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MECHANISTIC MODELING OF THE PYROLYSIS OF n-HEPTANE

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ABSTRACT

A mechanistic model of the thermal decomposition reactions of n-heptane at high conversions was proposed on the basis of observed product distributions and a complex free radical chain mechanism The predicted product distributions showed a reasonably good agreement with the experimental results of an earlier work by the authors of this paper (Thermochim Acta, 127 (1988) 247) The radical concentrations varied significantly with reaction time Furthermore, the appearance of allylic radicals (C_3H_5 and C_4H_7) is an indication of the presence of secondary reactions of olefinic primary products and hence of inhibition in n-heptane pyrolysis

NOMENCLATURE

C_i	concentration of ith species (gmol l^{-1})
t	reaction time (s)
S_{ij}	stoichiometric constant of ith species in the jth reaction
r_j	rate of ith reaction (mol l^{-1} s^{-1})
k_j	rate constant of forward reaction (s^{-1} or l mol^{-1} s^{-1})
k'_j	rate constant of reverse reaction (s^{-1} or l mol^{-1} s^{-1})
M'	total number of species
N	total number of reactions
A	pre-exponential factor (s^{-1} or l mol^{-1} s^{-1})
E	activation energy (cal mol^{-1})

INTRODUCTION

Expansion in the petrochemical industry, the prevailing decline in demand growth for ethylene, feedstock flexibility, unstable prices and fierce competition among manufacturers have provided the impetus for extensive

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research into the development of hydrocarbon pyrolysis models applicable to a wide range of feedstocks—from ethane and propane to whole crudes The intense competition of the past few years has resulted in marked improvements in the efficiency of olefine production [1]

Better understanding of the mechanisms of the pyrolysis of hydrocarbons would be of great economic importance, when one considers the costs of petrochemical plants Besides, models can be used in optimizing thermal cracking operations and in reducing costly and time-consuming experimental programs [2] Mechanistic modeling is widely used thanks to the availability of fast computers Though it is initially more expensive and time-consuming, its long term advantage is important, once it is developed, it is no longer necessary to employ an expensive pilot plant [3] Furthermore, mechanistic models account extensively for free radical reactions which play very significant roles in hydrocarbon pyrolysis Also, the pyrolysis of hydrocarbons under industrial conditions occur at high conversions where secondary reactions of radicals predominate

Mechanistic models have been used mainly in hydrocarbon pyrolysis studies at low conversions [4–7], there are few applications at high conversions [8,9] The scarcity of mechanistic models of hydrocarbon pyrolysis at high conversions may be due to the complexity of the mechanism, the number of reactive species increases with conversion leading to excessive computation time Also, most of the mechanistic modeling studies were on light hydrocarbons, there are few reported studies on the modeling of the pyrolysis of medium and heavy hydrocarbons [7,16,17] Two of the latter studies [16,17] were concerned with the prediction of the initial product distributions of the pyrolysis of n-heptane and other hydrocarbons at temperatures of 440–700 °C on the basis of the Rice–Kossiakoff (R–K) theory [10,11] Therefore, as far as the present authors are aware, there is no reported study on the mechanistic modeling of n-heptane pyrolysis up to the high conversion region

In the present study, a mechanistic model of n-heptane pyrolysis is proposed on the basis of experimental product distributions, R–K theory and literature information Modifications made to the R–K theory in accounting for the secondary reactions of higher α-olefins in an earlier work by the authors of this paper [12] are adapted in the present work

REACTION MECHANISM AND MODEL

To develop mechanistic models, an intrinsic reaction mechanism is determined on the basis of the most plausible set of elementary reactions (ER) Also, the development of well-balanced mechanistic models is possible due to accurate and detailed thermochemical kinetic data and increased availability of pyrolysis data [16]

Thermal cracking of n-heptane produced ethylene, propylene, methane, 1-butene, 1,3-butadiene and hydrogen as major products [12,18], relatively smaller amounts of ethane, propane, 3-methylbutene, 1-pentene, 1-hexene and benzene were also produced It is generally accepted that the pyrolyses of hydrocarbons proceed via a free radical chain mechanism In explaining the product distributions of n-heptane pyrolysis at high conversions Bajus et al [18] proposed the following mechanism based on the R–K theory

$$1\text{-}C_7H_{15}\xrightarrow{a}3C_2H_4+CH_3^{\cdot}$$

$$2\text{-}C_7H_{15}\xrightarrow{b}C_3H_6+C_2H_4+C_2H_5$$

$$3\text{-}C_7H_{15}^{\cdot}-\left[\begin{array}{l}\xrightarrow{c}1\text{-}C_6H_{12}+CH_3^{\cdot}\\ \xrightarrow{d}C_2H_4+1\text{-}C_4H_8+CH_3\end{array}\right.$$

$$4\text{-}C_7H_{15}\xrightarrow{e}1\text{-}C_5H_{10}+C_2H_5$$

However, Bajus et al [18] and other workers [12,16,19] found the R–K theory to be inadequate in accounting for the product distributions of the pyrolysis of hydrocarbons at high conversions

