Olefin Production from Heavy Liquid Hydrocarbon Thermal Cracking: Kinetics and Product Distribution

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ABSTRACT: *Thermal cracking of a heavy liquid hydrocarbon was performed in a laboratory scale tubular reactor. Central Composite Design (CCD), was used as an experimental design method. The design variables were Coil Outlet Temperature (COT), feed flow and rate steam ratio. Maximum yield of ethylene was 30.37 wt% at COT, residence time and steam ratio of 869^{o}C, 0.208 s and 1.22 g/g, respectively. Maximum yield of propylene was 15.37 wt% at COT, residence time and steam ratio of 825^{o}C, 0.147 s and 0.95 g/g, respectively. A mechanistic model based on free radical chain reactions was developed using experimental results. Developed reaction network contains 148 reactions for 43 species. Finally, the experimental data were compared with model results. Scatter diagrams showed good agreement between model and experimental data.*

KEY WORDS: *Thermal cracking, Heavy liquid hydrocarbon, Kinetic model.*

INTRODUCTION

Steam cracking of various hydrocarbons is the major rout for production of light olefins, ethylene and propylene, which are basic feedstocks for the petrochemical industries. Steam is used in this process to increase the olefin selectivity and decrease coke formation rate. The mixed hydrocarbon and steam are heated to primary cracking temperature (500 - 650°C). Then, it is cracked in fired tubular reactor where the reactions take place at higher temperatures.

Free-radical chain reactions are accepted as reaction mechanism of hydrocarbon thermal cracking [1]. The increase in prices of lighter hydrocarbons has brought about the tendency to the heavier hydrocarbon such as gasoil and residue as feedstocks for olefin production.

Thermal cracking of atmospheric gasoil was carried out by *Hirato et al.* [2]. Then, molecular-based model was developed. They also used the modified model for modeling of thermal cracking of naphtha and kerosene. *Belohlav et al.* [3] developed a model of pyrolysis of ethane, petroleum gases, and primary naphthas involve free radical reactions. The kinetic model optimization and verification was performed by the experimental set. Thermal cracking of kerosene for producing ethylene and propylene has been studied in an experimental setup

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by *Ghassabzadeh et al*. [4]. An applicable kinetic model was developed to predict yield distribution of products of the kerosene thermal cracking. Therefore, a reaction mechanism is generated on the basis of major reactions classes in the pyrolysis and feed compounds using some simplification assumptions in the model. *Zahedi et al.* [5] studied the thermal cracking of atmospheric gas oil. The obtained maximum yield of ethylene was equal to 30.9 wt% as well as the maximum yield of propylene was 12.2wt%. A mechanistic model was developed based on experimental data. *Depeyre et al.* [6] studied the effects of temperature, steam to gas oil ratio and residence time on major products in gas oil thermal cracking. The best yield of ethylene, 27% in mass, was obtained in the quartz reactor at 770 °C, residence time of 0.6 s, and mass ratio of steam to gas oil equal to 1. *Keyvanloo et al.* [7] studied the effect of main parameters and their quadratic and cubic interactions on the yield of light olefins in thermal cracking of naphtha by statistical design of experiments. They have found that the higher interactions should be considered in the modeling of naphtha steam cracking besides the effect of key factors.

Various multiobjective optimizations have been also carried out. The other authors [8-10] have also studied the thermal cracking and mathematical modeling of different feedstock.

In this paper, thermal cracking of a heavy liquid hydrocarbon was experimentally investigated and products yield distribution was studied. Several experiments were conducted to study the effects of operating parameters on product distribution. In order to generate systematic experimental data, response surface methodology was used. Then a mechanistic model based on free radical chain reactions was developed to predict product distribution.

EXPERIMENTAL SECTION

Feed Characteristics

The selected feed was a heavy liquid hydrocarbon. This feed is the mixture of three industrial residue which wants to be used as a new feedstock in Olefin 12 unit. It was a distilled fraction, 32 °C < bp < 324 °C, with a specific gravity of 0.77. Physicochemical characteristics, composition and mean molecular weight are presented in Table 1.

Table 1: Chemical composition and physicochemical characteristics of heavy liquid hydrocarbon feed.

Chemical composition (wt%)	
n - Paraffin	26.65
I - paraffin	28.29
Naphthene	17.84
Aromatics	19.3
Olefins	0.17
Physiochemical properties	
Hydrocarbon C_{15+}	7.75 wt%
Specific Gravity	0.769 g/g
Average Molecular Weight	g 148.35
Sulfur	wt ppm 2137
Mercury	1.13 wt ppb<
Lead	ppb wt 3.9<
Arsenic	6.5 wt ppb <

Thermal Cracking Set-up

A schematic diagram of the experimental set-up is shown in Fig. 1. The hydrocarbon and dilution water are fed into the preheaters by two dosing pumps and then mixture was injected into the reactor at the required flow rate. The setup is controlled by computer [1]. The reactor is a tube that is 1.2 m long and has an internal diameter of 10 mm and outer diameter of 12.7 mm. The temperature of each zone was controlled by separate proportional controllers. The axial temperature profile was measured using a type K thermocouple. Double-pipe heat exchanger was used to cool reactor effluents to the appropriate temperature. A fraction of the product gas is then withdrawn for the analysis via Varian Chrompack CP3800 gas chromatograph, whereas the remainder is sent directly to the flare.

Experimental Design and Collection of Data

CCD method was applied with three design factors, namely the hydrocarbon feed flow rate, the steam ratio and coil outlet temperature. The coded levels and the natural values of the factors are shown in Table 2. The experiments covered the following range of variables: temperature; 750- 900°C, and feed flow rate; 3 - 7 g/min and steam ratio; 0.5-1.4 g/g.

Table 2: Coded and natural levels of the design factors.

