industrial data. Literature data and plant output observations were combined to obtain a coke model for prediction of the rate of coking and thickness of coke along the reactor. The kinetic model in which sets of 7 precursors form coke via a set of parallel reactions is developed. This coking model was combined with a kinetic model for thermal cracking, a reactor model to simulate the run length of an industrial reactor for the cracking of naphtha. Detailed and accurate information can be obtained from this simulation. The growth of a coke layer and the effect on product yields, and so is the evolution of the external tube skin temperatures. The simulated and plant output run length agree in a good accuracy. It has been proven that unsaturates and aromatics have the most important role in coke formation. Simulation of this kind can be used to optimize reactor operation for various operating condition. They can be used as a guide for the adaption of the operating variables aiming at prolonging the run length of the reactor.

## 9. NOMENCLATURE

- $C_c$  Concentration of coke (mole/m<sup>3</sup>)
- $C_i$  Concentration of coke precursors (mole/m<sup>3</sup>)
- $C_p$  Heat capacity (J / mole . K)
- $A$  Cross section of area (m<sup>2</sup>)
- $D_t$  Tube diameter (m)
- $E_o$  Activation energy (J/mole.K)
- $F$  Molar flow rate (mole/hr)
- $Fr$  Friction factor
- $G$  Total mass flux of the process gas (kg/m<sup>2</sup>.S)
- $-\Delta H$  Heat of reaction (J/mole)
- $k_{oi}$  Pre exponential factor for coke formation (Kg coke/(m<sup>2</sup>)(hr)(kmol/m<sup>3</sup>)<sup>3</sup>)
- $M_m$  Average molecular weight (kg/mole)
- $N_{ij}$  Stoichiometry factor
- $P_t$  Total pressure (bar)
- $Q$  Heat flux (W/m<sup>2</sup>)
- $R$  Radius (m)
- $r_{ci}$  Coking reaction rate of precursor i (mole/m<sup>3</sup>.s)
- $Re$  Reynolds number
- $r_c$  Coking reaction rate (mole / m<sup>3</sup> s)

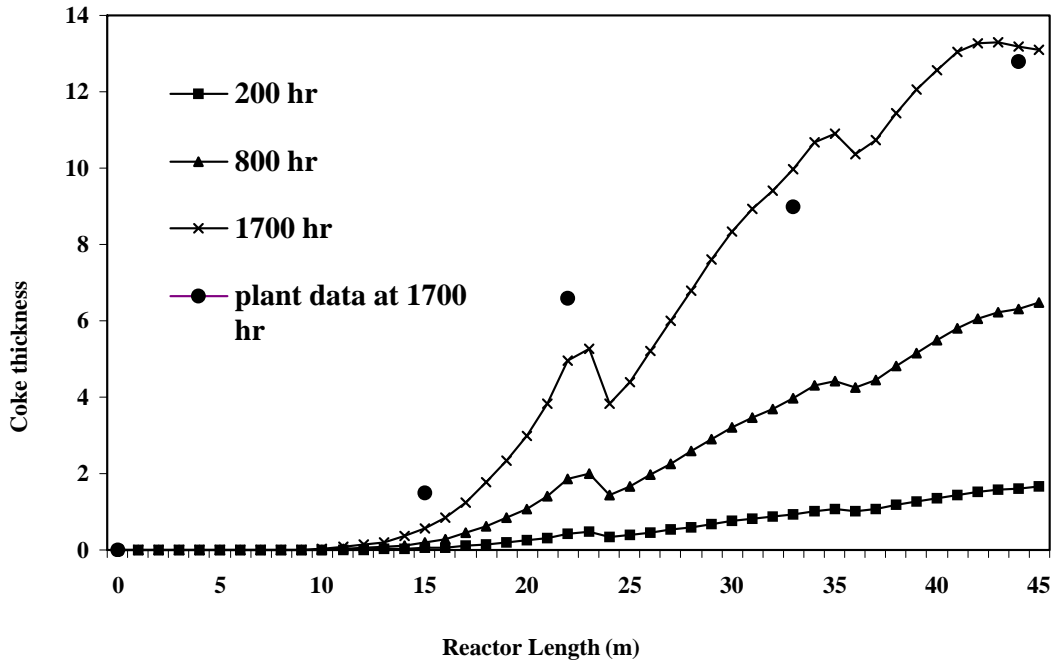


Figure 6. Profile of coke thickness along the cracking coils vs run time.