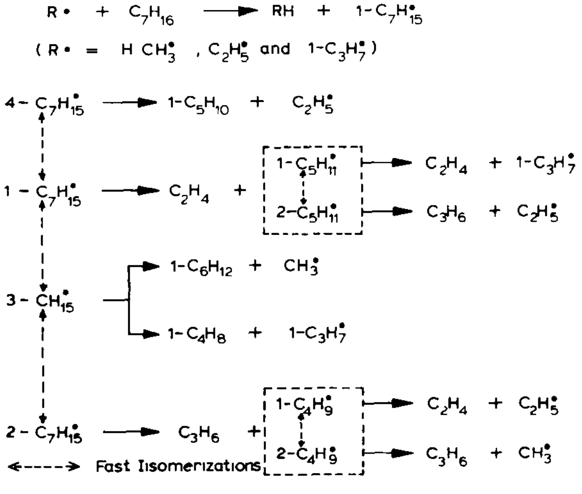
The major initiation reactions of n-heptane pyrolysis at high conversions are not only the unimolecular scission of primary and secondary C–C bonds

$C_7H_{16}\rightarrow R+R'$

($R^{\cdot}$ and R' are alkyl radicals) but also the cleavage of the C–H bonds to form heptyl radicals

$C_7H_{16}\rightarrow H+C_7H_{15}^{\cdot}$

Furthermore, smaller radicals ($H^{\cdot}$, $CH_3^{\cdot}$, $C_2H_5^{\cdot}$ and $C_3H_7^{\cdot}$) will abstract a hydrogen radical from n-heptane to form more light saturated molecules (H_2, CH_4, C_2H_6, C_3H_8) and heptyl radicals Heptyl radicals will in turn undergo fast isomerization reactions followed immediately by unimolecular decompositions to form olefins and some lighter alkyl radicals



Also, olefins participate in secondary reactions at higher conversions, these are

(i) addition of light radicals to alkenes

$$R'^{\cdot} + C_NH_{2N} \rightarrow R'C_NH^{\cdot}_{2N} \rightarrow \text{(lighter olefins + radicals)}$$
$$(R'^{\cdot} = H, CH_3)$$

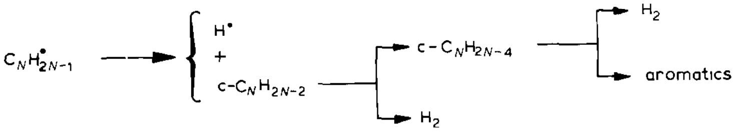
(ii) H-abstractions from alkenes by reactive radicals

$$R'^{\cdot} + C_NH_{2N} \rightarrow R'H + C_NH_{2N-1}$$

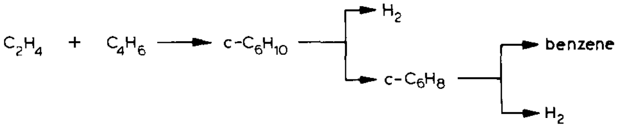
$$C_NH^{\cdot}_{2N-1} \rightarrow \left\{\begin{array}{l}\text{olefins}\\ \text{di-olefins}\\ \text{cyclo-olefins}\end{array}\right. + R''^{\cdot}$$

$$(R'^{\cdot} = H\,, CH^{\cdot}_3, C_2H^{\cdot}_5, R''^{\cdot} = H^{\cdot}, C_2H^{\cdot}_5, C_2H^{\cdot}_3, C_3H^{\cdot}_5)$$

The alkenyl radicals may undergo dehydrocyclization reactions to form cyclo-olefins which can in turn dehydrogenate to form aromatics The formation of benzene as a secondary product in n-heptane pyrolysis [12,18] supports this assertion



Another reaction that may lead to benzene is Diels–Alder reaction of the form



This concerted molecular reaction can occur as fast as free radical reactions even with a smaller amount of 1,3-butadiene [35] The proposed model is shown in Table 1 Some molecular reactions are included in the model because their exclusion will lead to misleading conclusions of rate parameters, particularly for olefins and di-olefins [21] In developing this model, an initial minimum set of ER is used and later expanded by addition of new ER until experimental and predicted distributions have shown good agreement

SELECTION OF KINETIC RATE PARAMETERS

Kinetic rate parameters of the ER listed in Table 1 are compiled from several sources Large numbers of accurate and reliable rate parameters of