Design factor	-1.68	-1	0	+1	1.68
Coil outlet temperature	750	780	825	869	900
Feed flow rate (g/min)	3.0	3.8	5.0	6.2	7.0
Steam ratio (g/g)	0.5	0.68	0.95	1.22	1.4

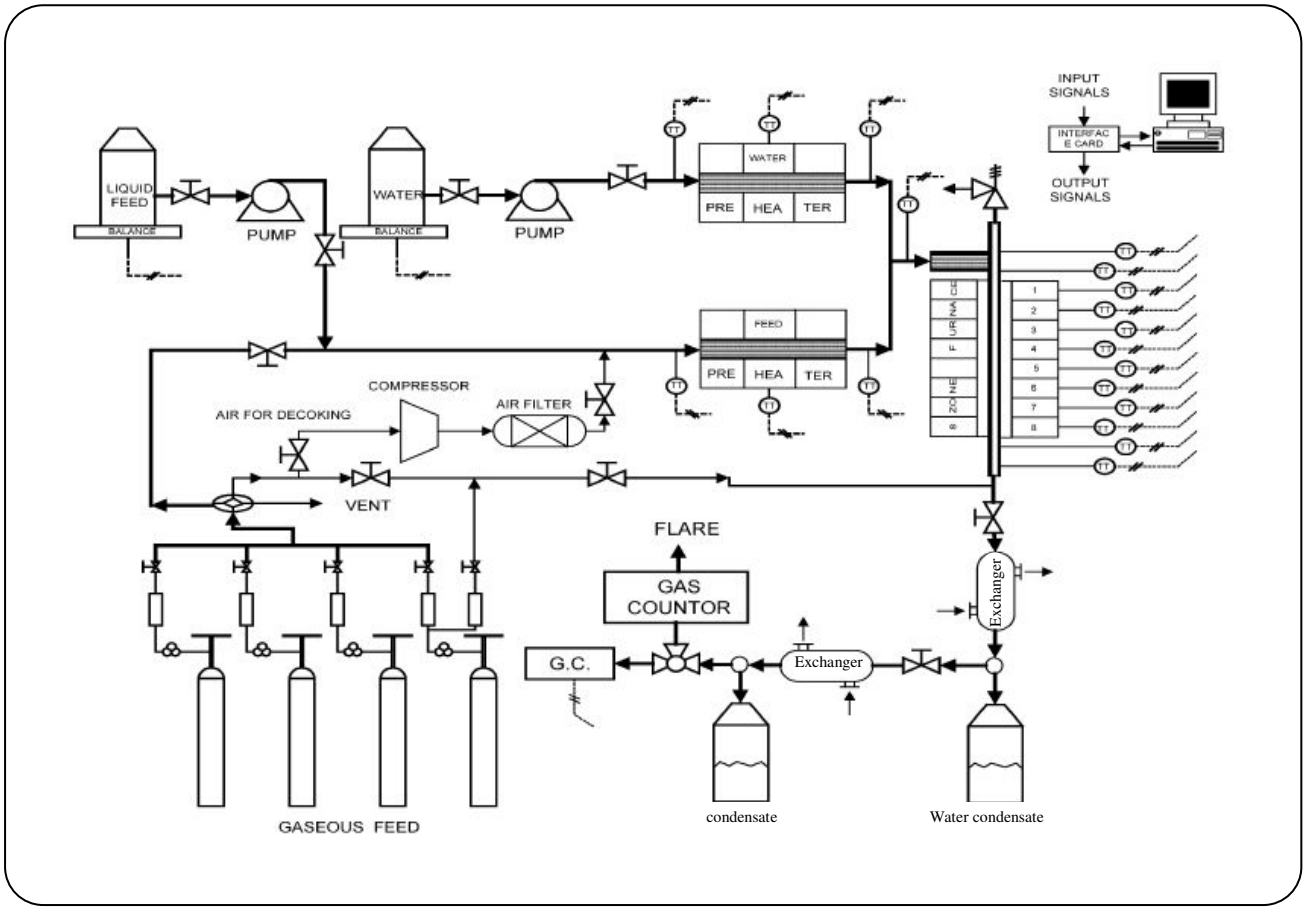

Fig. 1: Schematic diagram of the thermal cracking setup.

Eight response variables concerned including product yield of the main primary products (wt %). Results of the experiments and the design matrix are shown in Table 3.

The Relative Absolute Error (RAE), between predicted and experimental data for every output data of models was defined as an objective function (Eq. (1)).

$$RAE = \frac{\left|Y_{experimental} - Y_{predicted}\right|}{Y_{experimental}} \quad (1)$$

MATHEMATICAL MODEL

Reactor model

A one-dimensional plug flow model is used to simulate the reactor of thermal cracking setup. The set of continuity equations for the process gas species is solved simultaneously with the energy, momentum equations [11, 12]. These equations are as follows:

Mass balance:

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

Table 3: Design matrix and results of the central composite design.

Run	1	2	3	4	5	6	7	8	9
COT(°C)	750	900	869	780	825	869	869	780	825
Feed flow rate (g/min)	5	5	6.2	6.2	5	3.8	6.2	3.8	5
Steam ratio (g/g)	0.95	0.95	1.22	0.68	0.95	0.68	0.68	0.68	0.95
Experimental Data									
CH_4	8.72	16.3	15.00	8.34	13.25	15.77	14.93	9.35	13.27
C_2H_6	3.72	1.82	1.93	2.5	2.27	2.2	2.00	3.41	2.23
C_2H_4	19.75	29.9	28.34	18.53	25.8	30.09	27.8	20.74	25.3
C_3H_8	1.75	0.67	0.93	1.49	1.22	0.84	0.94	1.18	1.25
C_3H_6	13.21	9.45	12.05	14.03	14.31	10.4	11.85	13.31	14.41
C_4H_8	3.71	1.47	1.95	3.51	2.26	1.74	2.07	3.44	2.26
H_2	0.9	1.43	1.31	0.89	1.18	1.4	1.33	0.95	1.2
C_{5+}	40.18	29.72	29.23	43.09	31.06	27.9	28.73	41.1	31.26
Run	10	11	12	13	14	15	16	17	
COT(°C)	780	869	825	825	825	825	780	825	
Feed flow rate (g/min)	3.8	3.8	5	7	3	5	6.2	5	
Steam ratio (g/g)	1.22	1.22	0.5	0.95	0.95	0.95	1.22	1.4	
Experimental Data132.8									
CH_4	9.67	15.94	12.76	10.7	15.32	13.28	8.6	14.8	
C_2H_6	3.45	2.06	2.61	1.97	2.69	2.19	2.51	2.17	
C_2H_4	21.73	30.37	24.74	23.45	28.4	25.07	191	26.12	
C_3H_8	1.14	0.83	1.42	1.63	0.84	1.28	1.4	1.2	
C_3H_6	13.38	10.62	13.71	15.37	13.49	14.55	14.17	15.12	
C_4H_8	3.4	0.9	2.49	2.93	2.15	2.24	3.52	2.1	
H_2	0.92	1.37	1.26	1.15	1.37	1.21	0.87	0.99	
C_{5+}	39.52	28.12	31.9	33.87	28.15	31.87	42.19	30.61	