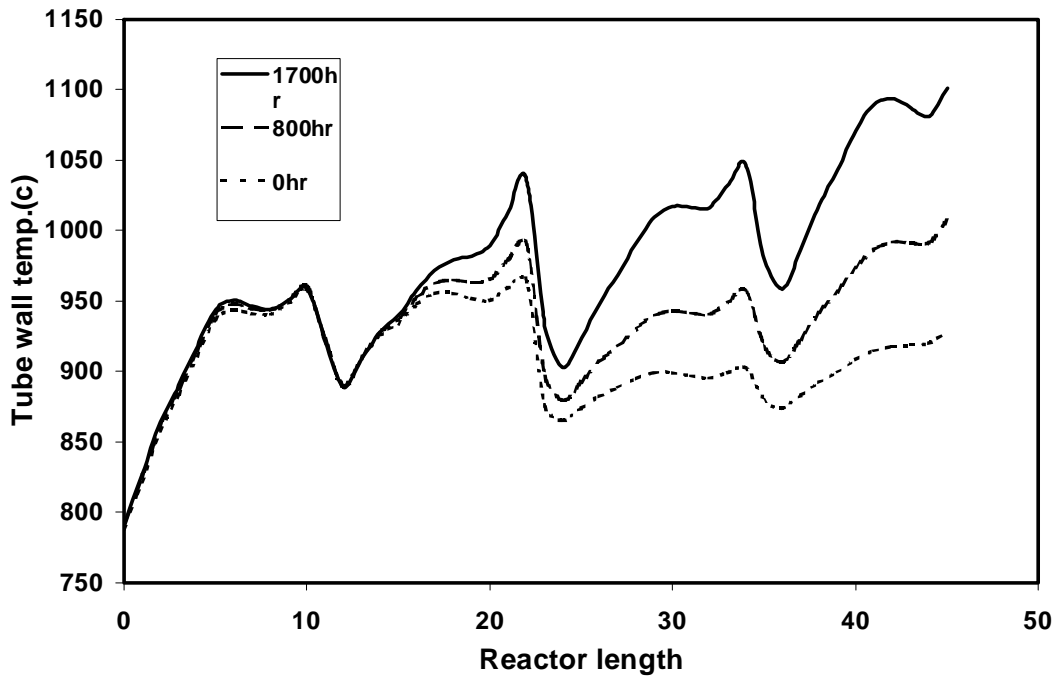


Figure 7. Evolution with time of external tube skin temperature profile along coil length.