TABLE 1

Mechanistic model for the pyrolysis of n-heptane

No	Reaction		$\log_{10} A$	E
Initiation				
1	CH_4	$\rightarrow H+CH_3$	15.3	104000
2	C_2H_6	$\rightarrow H+C_2H_5$	16.0	98000
3	C_2H_6	$\rightarrow CH_3+CH_3$	16.0	88000
4	C_3H_8	$\rightarrow H+1\text{-}C_3H_7$	16.0	98000
5	C_3H_8	$\rightarrow CH_3+C_2H_5$	16.3	85000
6	C_4H_{10}	$\rightarrow CH_3+1\text{-}C_3H_7$	16.3	85000
7	C_4H_{10}	$\rightarrow C_2H_5+C_2H_5$	16.3	81400
8	C_6H_{14}	$\rightarrow CH_3+1\text{-}C_5H_{11}$	17.2	85400
9	C_6H_{14}	$\rightarrow C_2H_5+1\text{-}C_4H_9$	16.5	82400
10	C_6H_{14}	$\rightarrow 1\text{-}C_3H_7+1\text{-}C_3H_7$	16.1	82400
11	C_7H_{16}	$\rightarrow CH_3+1\text{-}C_6H_{13}$	17.4	85040
12	C_7H_{16}	$\rightarrow C_2H_5+1\text{-}C_5H_{11}$	16.8	82300
13	C_7H_{16}	$\rightarrow 1\text{-}C_3H_7+1\text{-}C_4H_9$	16.8	81800
14	C_2H_4	$\rightarrow H+C_2H_3$	13.0	108000
15	C_3H_6	$\rightarrow H+C_3H_5$	15.0	88000
16	C_3H_6	$\rightarrow CH_3+C_2H_3$	15.5	89000
17	$1\text{-}C_4H_8$	$\rightarrow CH_3+C_3H_5$	16.0	74000
18	$1\text{-}C_4H_8$	$\rightarrow$ H + 1-M-AL	16.0	90000
19	$1\text{-}C_5H_{10}$	$\rightarrow C_2H_5+C_3H_5$	16.6	74800
H-Abstraction				
20	$H+CH_4$	$\rightarrow H_2+CH_3$	11.1	12600
21	$H+C_2H_6$	$\rightarrow H_2+C_2H_5$	11.1	9700
22	$H+C_3H_8$	$\rightarrow H_2+1\text{-}C_3H_7$	11.1	9700
23	$H+C_3H_8$	$\rightarrow H_2+2\text{-}C_3H_7$	11.0	8300
24	$H+C_4H_{10}$	$\rightarrow H_2+1\text{-}C_4H_9$	11.1	9700
25	$H+C_4H_{10}$	$\rightarrow H_2+2\text{-}C_4H_9$	11.0	8400
26	$H+C_6H_{14}$	$\rightarrow H_2+1\text{-}C_6H_{13}$	11.0	9700
27	$H+C_6H_{14}$	$\rightarrow H_2+2\text{-}C_6H_{13}$	10.7	8400
28	$H+C_6H_{14}$	$\rightarrow H_2+3\text{-}C_6H_{13}$	10.4	8400
29	$H+C_7H_{16}$	$\rightarrow H_2+1\text{-}C_7H_{15}$	11.0	9700
30	$H+C_2H_4$	$\rightarrow H_2+C_2H_3$	8.5	4500
31	$H+C_3H_6$	$\rightarrow H_2+C_3H_5$	8.5	4500
32	$H+1\text{-}C_4H_8$	$\rightarrow H_2$ + 1-M-AL	8.5	4500
33	$H+1\text{-}C_4H_8$	$\rightarrow H_2$ + 3-BEN	9.1	11600
34	$H+1\text{-}C_5H_{10}$	$\rightarrow H_2$ + 1-E-AL	7.7	4500
35	$H+1\text{-}C_5H_{10}$	$\rightarrow H_2$ + 1-M-BEN	8.5	11000
36	$H+1\text{-}C_5H_{10}$	$\rightarrow H_2$ + 4-PEN	9.0	11600
37	CH_3+H_2	$\rightarrow CH_4+H$	9.5	10200
38	CH_3+CH_4	$\rightarrow CH_4+CH_3$	8.6	14000
39	$CH_3+C_2H_6$	$\rightarrow CH_4+C_2H_5$	9.0	10600
40	$CH_3+C_3H_8$	$\rightarrow CH_4+1\text{-}C_3H_7$	9.0	11500
41	$CH_3+C_3H_8$	$\rightarrow CH_4+2\text{-}C_3H_7$	8.9	10100
42	$CH_3+C_4H_{10}$	$\rightarrow CH_4+1\text{-}C_4H_9$	9.1	11600
43	$CH_3+C_4H_{10}$	$\rightarrow CH_4+2\text{-}C_4H_9$	8.9	9500
44	$CH_3+C_6H_{14}$	$\rightarrow CH_4+1\text{-}C_6H_{13}$	9.1	11600

(continued)

TABLE 1 (continued)