Energy balance:

$$\sum_j F_j C_{pj} \frac{dT}{dz} = Q(z)\pi d_t + \frac{\pi d_t^2}{4}\sum_i r_{ri}\left(-\Delta H\right)_i \qquad (3)$$

Momentum balance:

$$\left(\frac{1}{M_m P_t} - \frac{P_t}{\eta G^2 RT}\right)\frac{dP_t}{dz} = \frac{d}{dz}\left(\frac{1}{M_m}\right) + \frac{1}{M_m}\left(\frac{1}{T}\frac{dT}{dz} + F_r\right) \qquad (4)$$

Which F_r is the friction factor and is calculated as follow:

$$F_r = 0.092\frac{Re^{-0.2}}{d_t} + \frac{\zeta}{\pi R_b} \qquad (5)$$

and for the tube bends as

$$\zeta = \left(0.7 + 0.35\frac{\Lambda}{90^\circ}\right)\left(0.051 + 0.19\frac{d_t}{R_b}\right) \qquad (6)$$

Where R_b and Λ represents the radius of the tube bend and angle of bend, respectively. *Towfighi et al.* [12] have shown the detail description of the applied mathematical model.

Kinetic model

There are three kinds of model to state kinetic model which are empirical, molecular, and mechanistic models. Due to the flexibility and accuracy, mechanistic radical kinetic models were widely accepted for thermal cracking reaction [13,14]. As shown in Table 1, the feed analysis contains n-paraffins, iso-paraffins, naphthenes and aromatics.

The proposed kinetic model is semi-mechanistic model of radical decomposition based on the simplified theory of radical and pure molecular reactions. The radical reactions contain chain-initiation reactions, chain-propagation reactions, chain-termination reactions, secondary reaction, and isomerization reaction [15-16]. Molecular reactions contain dehydrogenation, Diels-Alder molecular reaction and isomerization reaction. The developed model delete consists of the following reaction:

• Radical reaction

1- Chain-initiation reaction, for example:

$C_9H_{20} \longrightarrow C_5H_{11}^0 + 1\text{-}C_4H_9^0$

2- Chain-propagation reaction, for example:

a) $C_9H_{19}^0 \longrightarrow C_2H_4 + C_7H_{15}^0$

b) $C_9H_{20} + H^0 \longrightarrow C_9H_{19}^0 + H_2$

3- Chain-termination reaction, for example:

$C_2H_5^0 + H^0 \longrightarrow C_2H_6$

4- Secondary reaction, for example:

a) $C_3H_6 + H^0 \longrightarrow C_3H_5^0 + H_2$

b) $C_2H_4 + H^0 \longrightarrow C_2H_5^0$

• Molecular reaction

1- Olefin isomerization, for example:

$1\text{-}C_6H_{11}^0 \longrightarrow 2\text{-}C_6H_{11}^0$

2- Dehydrogenation reaction, for example:

$C_3H_8 \longrightarrow C_3H_6 + H_2$

3- Diels – Alder Molecular reaction, for example:

$C_4H_6 + C_2H_4 \longrightarrow C_6H_6 + 2H_2$

4- Other molecular reaction, for example:

$C_3H_8 \longrightarrow C_2H_4 + CH_4$

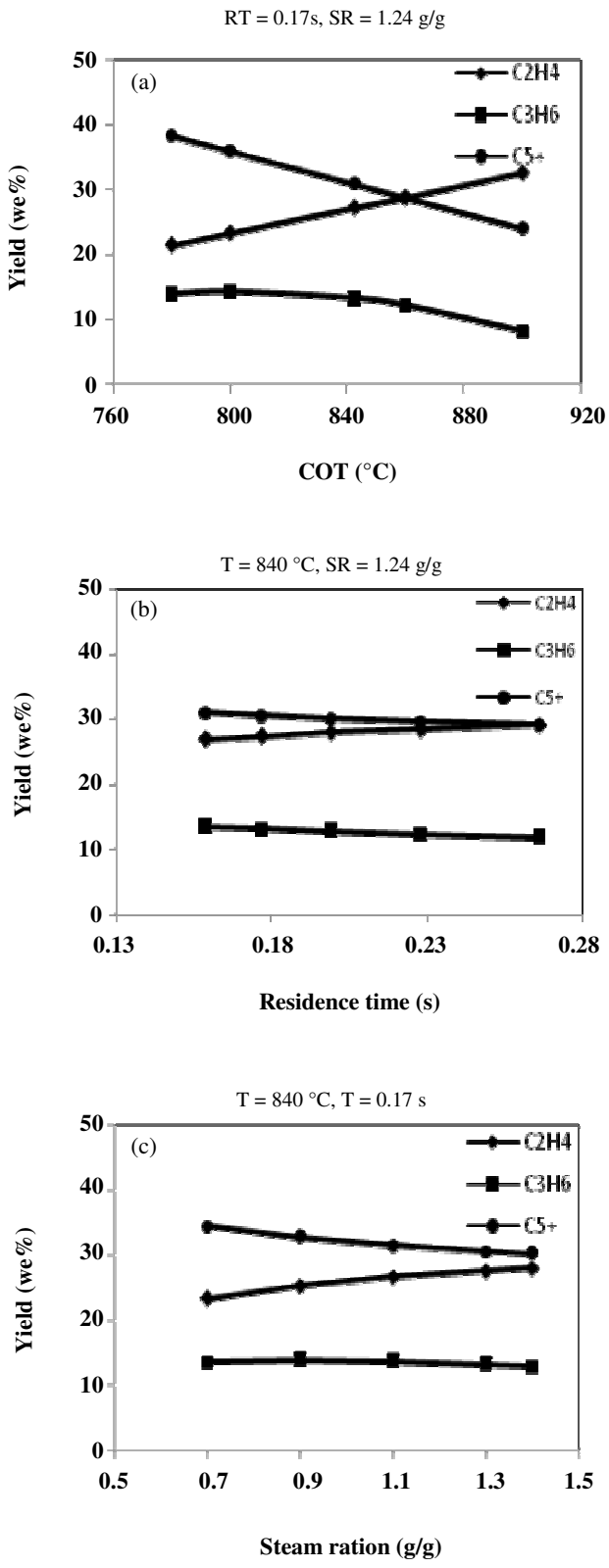

Fig. 2: Effect of (a) COT(°C), (b) residence time(s) and (c) steam ratio (g/g) on the yield of C_2H_4, C_2H_6, C_5^+.