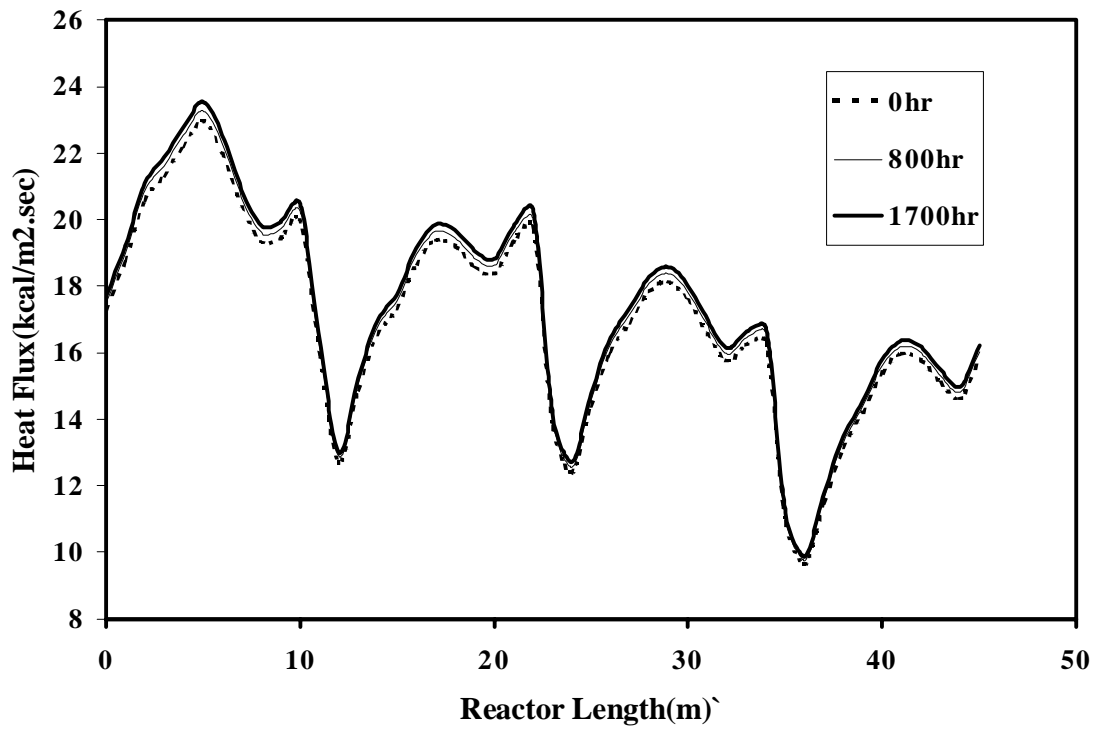


Figure 8. Evolution with time of heat flux profile along coil length.

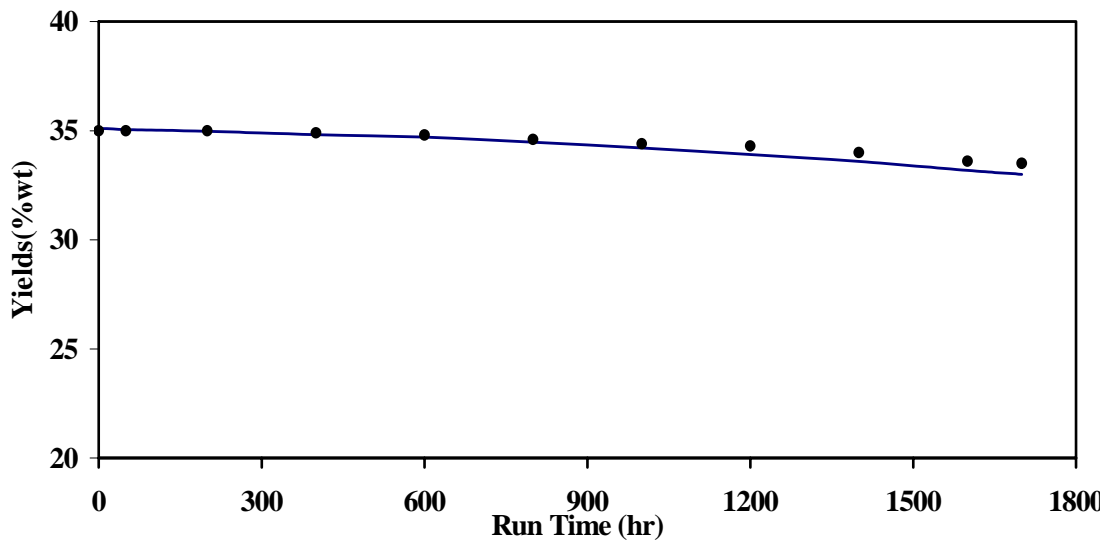


Figure 9. Comparison of industrial and simulation of average Ethylene yield yield versus run time.