No	Reaction		$\log_{10} A$	E
45	$CH_3 + C_6H_{14}$	$\rightarrow CH_4 + 2\text{-}C_6H_{13}$	8 9	9500
46	$CH_3 + C_6H_{14}$	$\rightarrow CH_4 + 3\text{-}C_6H_{13}$	8 6	9500
47	$CH_3 + C_7H_{16}$	$\rightarrow CH_4 + 1\text{-}C_7H_{15}$	8 8	11600
48	$CH_3 + C_2H_4$	$\rightarrow CH_4 + C_2H_3$	8 6	8000
49	$CH_3 + C_3H_6$	$\rightarrow CH_4 + C_3H_5$	7 3	4500
50	$CH_3 + 1\text{-}C_4H_8$	$\rightarrow CH_4 + 1\text{-M-AL}$	7 3	4500
51	$CH_3 + 1\text{-}C_4H_8$	$\rightarrow CH_4 + 3\text{-BEN}$	9 0	11600
52	$CH_3 + 1\text{-}C_5H_{10}$	$\rightarrow CH_4 + 1\text{-E-AL}$	7 7	4500
53	$CH_3 + 1\text{-}C_5H_{10}$	$\rightarrow CH_4 + 1\text{-M-BEN}$	8 9	9500
54	$CH_3 + 1\text{-}C_5H_{10}$	$\rightarrow CH_4 + 4\text{-PEN}$	9 1	11600
55	$C_2H_5 + H_2$	$\rightarrow C_2H_6 + H$	8 5	10800
56	$C_2H_5 + CH_4$	$\rightarrow C_2H_6 + CH_3$	8 0	11000
57	$C_2H_5 + C_2H_6$	$\rightarrow C_2H_6 + C_2H_5$	9 0	11500
58	$C_2H_5 + C_3H_8$	$\rightarrow C_2H_6 + 1\text{-}C_3H_7$	9 1	12600
59	$C_2H_5 + C_3H_8$	$\rightarrow C_2H_6 + 2\text{-}C_3H_7$	8 9	10400
60	$C_2H_5 + C_4H_{10}$	$\rightarrow C_2H_6 + 1\text{-}C_4H_9$	9 3	12600
61	$C_2H_5 + C_4H_{10}$	$\rightarrow C_2H_6 + 2\text{-}C_4H_9$	8 65	10400
62	$C_2H_5 + C_6H_{14}$	$\rightarrow C_2H_6 + 1\text{-}C_6H_{13}$	8 0	12600
63	$C_2H_5 + C_6H_{14}$	$\rightarrow C_2H_6 + 2\text{-}C_6H_{13}$	8 0	10400
64	$C_2H_5 + C_6H_{14}$	$\rightarrow C_2H_6 + 3\text{-}C_6H_{13}$	7 7	10400
65	$C_2H_5 + C_2H_4$	$\rightarrow C_2H_6 + C_2H_3$	8 5	11400
66	$C_2H_5 + C_3H_6$	$\rightarrow C_2H_6 + C_3H_5$	7 3	4500
67	$C_2H_5 + 1\text{-}C_4H_8$	$\rightarrow C_2H_6 + 1\text{-M-AL}$	7 3	4500
68	$C_2H_5 + 1\text{-}C_4H_8$	$\rightarrow C_2H_6 + 3\text{-BEN}$	9 0	11600
69	$C_2H_5 + 1\text{-}C_5H_{10}$	$\rightarrow C_2H_6 + 1\text{-E-AL}$	7 3	4500
70	$C_2H_5 + 1\text{-}C_5H_{10}$	$\rightarrow C_2H_6 + 1\text{-M-BEN}$	8 7	9800
71	$C_2H_5 + 1\text{-}C_5H_{10}$	$\rightarrow C_2H_6 + 4\text{-PEN}$	8 4	9800
72	$1\text{-}C_3H_7 + H_2$	$\rightarrow C_3H_8 + H$	9 8	14600
73	$1\text{-}C_3H_7 + CH_4$	$\rightarrow C_3H_8 + CH_3$	8 3	15000
74	$1\text{-}C_3H_7 + C_2H_6$	$\rightarrow C_3H_8 + C_2H_5$	8 0	10000
75	$1\text{-}C_3H_7 + C_3H_8$	$\rightarrow C_3H_8 + 2\text{-}C_3H_7$	8 0	10000
76	$1\text{-}C_3H_7 + C_4H_{10}$	$\rightarrow C_3H_8 + 2\text{-}C_4H_9$	8 3	10200
77	$1\text{-}C_3H_7 + C_6H_{14}$	$\rightarrow C_3H_8 + 1\text{-}C_6H_{13}$	8 0	12600
78	$1\text{-}C_3H_7 + C_6H_{14}$	$\rightarrow C_3H_8 + 2\text{-}C_6H_{13}$	8 0	10400
79	$1\text{-}C_3H_7 + C_6H_{14}$	$\rightarrow C_3H_8 + 3\text{-}C_6H_{13}$	7 7	10400
80	$1\text{-}C_3H_7 + C_2H_4$	$\rightarrow C_3H_8 + C_2H_3$	8 0	15000
81	$1\text{-}C_3H_7 + C_3H_6$	$\rightarrow C_3H_8 + C_3H_5$	8 0	9200
82	$C_2H_3 + H_2$	$\rightarrow C_2H_4 + H$	9 9	7400
83	$C_2H_3 + CH_4$	$\rightarrow C_2H_4 + CH_3$	9 0	16000
84	$C_2H_3 + C_2H_6$	$\rightarrow C_2H_4 + C_2H_5$	9 0	16000
85	$C_2H_3 + C_3H_8$	$\rightarrow C_2H_4 + 1\text{-}C_3H_7$	9 5	18800
86	$C_2H_3 + C_3H_8$	$\rightarrow C_2H_4 + 2\text{-}C_3H_7$	9 0	16200
87	$C_2H_3 + C_4H_{10}$	$\rightarrow C_2H_4 + 1\text{-}C_4H_9$	9 0	18800
88	$C_2H_3 + C_4H_{10}$	$\rightarrow C_2H_4 + 2\text{-}C_4H_9$	8 9	16800
89	$C_2H_3 + C_6H_{14}$	$\rightarrow C_2H_4 + 1\text{-}C_6H_{13}$	9 0	18000
90	$C_2H_3 + C_6H_{14}$	$\rightarrow C_2H_4 + 2\text{-}C_6H_{13}$	8 9	16800
91	$C_2H_3 + C_6H_{14}$	$\rightarrow C_2H_4 + 3\text{-}C_6H_{13}$	8 9	16800
92	$C_2H_3 + C_3H_6$	$\rightarrow C_2H_4 + C_3H_5$	9 5	14500
93	$C_2H_3 + 1\text{-}C_4H_8$	$\rightarrow C_2H_4 + 1\text{-M-AL}$	8 0	13000
94	$C_2H_3 + 1\text{-}C_5H_{10}$	$\rightarrow C_2H_4 + 1\text{-E-AL}$	9 0	13000