Table 4: Comparison of simulated and experimental product distributions.

	Test 1		Test 2		Test 3	
Parameter	Experiment	model	Experiment	model	Experiment	model
COT(°C)	830	830	885	885	765	765
Feed flow rate(g/min)	5.1	5.1	6.5	6.5	4.1	4.1
Steam ratio (g/g)	0.7	0.7	1.15	1.15	0.9	0.9
Yield (wt %)						
CH_4	14	12.57	15.4	14.6	9.22	8.53
C_2H_6	2.14	2.1	1.8	1.91	3.00	2.87
C_2H_4	26.9	24.8	28.2	30.2	19.7	20.34
C_3H_6	14	14.54	9.65	9.35	13.41	14.06
C_5^+	32.7	34.6	31.9	33.6	41.3	43.7

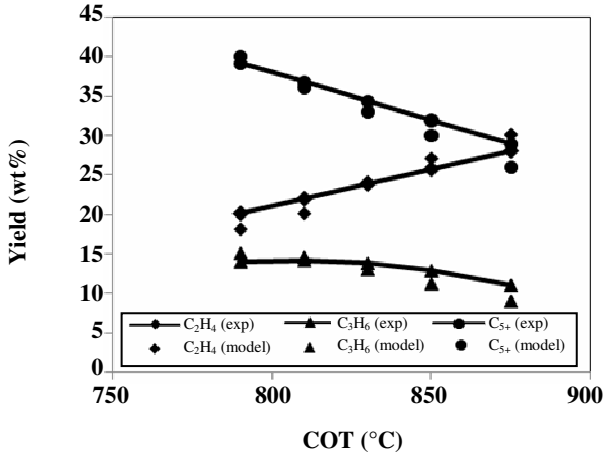

Fig. 3: Effect of COT (^oC) on C_2H_4, C_3H_6 and C_5^+ yields predicted by developed model.

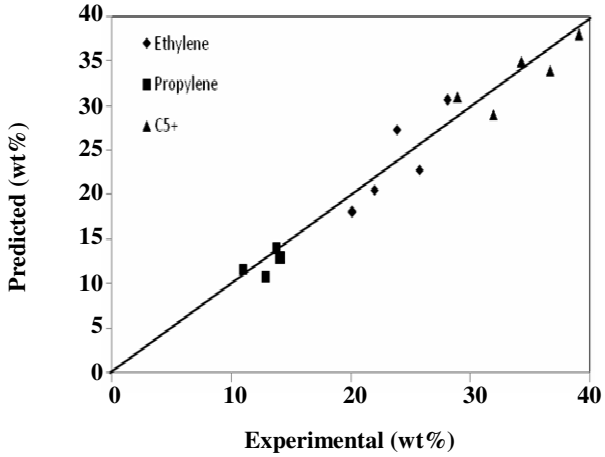

Fig. 4: Scatter diagram of C_2H_4, C_3H_6 and C_5^+ yield.

To avoid complexity in reaction network, the detected species of heavy liquid hydrocarbon were lumped to four pseudo components as n-C_9H_{20} and i-C_9H_{20} for normal paraffins and iso paraffins, C_9H_{18} for naphthenes, and $C_{10}H_{14}$ for aromatics. Based on pseudo components, reaction network includes 148 reactions for 43 species. The developed reaction network is presented in Table 5 Due to differences between radicals and molecules concentrations, the governing mass, energy and momentum balance equations can be solved with Gear method.

RESULTS AND DISCUSSION

The effect of temperature, Residence Time (RT) and Steam Ratio (SR) on product distribution of ethylene, propylene and C_5^+ is shown in Fig. 2. As shown in Fig. 2(a), increasing the temperature improves the ethylene yield. The main part of C_{5+} is untreated feed. By increasing the temperature, the conversion increases which leads to the sharp decline in the yield of C_{5+} and increase in the yield of ethylene as shown in Fig. 2(a). The yield of propylene increases slightly and reaches a maximum and then

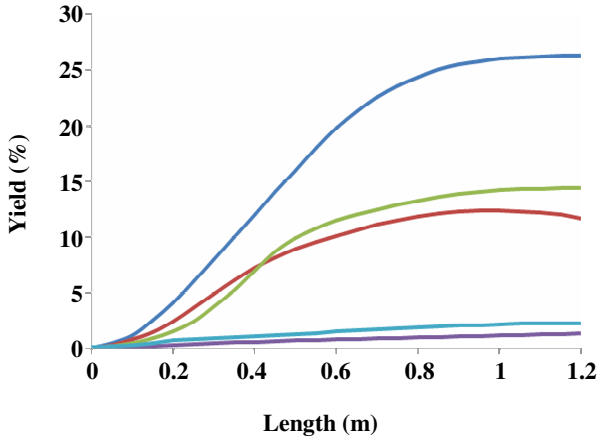

Fig. 5: Profile of yields of main products along the reactor at residence time=0.3 sec, COT=850 °C, steam ratio=0.6.

it decreases. This is due to the fact that propylene was produced at primary reaction and after duration of time, it was consumed in secondary reactions [7]. Fig. 2(b) shows that with the increase of residence time, the ethylene yield increases, whereas both propylene yield and C_5^+ yield decreases. In order to achieve high ethylene yield, the residence time should be increased. However, the yield of propylene should be considered.

Fig. 2(c) shows the effect of steam ratio on the yields of ethylene, propylene and heavy compound. It is shown that yield of ethylene increases with increasing the steam ratio, while C_5^+ and propylene decrease. In Table 3, the maximum yield of ethylene is 30.37 wt% at COT, residence time and steam ratio of 869 °C, 0.208 sec and 1.22 (g/g), respectively. The maximum yield of propylene is 15.37 wt% at COT, residence time and steam ratio of 825 °C, 0.147 sec and 0.95 (g/g), respectively.