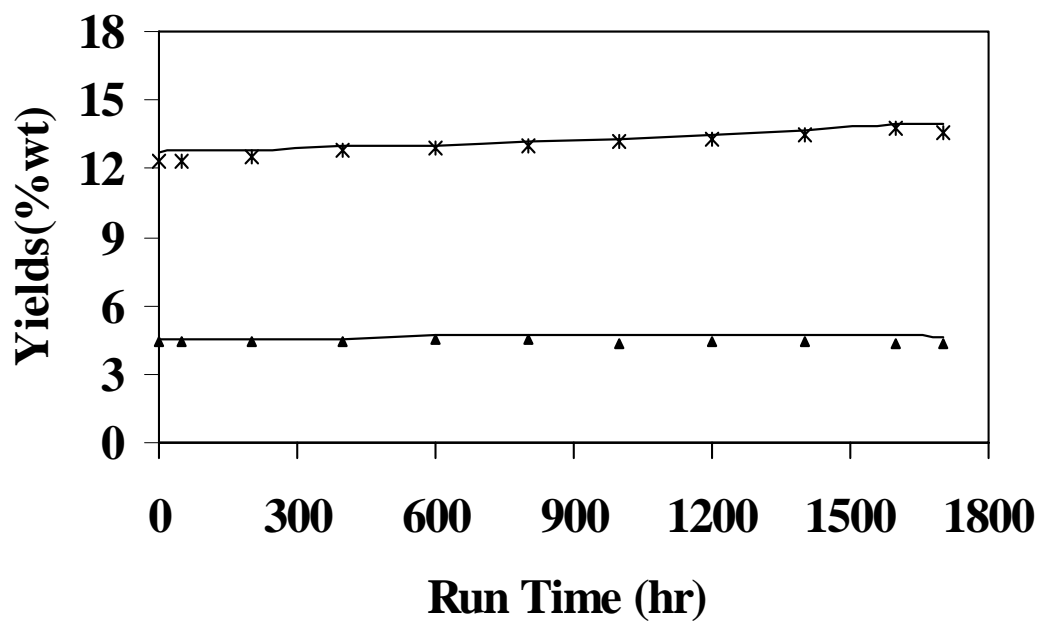


Figure 10. Evolution of Propylene and Butadiene Yield along the run time of cracking coils (Simulation- Line, Plant data- points).

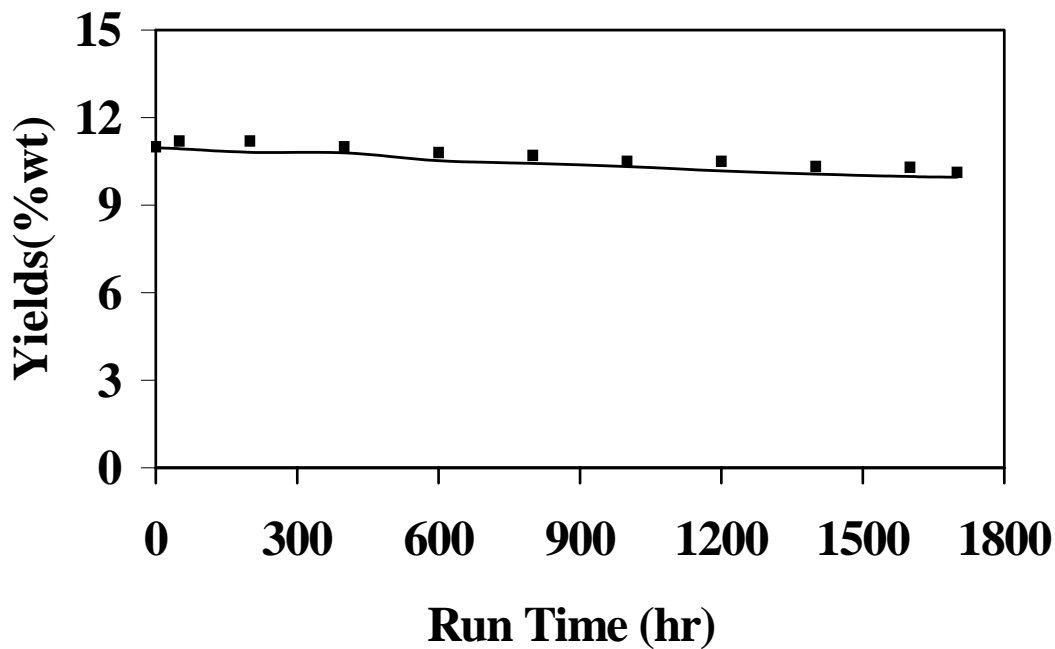


Figure 11. Comparison of industrial and simulation total aromatic yield vs run time.

$R_b$	Radius of the tube bend (m)
T	Time (hr)
T	Temperature (k)
Z	Axial reactor coordinate (m)

### Greek Letters

$\alpha$	coking factor
$\alpha_i$	coefficient of coke precursors in coking rate
$\Lambda$	angle of bend <sup>0</sup>
$\zeta$	parameter of tube bend

### Subscripts

B	Benzene
T	Toluene
X	Xylene
S	Styrene

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