TABLE 1 (continued)

No	Reaction		$\log_{10} A$	E
95	C_2H_3 + 1-C_5H_{10}	→ C_2H_4 + 1-M-BEN	9 0	16000
96	C_2H_3 + 1-C_5H_{10}	→ C_2H_4 + 4-PEN	9 0	16000
97	$C_3H_5 + H_2$	→ $C_3H_6 + H$	9 9	7400
98	$C_3H_5 + CH_4$	→ $C_3H_6 + CH_3$	9 0	16000
99	$C_3H_5 + C_2H_6$	→ $C_3H_6 + C_2H_5$	9 0	16000
100	$C_3H_5 + C_3H_8$	→ C_3H_6 + 1-C_3H_7	9 0	18800
101	$C_3H_5 + C_3H_8$	→ C_3H_6 + 2-C_3H_7	8 9	16200
102	$C_3H_5 + C_4H_{10}$	→ C_3H_6 + 1-C_4H_9	8 6	18800
103	$C_3H_5 + C_4H_{10}$	→ C_3H_6 + 2-C_4H_9	8 9	16800
104	$C_3H_5 + C_6H_{14}$	→ C_3H_6 + 1-C_6H_{13}	8 6	18800
105	$C_3H_5 + C_6H_{14}$	→ C_3H_6 + 2-C_6H_{13}	8 9	16800
106	$C_3H_5 + C_6H_{14}$	→ C_3H_6 + 3-C_6H_{13}	8 9	16800
107	$C_3H_5 + C_2H_4$	→ $C_3H_6 + C_2H_3$	9 5	18000
108	$C_3H_5 + C_3H_6$	→ $C_3H_6 + C_3H_5$	9 0	14500
109	C_3H_5 + 1-C_4H_8	→ C_3H_6 + 1-M-AL	7 9	13500
110	C_3H_5 + 1-C_5H_{10}	→ C_3H_6 + 1-E-AL	9 0	10500
111	C_3H_5 + 1-C_5H_{10}	→ C_3H_6 + 1-M-BEN	9 0	13500
112	C_3H_5 + 1-C_5H_{10}	→ C_3H_6 + 4-PEN	9 0	13500
Addition				
113	$H + C_2H_4$	→ C_2H_5	10 6	1600
114	$H + C_3H_6$	→ 1-C_3H_7	9 9	2900
115	$H + C_3H_6$	→ 2-C_3H_7	9 9	1200
116	H + 1-C_4H_8	→ 1-C_4H_9	9 9	2000
117	H + 1-C_4H_8	→ 2-C_4H_9	9 9	500
118	H + 1-C_5H_{10}	→ 1-C_5H_{11}	9 9	2000
119	H + 1-C_5H_{10}	→ 2-C_5H_{11}	9 9	500
120	$H + C_2H_2$	→ C_2H_3	10 6	1300
121	$CH_3 + C_2H_4$	→ 1-C_3H_7	8 5	7800
122	$CH_3 + C_3H_6$	→ 2-C_4H_9	8 5	7400
123	$CH_3 + C_3H_6$	→ 1-C_4H_9	8 5	9100
124	CH_3 + 1-C_4H_8	→ 3-C_5H_{11}	8 3	7200
125	CH_3 + 1-C_4H_8	→ 2-M-B	8 3	9200
126	CH_3 + 1-C_5H_{10}	→ 3-C_6H_{13}	8 3	7200
127	CH_3-1-C_5H_{10}	→ 2-M-P	8 3	9100
128	$CH_3 + C_2H_2$	→ C_3H_5	7 4	7700
129	$C_2H_5 + C_2H_4$	→ 1-C_4H_9	7 33	7600
130	$C_2H_5 + C_3H_6$	→ 2-C_5H_{11}	7 1	7500
131	$C_2H_5 + C_3H_6$	→ 2-M-B	7 1	9200
132	C_2H_5 + 1-C_4H_8	→ 3-C_6H_{13}	7 1	7500
133	C_2H_5 + 1-C_4H_8	→ 2-E-B	7 1	9200
134	C_2H_5 + 1-C_5H_{10}	→ 4-C_7H_{15}	7 1	7500
135	C_2H_5 + 1-C_5H_{10}	→ 2-E-P	7 1	8300
136	$C_2H_5 + C_2H_2$	→ 1-M-AL	7 4	7000
137	1-$C_3H_7 + C_2H_4$	→ 1-C_5H_{11}	7 4	8000
138	1-$C_3H_7 + C_3H_6$	→ 2-C_6H_{13}	9 1	8600
139	$C_2H_3 + C_2H_4$	→ 3-BEN	7 0	8000
140	$C_2H_3 + C_3H_6$	→ 1-M-BEN	7 0	8000
141	C_2H_3 + 1-C_4H_8	→ 1-E-BEN	7 0	8000

(continued)

TABLE 1 (continued)