The model was developed to determine the product yields in the total mentioned ranges. Fig. 3 shows the effect of temperature on ethylene, propylene and C_5^+ yields in both experiment and model results. Results of the experiment and model for different conditions are shown in Table 4. As it was shown, there is a good consistency between experimental and model data.

Fig. 4 shows a typical scatter diagram for products distribution of heavy liquid hydrocarbon. It indicates a good agreement between the predicted and experimental data.

The main product yields vs. the length of the reactor are shown in Fig. 5. In general, the yields of ethylene, methane, ethane and hydrogen products increase continuously along the reactor. Due to the secondary reactions the yield of propylene increases and reaches a maximum value and then decreases.

CONCLUSIONS

The goal of this study was to obtain experimental data on thermal cracking of a heavy liquid hydrocarbon and to develop a kinetic model in order to predict product distribution of olefins. Central composite design was used to carry out the experiments. Regarding the results, the maximum yield of ethylene and propylene was obtained 30.37 wt% and 15.37 wt%, respectively. Increasing temperature, residence time and steam ratio increases the ethylene yield. But there is a limitation for propylene by increasing the operating parameters and its optimum amount was found at 825°C.

Finally, the developed kinetic model was compared with experimental data. There was a good agreement between model results, which is based on free radical chain reactions, and experimental data. Furthermore, the trends of main products were studied along the reactor.

Acknowledgements

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Notation

COT	Coil outlet temperature, °C
C_{Pj}	Specific heat capacity of jth component, J/mol K
d_t	Diameter of reactor tube, m
F_j	Molar flow rate of jth component, mol/s
M_m	Molecular weight of mixture, g/mol
Q	Heat flux, kW/m^3
r_{ri}	Rate of reactions, mol/m^3·s
Re	Reynolds number

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Table 5: The developed reaction network.

No.	Reaction	Parameters Adopted	
		LOG (A)[1]	E[2]
1. Paraffin → Radical + Radical			
1	$C_9H_{20} \rightarrow C_5H_{11}^{\bullet} + 1\text{-}C_4H_9^{\bullet}$	14.5	80.0
2	$C_9H_{20} \rightarrow C_6H_{13}^{\bullet} + 1\text{-}C_3H_7^{\bullet}$	14.5	80.0
3	$C_9H_{20} \rightarrow C_7H_{15}^{\bullet} + C_2H_5^{\bullet}$	14.5	80.0
4	$C_9H_{20} \rightarrow C_8H_{17}^{\bullet} + CH_3^{\bullet}$	14.5	80.0
5	$C_9H_{20} \rightarrow C_9H_{19}^{\bullet} + H^{\bullet}$	14.5	85.0
6	$i\text{-}C_9H_{20} \rightarrow CH_3^{\bullet} + i\text{-}C_8H_{17}^{\bullet}$	14.5	80.0
7	$i\text{-}C_9H_{20} \rightarrow C_2H_5^{\bullet} + i\text{-}C_7H_{15}^{\bullet}$	14.5	80.0
8	$i\text{-}C_9H_{20} \rightarrow 1\text{-}C_3H_7^{\bullet} + i\text{-}C_6H_{13}^{\bullet}$	14.5	80.0
9	$i\text{-}C_9H_{20} \rightarrow 1\text{-}C_4H_9^{\bullet} + i\text{-}C_5H_{11}^{\bullet}$	14.5	80.0
10	$i\text{-}C_9H_{20} \rightarrow i\text{-}C_4H_9^{\bullet} + C_5H_{11}^{\bullet}$	14.5	80.0
11	$i\text{-}C_9H_{20} \rightarrow 2\text{-}C_3H_7^{\bullet} + C_6H_{13}^{\bullet}$	14.5	80.0
12	$i\text{-}C_9H_{20} \rightarrow H^{\bullet} + i\text{-}C_9H_{19}^{\bullet}$	14.5	83.0
13	$C_9H_{18} \rightarrow 1\text{-}C_4H_7^{\bullet} + C_5H_{11}^{\bullet}$	14.0	75.0
2. Radical → Radical + Radical			
14	$C_9H_{19}^{\bullet} \rightarrow C_2H_4 + C_7H_{15}^{\bullet}$	13.2	30.0
15	$C_9H_{19}^{\bullet} \rightarrow C_3H_6 + C_6H_{13}^{\bullet}$	13.0	30.0
16	$C_9H_{19}^{\bullet} \rightarrow 1\text{-}C_4H_8 + C_5H_{11}^{\bullet}$	12.6	29.0
17	$C_9H_{19}^{\bullet} \rightarrow C_5H_{10} + 1\text{-}C_4H_9^{\bullet}$	13.0	35.0
18	$C_8H_{17}^{\bullet} \rightarrow C_2H_4 + C_6H_{13}^{\bullet}$	13.4	31.0
19	$C_8H_{17}^{\bullet} \rightarrow C_3H_6 + C_5H_{11}^{\bullet}$	13.3	30.0
20	$C_8H_{17}^{\bullet} \rightarrow 1\text{-}C_4H_8 + 1\text{-}C_4H_9^{\bullet}$	12.6	29.0
21	$C_8H_{17}^{\bullet} \rightarrow C_5H_{10} + 1\text{-}C_3H_7^{\bullet}$	14.0	32.5
22	$C_7H_{15}^{\bullet} \rightarrow C_2H_4 + C_5H_{11}^{\bullet}$	13.6	45.0
23	$C_7H_{15}^{\bullet} \rightarrow C_3H_6 + C_4H_9^{\bullet}$	13.3	31.0
24	$C_7H_{15}^{\bullet} \rightarrow 1\text{-}C_4H_8 + 1\text{-}C_3H_7^{\bullet}$	13.0	29.0
25	$C_7H_{15}^{\bullet} \rightarrow C_5H_{10} + C_2H_5^{\bullet}$	14.1	32.5
26	$C_6H_{13}^{\bullet} \rightarrow C_2H_4 + 1\text{-}C_4H_9^{\bullet}$	13.4	30.0
27	$C_6H_{13}^{\bullet} \rightarrow C_3H_6 + 1\text{-}C_3H_7^{\bullet}$	13.2	29.0
28	$C_6H_{13}^{\bullet} \rightarrow 1\text{-}C_4H_8 + C_2H_5^{\bullet}$	12.6	31.0