No	Reaction		$\log_{10} A$	E
142	$C_3H_5 + C_2H_4$	→ 4-PEN	7 7	8000
143	$C_3H_5 + C_3H_6$	→ 1-M-PEN	7 0	8000
Radical isomerization				
144	1-C_5H_{11}	→ 2-C_5H_{11}	11 0	20000
145	2-C_5H_{11}	→ 1-C_5H_{11}	11 1	22900
146	1-C_6H_{13}	→ 2-C_6H_{13}	11 0	13700
147	2-C_6H_{13}	→ 1-C_6H_{13}	11 1	16600
148	1-C_6H_{13}	→ 3-C_6H_{13}	11 0	20000
149	3-C_6H_{13}	→ 1-C_6H_{13}	11 1	22900
150	1-C_7H_{15}	→ 3-C_7H_{15}	9 2	11100
151	3-C_7H_{15}	→ 1-C_7H_{15}	11 1	22900
152	1-C_7H_{15}	→ 4-C_7H_{15}	11 1	20500
153	4-C_7H_{15}	→ 1-C_7H_{15}	11 1	22900
154	2-C_7H_{15}	→ 3-C_7H_{15}	11 1	13900
155	3-C_7H_{15}	→ 2-C_7H_{15}	11 2	16800
Decomposition				
156	C_2H_5	→ $H + C_2H_4$	13 9	41700
157	1-C_3H_7	→ $H + C_3H_6$	13 2	38000
158	1-C_3H_7	→ $CH_3 + C_2H_4$	13 2	32000
159	2-C_3H_7	→ $H + C_3H_6$	13 6	40300
160	1-C_4H_9	→ H + 1-C_4H_8	13 0	38000
161	1-C_4H_9	→ $C_2H_5 + C_2H_4$	13 6	29000
162	1-C_4H_9	→ $C_3H_6 + CH_3$	12 1	21700
163	2-C_4H_9	→ H + 1-C_4H_8	13 3	39800
164	2-C_4H_9	→ $CH_3 + C_3H_6$	13 4	31900
165	1-C_4H_9	→ H + 1-C_4H_8	13 7	36600
166	1-C_4H_9	→ $CH_3 + C_3H_6$	13 9	33000
167	1-C_5H_{11}	→ 1-$C_3H_7 + C_2H_4$	12 6	28700
168	2-C_5H_{11}	→ $C_2H_5 + C_3H_6$	12 6	27900
169	3-C_5H_{11}	→ CH_3 + 1-C_4H_8	13 5	31500
170	2-M-B	→ CH_3 + 1-C_4H_8	13 5	31500
171	2-M-B	→ $C_2H_5 + C_3H_6$	12 5	27900
172	1-C_6H_{13}	→ 1-$C_4H_9 + C_2H_4$	12 6	27900
173	2-C_6H_{13}	→ 1-$C_3H_7 + C_3H_6$	12 6	27900
174	3-C_6H_{13}	→ C_2H_5 + 1-C_4H_8	12 6	27900
175	3-C_6H_{13}	→ CH_3 + 1-C_5H_{10}	13 4	31500
176	2-M-P	→ 1-$C_3H_7 + C_3H_6$	12 5	27900
177	2-E-B	→ C_2H_5 + 1-C_4H_8	12 5	27900
178	1-C_7H_{15}	→ 1-$C_5H_{11} + C_2H_4$	13 6	29100
179	2-C_7H_{15}	→ C_3H_6 + 1-C_4H_9	13 1	28000
180	3-C_7H_{15}	→ CH_3 + 1-C_6H_{12}	13 8	33500
181	3-C_7H_{15}	→ 1-C_3H_7 + 1-C_4H_8	12 5	29500
182	4-C_7H_{15}	→ C_2H_5 + 1-C_5H_{10}	12 5	27900
183	2-E-P	→ C_2H_5 + 1-C_5H_{10}	12 5	27900
184	2-E-P	→ 1-C_3H_7 + 1-C_4H_8	12 5	27900
185	C_2H_3	→ $H + C_2H_2$	9 0	31500
186	C_3H_5	→ $CH_3 + C_2H_2$	10 5	36200
187	1-M-AL	→ $H + C_4H_6$	14 8	49300
188	1-M-AL	→ $C_2H_3 + C_2H_4$	13 7	38000

TABLE 1 (continued)

No	Reaction		$\log_{10} A$	E
189	3-BEN	$\rightarrow C_2H_3 + C_2H_4$	13 0	34000
190	1-E-AL	$\rightarrow CH_3 + C_4H_6$	13 0	32000
191	1-M-BEN	$\rightarrow C_2H_3 + C_3H_6$	13 0	34000
192	4-PEN	$\rightarrow C_3H_5 + C_2H_4$	13 0	34000
193	1-M-PEN	$\rightarrow C_3H_5 + C_3H_6$	13 5	26000
194	1-E-BEN	$\rightarrow CH_3 + C_5H_8$	13 0	34000
Termination				
195	$H + H$	$\rightarrow H_2$	9 0	0 0
196	$H + C_2H_3$	$\rightarrow C_2H_4$	10 0	0 0
197	$H + C_3H_5$	$\rightarrow C_3H_6$	10 3	0 0
198	$CH_3 + CH_3$	$\rightarrow C_2H_6$	10 7	0 0
199	$CH_3 + C_2H_5$	$\rightarrow C_3H_8$	10 5	0 0
200	$CH_3 + C_2H_3$	$\rightarrow C_3H_6$	10 0	0 0
201	$CH_3 + C_3H_5$	$\rightarrow 1\text{-}C_4H_8$	10 3	0 0
202	$C_2H_5 + C_2H_5$	$\rightarrow C_4H_{10}$	9 6	0 0
203	$C_2H_5 + C_2H_3$	$\rightarrow 1\text{-}C_4H_8$	9 0	0 0
204	$C_2H_5 + C_3H_5$	$\rightarrow 1\text{-}C_5H_{10}$	9 5	0 0
205	C_2H_5 + 1-E-AL	→ TAR	9 0	0 0
206	$1\text{-}C_3H_7 + 1\text{-}C_3H_7$	$\rightarrow C_6H_{14}$	9 5	0 0
207	$C_2H_3 + C_2H_3$	$\rightarrow C_4H_6$	10 1	0 0
208	$C_2H_3 + C_3H_5$	$\rightarrow C_5H_8$	9 0	0 0
209	C_2H_3 + 1-M-AL	$\rightarrow C_6H_{10}$	9 0	0 0
210	$C_2H_3 + C_3H_5$	$\rightarrow C_6H_{10}$	9 5	0 0
211	C_3H_5 + 1-M-AL	→ TAR	8 5	0 0
212	C_3H_5 + 1-E-AL	→ TAR	8 5	0 0
213	1-M-AL + 1-M-AL	→ TAR	8 5	0 0
214	1-M-AL + 1-E-AL	→ TAR	8 5	0 0
215	1-E-AL + 1-E-AL	→ TAR	8 5	0 0
Disproportionation				
216	$CH_3 + C_2H_5$	$\rightarrow CH_4 + C_2H_4$	8 4	0 0
217	$CH_3 + C_2H_3$	$\rightarrow CH_4 + C_2H_2$	9 0	0 0
218	$CH_3 + C_3H_5$	$\rightarrow CH_4 + C_3H_4$	9 0	0 0
219	CH_3 + 1-M-AL	$\rightarrow CH_4 + C_4H_6$	9 9	0 0
220	$C_2H_5 + C_2H_5$	$\rightarrow C_2H_6 + C_2H_4$	7 7	0 0
221	$C_2H_5 + C_2H_3$	$\rightarrow C_2H_6 + C_2H_2$	8 0	0 0
222	$C_2H_5 + C_2H_3$	$\rightarrow C_2H_6 + C_2H_4$	8 5	0 0
223	$C_2H_5 + C_3H_5$	$\rightarrow C_2H_6 + C_3H_4$	8 6	0 0
224	$C_2H_5 + C_3H_5$	$\rightarrow C_2H_6 + C_3H_6$	8 6	0 0
225	C_2H_5 + 1-M-AL	$\rightarrow C_2H_6 + C_4H_6$	9 1	0 0
226	C_2H_5 + 1-M-AL	$\rightarrow C_2H_4 + 1\text{-}C_4H_8$	8 5	0 0
227	$C_2H_3 + C_2H_3$	$\rightarrow C_2H_4 + C_2H_2$	9 5	0 0
228	$C_2H_3 + C_3H_5$	$\rightarrow C_2H_4 + C_3H_4$	9 0	0 0
229	C_2H_3 + 1-M-AL	$\rightarrow C_2H_4 + C_4H_6$	9 0	0 0
230	$C_3H_5 + C_3H_5$	$\rightarrow C_3H_6 + C_3H_4$	9 5	0 0
231	C_3H_5 + 1-M-AL	$\rightarrow C_3H_6 + C_4H_6$	9 8	0 0
232	C_3H_5 + 1-M-AL	$\rightarrow C_3H_4 + 1\text{-}C_4H_8$	9 0	0 0
233	1-M-AL + 1-M-AL	$\rightarrow C_4H_6 + 1\text{-}C_4H_8$	9 5	0 0

(continued)

TABLE 1 (continued)

No	Reaction		$\log_{10} A$	E
Aromatization				
234	$C_4H_6 + C_2H_4$	$\rightarrow$ CH	7 5	27500
235	$C_4H_6 + C_3H_6$	$\rightarrow$ MCH	7 8	27500
236	$C_4H_6 + 1\text{-}C_4H_8$	$\rightarrow$ ECH	7 4	30000
237	$C_4H_6 + C_4H_6$	$\rightarrow$ VCH	7 4	26800
238	CH	$\rightarrow H_2 +$ CHD	11 5	50900
239	MCH	$\rightarrow H_2 +$ MCHD	10 5	49500
240	MCH	$\rightarrow CH_4 +$ CHD	13 6	61100
241	ECH	$\rightarrow H_2 +$ ECHD	10 5	49500
242	VCH	$\rightarrow H_2 +$ VCHD	10 6	48400
243	CHD	$\rightarrow H_2 +$ benzene	12 0	42500
244	MCHD	$\rightarrow H_2 +$ toluene	12 5	43000
245	ECHD	$\rightarrow H_2 +$ E-benzene	12 5	43000
246	VCHD	$\rightarrow H_2 +$ styrene	12 0	43000