1. Unit of A is: s^{-1} or $L\ mol^{-1}s^{-1}$

2. Unit of E is: kCal / mol

Table 5 (Continued)

No.	Reaction	Parameters Adopted	
		LOG (A)[1]	E[2]
29	$C_6H_{13}^{\bullet} \rightarrow C_5H_{10} + CH_3^{\bullet}$	14.0	32.5
30	$1\text{-}C_4H_7^{\bullet} \rightarrow C_4H_6 + H^{\bullet}$	11.0	49.3
31	$1\text{-}C_4H_7^{\bullet} \rightarrow C_2H_4 + C_2H_3^{\bullet}$	14.1	39.0
32	$C_5H_{11}^{\bullet} \rightarrow C_2H_4 + 1\text{-}C_3H_7^{\bullet}$	13.5	28.4
33	$C_5H_{11}^{\bullet} \rightarrow C_3H_6 + C_2H_5^{\bullet}$	13.7	38.0
34	$C_5H_{11}^{\bullet} \rightarrow C_4H_8 + CH_3^{\bullet}$	13.5	31.5
35	$C_5H_{11}^{\bullet} \rightarrow C_5H_{10} + H^{\bullet}$	13.7	38.6
36	$1\text{-}C_4H_9^{\bullet} \rightarrow C_2H_4 + C_2H_5^{\bullet}$	12.2	29.0
37	$1\text{-}C_4H_9^{\bullet} \rightarrow C_3H_6 + CH_3^{\bullet}$	13.3	34.0
38	$1\text{-}C_4H_9^{\bullet} \rightarrow 1\text{-}C_4H_8 + H^{\bullet}$	13.0	36.6
39	$2\text{-}C_3H_7^{\bullet} \rightarrow C_3H_6 + H^{\bullet}$	13.3	38.7
40	$1\text{-}C_3H_7^{\bullet} \rightarrow C_2H_4 + CH_3^{\bullet}$	13.6	32.6
41	$1\text{-}C_3H_7^{0} \rightarrow C_3H_6 + H^{0}$	13.3	38.4
42	$C_2H_3^{\bullet} \rightarrow C_2H_2 + H^{\bullet}$	9.3	31.5
43	$i\text{-}C_9H_{19}^{\bullet} \rightarrow C_2H_4 + i\text{-}C_7H_{15}^{\bullet}$	13.1	32.5
44	$i\text{-}C_9H_{19}^{\bullet} \rightarrow C_3H_6 + i\text{-}C_6H_{13}^{\bullet}$	12.5	30.0
45	$i\text{-}C_9H_{19}^{\bullet} \rightarrow C_3H_6 + C_6H_{13}^{\bullet}$	13.1	32.0
46	$i\text{-}C_9H_{19}^{\bullet} \rightarrow 1\text{-}C_4H_8 + i\text{-}C_5H_{11}^{\bullet}$	12.8	30.0
47	$i\text{-}C_9H_{19}^{\bullet} \rightarrow i\text{-}C_4H_8 + C_5H_{11}^{\bullet}$	13.0	29.0
48	$i\text{-}C_9H_{19}^{\bullet} \rightarrow C_5H_{10} + i\text{-}C_4H_9^{\bullet}$	13.5	31.0
49	$i\text{-}C_8H_{17}^{\bullet} \rightarrow C_2H_4 + i\text{-}C_6H_{13}^{\bullet}$	13.2	32.0
50	$i\text{-}C_8H_{17}^{\bullet} \rightarrow C_3H_6 + i\text{-}C_5H_{11}^{\bullet}$	13.3	31.0
51	$i\text{-}C_8H_{17}^{\bullet} \rightarrow C_3H_6 + C_5H_{11}^{\bullet}$	13.3	30.0
52	$i\text{-}C_8H_{17}^{\bullet} \rightarrow 1\text{-}C_4H_8 + i\text{-}C_4H_9^{\bullet}$	12.5	30.0
53	$i\text{-}C_8H_{17}^{\bullet} \rightarrow i\text{-}C_4H_8 + 1\text{-}C_4H_9^{\bullet}$	12.5	31.0
54	$i\text{-}C_8H_{17}^{\bullet} \rightarrow C_5H_{10} + 2\text{-}C_3H_7^{\bullet}$	13.5	30.1
55	$i\text{-}C_7H_{15}^{\bullet} \rightarrow C_2H_4 + i\text{-}C_5H_{11}^{\bullet}$	13.5	43.0
56	$i\text{-}C_7H_{15}^{\bullet} \rightarrow C_3H_6 + i\text{-}C_4H_9^{\bullet}$	13.1	30.0
57	$i\text{-}C_7H_{15}^{\bullet} \rightarrow C_3H_6 + 1\text{-}C_4H_9^{\bullet}$	13.0	32.5
58	$i\text{-}C_7H_{15}^{\bullet} \rightarrow 1\text{-}C_4H_8 + 2\text{-}C_3H_7^{\bullet}$	13.0	29.5

Table 5 (Continued)

No.	Reaction	Parameters Adopted	
		LOG (A)[1]	E[2]
59	$i\text{-}C_7H_{15}^{\bullet} \rightarrow i\text{-}C_4H_8 + 1\text{-}C_3H_7^{\bullet}$	12.5	31.0
60	$i\text{-}C_6H_{13}^{\bullet} \rightarrow C_2H_4 + i\text{-}C_4H_9^{\bullet}$	13.2	31.0
61	$i\text{-}C_6H_{13}^{\bullet} \rightarrow C_3H_6 + 2\text{-}C_3H_7^{\bullet}$	13.4	31.0
62	$i\text{-}C_6H_{13}^{\bullet} \rightarrow C_3H_6 + 1\text{-}C_3H_7^{\bullet}$	13.1	29.0
63	$i\text{-}C_6H_{13}^{\bullet} \rightarrow i\text{-}C_4H_8 + C_2H_5^{\bullet}$	13.4	32.5
64	$i\text{-}C_5H_{11}^{\bullet} \rightarrow C_2H_4 + 2\text{-}C_3H_7^{\bullet}$	13.0	29.0
65	$i\text{-}C_5H_{11}^{\bullet} \rightarrow C_3H_6 + C_2H_5^{\bullet}$	13.1	31.0
66	$i\text{-}C_5H_{11}^{\bullet} \rightarrow 1\text{-}C_4H_8 + CH_3^{\bullet}$	13.7	32.8
67	$i\text{-}C_5H_{11}^{\bullet} \rightarrow i\text{-}C_4H_8 + CH_3^{\bullet}$	13.0	30.0
68	$i\text{-}C_4H_9^{\bullet} \rightarrow C_3H_6 + CH_3^{\bullet}$	14.0	32.8
69	$i\text{-}C_4H_9^{\bullet} \rightarrow i\text{-}C_4H_8 + H^{\bullet}$	13.5	30.0
70	$i\text{-}C_4H_9^{\bullet} \rightarrow 2\text{-}C_4H_8 + H^{\bullet}$	13.0	30.2
3. Paraffin + Radical → Paraffin + Radical			
71	$C_9H_{20} + H^{\bullet} \rightarrow C_9H_{19}^{\bullet} + H_2$	12.0	15.0
72	$C_9H_{20} + CH_3^{\bullet} \rightarrow C_9H_{19}^{\bullet} + CH_4$	11.5	9.5
73	$C_9H_{20} + C_2H_5^{\bullet} \rightarrow C_9H_{19}^{\bullet} + C_2H_6$	11.6	10.0
74	$C_9H_{20} + 1\text{-}C_3H_7^{\bullet} \rightarrow C_9H_{19}^{\bullet} + C_3H_8$	11.1	11.0
75	$C_9H_{20} + C_2H_3^{\bullet} \rightarrow C_9H_{19}^{\bullet} + C_2H_4$	11.5	9.0
76	$i\text{-}C_9H_{20} + H^{\bullet} \rightarrow H_2 + i\text{-}C_9H_{19}^{\bullet}$	11.0	12.5
77	$i\text{-}C_9H_{20} + CH_3^{\bullet} \rightarrow CH_4 + i\text{-}C_9H_{19}^{\bullet}$	11.5	9.0
78	$i\text{-}C_9H_{20} + C_2H_3^{\bullet} \rightarrow C_2H_4 + i\text{-}C_9H_{19}^{\bullet}$	12.0	9.5
79	$i\text{-}C_9H_{20} + C_2H_5^{\bullet} \rightarrow C_2H_6 + i\text{-}C_9H_{19}^{\bullet}$	11.1	10.0
80	$i\text{-}C_9H_{20} + 1\text{-}C_3H_7^{\bullet} \rightarrow C_3H_8 + i\text{-}C_9H_{19}^{\bullet}$	10.1	9.0
81	$i\text{-}C_9H_{20} + 2\text{-}C_3H_7^{\bullet} \rightarrow C_3H_8 + i\text{-}C_9H_{19}^{\bullet}$	10.5	8.0
82	$C_3H_8 + H^{\bullet} \rightarrow 1\text{-}C_3H_7^{\bullet} + H_2$	10.5	9.7
83	$C_3H_8 + CH_3^{\bullet} \rightarrow 1\text{-}C_3H_7^{\bullet} + CH_4$	9.0	12.5
84	$C_3H_8 + C_2H_5^{\bullet} \rightarrow 1\text{-}C_3H_7^{\bullet} + C_2H_6$	8.5	12.3
85	$C_2H_6 + H^{\bullet} \rightarrow C_2H_5^{\bullet} + H_2$	11.1	10.5
86	$C_2H_6 + CH_3^{\bullet} \rightarrow C_2H_5^{\bullet} + CH_4$	11.6	16.5
87	$C_2H_6 + 1\text{-}C_3H_7^{\bullet} \rightarrow C_2H_5^{\bullet} + C_3H_8$	8.0	10.0
88	$CH_4 + H^{\bullet} \rightarrow CH_3^{\bullet} + H_2$	11.5	12.5

Table 5 (Continued)

No.	Reaction	Parameters Adopted	
		LOG (A)[1]	E[2]
89	$CH_4 + C_2H_5^{\bullet} \rightarrow CH_3^{\bullet} + C_2H_6$	7.0	11.0
90	$CH_4 + 1\text{-}C_3H_7^{\bullet} \rightarrow CH_3^{\bullet} + C_3H_8$	8.3	18.0
91	$H_2 + CH_3^{\bullet} \rightarrow H^{\bullet} + CH_4$	8.9	10.9
92	$H_2 + C_2H_5^{\bullet} \rightarrow H^{\bullet} + C_2H_6$	9.5	13.0
93	$H_2 + 1\text{-}C_3H_7^{\bullet} \rightarrow H^{\bullet} + C_3H_8$	9.0	15.6
94	$H_2 + 2\text{-}C_3H_7^{\bullet} \rightarrow H^{\bullet} + C_3H_8$	9.5	15.0
95	$H_2 + C_3H_5^{\bullet} \rightarrow H^{\bullet 0} + C_3H_6$	10.5	20.0
96	$H_2 + 1\text{-}C_4H_9^{\bullet} \rightarrow H^{\bullet} + C_4H_{10}$	9.5	16.5
97	$H_2 + 2\text{-}C_4H_9^{\bullet} \rightarrow H^{\bullet} + C_4H_{10}$	9.7	17.5
98	$H_2 + i\text{-}C_4H_9^{\bullet} \rightarrow H^{\bullet} + C_4H_{10}$	9.5	16.5
99	$C_2H_6 + 1\text{-}C_4H_9^{\bullet} \rightarrow C_2H_5 + C_4H_{10}$	8.5	12.5
100	$C_2H_6 + 2\text{-}C_4H_9^{\bullet} \rightarrow C_2H_5 + C_4H_{10}$	8.0	12.9
101	$C_2H_6 + i\text{-}C_4H_9^{\bullet 0} \rightarrow C_2H_5 + i\text{-}C_4H_{10}$	8.5	12.5
4. Radical + Radical $\rightarrow$ Paraffin			
102	$1\text{-}C_3H_7^{\bullet} + H^{\bullet} \rightarrow C_3H_8$	11.0	0
103	$C_2H_5^{\bullet} + H^{\bullet} \rightarrow C_2H_6$	11.5	0
104	$2\text{-}C_3H_7^{\bullet} + H^{\bullet} \rightarrow C_3H_8$	11.0	0
105	$1\text{-}C_4H_9^{\bullet} + H^{\bullet} \rightarrow C_4H_{10}$	11.0	0
106	$i\text{-}C_4H_9^{\bullet} + H^{\bullet} \rightarrow i\text{-}C_4H_{10}$	11.0	0
107	$C_5H_{11}^{\bullet} + H^{\bullet} \rightarrow C_5H_{12}$	11.0	0
108	$2\text{-}C_3H_7^{\bullet} + CH_3^{\bullet} \rightarrow i\text{-}C_4H_{10}$	10.3	0
109	$C_6H_{13}^{\bullet} + H^{\bullet} \rightarrow C_6H_{14}$	11.0	0
110	$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_6$	11.3	0
5. Secondary Reaction I; Olefin + Radical $\rightarrow$ Paraffin + Olefinic Radical			
111	$C_3H_6 + H^{\bullet} \rightarrow C_3H_5^{\bullet} + H_2$	10.7	5.0
112	$C_3H_6 + CH_3^{\bullet} \rightarrow C_3H_5^{\bullet} + CH_4$	7.5	8.0
113	$C_3H_6 + C_2H_5^{\bullet} \rightarrow C_3H_5^{\bullet} + C_2H_6$	8.0	10.5
114	$C_3H_8 + C_3H_5^{\bullet} \rightarrow C_3H_6 + 1\text{-}C_3H_7^{\bullet}$	9.0	20.5
115	$1\text{-}C_4H_8 + H^{\bullet} \rightarrow C_4H_7^{\bullet} + H_2$	11.0	5.0
116	$1\text{-}C_4H_8 + CH_3^{\bullet} \rightarrow C_4H_7^{\bullet} + CH_4$	8.0	7.3
117	$1\text{-}C_4H_8 + C_2H_5^{\bullet} \rightarrow C_4H_7^{\bullet} + C_2H_6$	8.0	8.3
118	$C_3H_8 + C_4H_7^{\bullet} \rightarrow C_4H_8 + 1\text{-}C_3H_7^{\bullet}$	9.69	6.0

Table 5 (Continued)

No.	Reaction	Parameters Adopted	
		LOG (A)[1]	E[2]
119	$C_5H_{10} + H^{\bullet 0} \rightarrow C_5H_9^{\bullet} + H_2$	12.0	8.0
120	$C_5H_{10} + CH_3^{\bullet} \rightarrow C_5H_9^{\bullet} + CH_4$	9.7	12.5
121	$C_5H_{10} + C_2H_5^{\bullet} \rightarrow C_5H_9^{\bullet} + C_2H_6$	9.6	14.5
122	$C_3H_8 + C_5H_9^{\bullet} \rightarrow C_5H_{10} + 1\text{-}C_3H_7^{\bullet}$	9.69	16.0
6. Secondary Reaction II			
123	$C_2H_4 + H^{\bullet} \rightarrow C_2H_3^{\bullet} + H_2$	8.9	4.0
124	$C_2H_4 + CH_3^{\bullet} \rightarrow C_2H_3^{\bullet} + CH_4$	10.0	12.0
125	$C_2H_4 + C_2H_5^{\bullet} \rightarrow C_2H_3^{\bullet} + C_2H_6$	9.4	25.0
126	$C_2H_4 + H^{\bullet} \rightarrow C_2H_5^{\bullet}$	9.9	1.5
127	$C_2H_4 + CH_3^{\bullet} \rightarrow 1\text{-}C_3H_7^{\bullet}$	8.6	7.9
128	$C_2H_4 + C_2H_5^{\bullet} \rightarrow 1\text{-}C_4H_9^{\bullet}$	7.8	7.6
129	$C_2H_4 + C_2H_3^{\bullet} \rightarrow C_4H_6 + H^{\bullet}$	11.0	50.0
130	$C_2H_4 + C_2H_3^{\bullet} \rightarrow C_4H_7^{\bullet}$	7.7	5.5
131	$C_3H_6 + H^{\bullet} \rightarrow 1\text{-}C_3H_7^{\bullet}$	10.1	3.0
132	$C_3H_6 + CH_3^{\bullet} \rightarrow 1\text{-}C_4H_9^{\bullet}$	8.5	7.4
133	$1\text{-}C_4H_8 + H^0 \rightarrow 1\text{-}C_4H_9^{\bullet}$	9.9	1.2
134	$1\text{-}C_4H_8 + CH_3^{\bullet} \rightarrow C_5H_{11}^{\bullet}$	8.3	7.2
7. Molecular Reaction I			
135	$C_3H_8 \rightarrow C_3H_6 + H_2$	12.0	50.0
136	$C_4H_6 + C_2H_4 \rightarrow C_6H_6 + 2H_2$	9.9	34.6
137	$C_4H_6 + C_3H_6 \rightarrow C_7H_8 + 2H_2$	9.0	35.6
138	$C_4H_6 + 1\text{-}C_4H_8 \rightarrow C_8H_{10} + 2H_2$	14.8	60.0
139	$C_4H_6 + C_4H_6 \rightarrow C_8H_8 + 2H_2$	9.2	29.8
8. Molecular Reaction II 7			
140	$4C_6H_6 \rightarrow 3(C_4H)_X + 9H_2$	15.3	50.7
141	$4C_7H_8 \rightarrow 7(C_4H)_X + 12.5\ H_2$	15.3	50.7
142	$C_8H_{10} \rightarrow 2(C_4H)_X + 4H_2$	15.3	50.7
143	$C_8H_8 \rightarrow 2(C_4H)_X + 3H_2$	15.3	50.7
144	$2C_2H_6 \rightarrow C_3H_8 + CH_4$	12.5	65.0
145	$C_3H_6 + C_2H_6 \rightarrow C_4H_8 + CH_4$	14.0	60.0
146	$C_3H_8 \rightarrow C_2H_4 + CH_4$	10.6	50.0
147	$C_3H_8 \rightarrow C_3H_6 + H_2$	10.7	51.0
148	$2C_3H_6 \rightarrow 3C_2H_4$	12.8	64.0

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