Nomenclature

Symbol	Name
1-M-AL	1-Methyl-allyl
3-BEN	3-Butenyl
1-E-AL	1-Ethyl-allyl
1-M-BEN	1-Methyl-3-butenyl
4-PEN	4-Pentenyl
2-M-B	2-Methyl-3-butenyl
2-M-P	2-Methyl-4-pentenyl
2-E-B	2-Ethyl-3-butenyl
2-E-P	2-Ethyl-4-pentenyl
1-E-BEN	1-Ethyl-3-butenyl
1-M-PEN	1-Methyl-4-pentenyl
CH	Cyclohexene
MCH	Methylcyclohexene
ECH	Ethylcyclohexene
VCH	Vinylcyclohexene
CHD	Cyclohexadiene
MCHD	Methylcyclohexadiene
ECHD	Ethylcyclohexadiene
VCHD	Vinylcyclohexadiene

radical reactions of n-alkanes are now available in the literature [7,9,13–15] Kunugi et al [22] also tabulated rate constants of free radical reactions of olefins However, many of these parameters were compiled at low temperatures Sundaram and Froment [9], on the other hand, listed the rate parameters of the pyrolysis reactions of light hydrocarbons (C_2–C_4 alkanes) at high conversions Rate parameters of ER not available in the literature can be estimated on the basis of the general methods proposed by Benson [23], some of the listed parameters used in the present work were estimated Furthermore, it is possible to estimate rate parameters by trial and error [24] The present authors had applied a non-linear regression technique in optimizing the rate parameters of molecular reactions in modeling cyclohexane pyrolysis [25], however, this method cannot be used here in view of the large number of ER being considered Also, some of these rate parameters considered were modified within reasonable limits

SIMULATION

In simulating the proposed mechanistic model, the system of ordinary differential equations (ODEs) are numerically integrated, the ODEs are the continuity equations of the species (radical and molecular) participating in the pyrolysis reactions and are given by

$$\frac{dC_i}{dt} = \sum_{j=1}^{N} S_{ij} r_j \qquad i = 1, 2, 3, \quad , M \tag{1}$$

where

$$r_j = k_j \prod_{i=1}^{M} C_i^{-S_{ij}} - k_j' \prod_{i=1}^{M} C_i^{S_{ij}} \tag{2}$$

and $S_{ij} < 0$ for reactants, $S_{ij} > 0$ for products

The ODEs generated for mechanistic models are non-linear and are also "stiff" as a result of the wide disparity between the concentrations of molecular and radical species (10^{-2} and 10^{-10} M, respectively) Considering the large number of ER in the proposed model, the formulation of eqns (1) and (2) was performed using a "chemical compiler", this was necessary to avoid inaccurate modeling of the hydrocarbon pyrolysis reactions

Numerous techniques are available in the literature for the numerical integration of stiff ODEs [26–29], Gear's DIFSUB [26] and Deuflhard and coworkers' "LARKIN" [27] stand out as the best The latter program package was used in the present work because its chemical compiler can generate all pertinent information (eqns (1) and (2)) together with the associated Jacobian matrix necessary for simulation In order to forestall the complex mathematics often encountered in the numerical integration of set of stiff ODEs, some workers [5,8,30] have applied the QSSA (quasi steady state assumption) to the radical species This method converts the ODEs representing radicals to algebraic equations (eqn (3)) which are then solved simultaneously with the remaining ODEs (of molecular species)

$$\frac{dC_i}{dt} = \sum_{j=1}^{N} S_{ij} r_j = 0 \tag{3}$$

Though the QSSA approach has been questioned by some authors [9,33], Edelson and Allara [33] reported a "surprising" agreement of the results predicted by Gear's method [26] and Snow's QSSA approach [30] Dente et al [32] and Come [31,34] have supplied detailed outlines on techniques that could be used in solving sets of stiff ODEs, these techniques involve the use of PSSA (pseudo steady state assumption) approach Dente et al [32] explained further that the PSSA approach can be used for actual calculations, but that the main problem in its applications, is to have a suitable method to solve the resulting algebraic non-linear equations for radical concentrations

The PSSA approach was not applied in the present study, instead a complete simultaneous numerical integration of the system of ODEs was carried out

RESULTS AND DISCUSSION

The proposed mechanistic model comprising 246 ER (Table 1) was simulated on an IBM 370/168 computer Table 2 shows the comparison of experimental and simulated product distributions, the major product distributions showed fairly good agreements

TABLE 2

Comparison of experimental and simulated product distributions (mol %)

	τ = 0 8 s		τ = 0 9 s		τ = 1 00 s	
	Exp	Sim	Exp	Sim	Exp	Sim
740 °C						
CH_4	9 55	18 03	10 07	18 67	14 17	19 25
C_2H_4	30 44	51 64	35 26	50 70	36 78	49 72
C_3H_6	9 86	4 30	9 95	4 10	9 85	3 91
$1\text{-}C_4H_8$	1 60	0 68	2 85	0 60	0 89	0 55
$1,3\text{-}C_4H_6$	2 40	2 00	3 20	1 96	1 59	1 93
760 °C						
CH_4	12 99	19 40	15 48	20 07	18 72	20 66
C_2H_4	38 36	48 55	40 30	46 95	39 24	45 40
C_3H_6	8 90	2 94	8 74	2 70	9 29	2 47
$1\text{-}C_4H_8$	0 89	0 33	1 12	0 29	0 94	0 26
$1,3\text{-}C_4H_6$	1 51	1 67	1 83	1 65	2 15	1 61
	τ = 0 7 s		τ = 0 8 s		τ = 0 9 s	
780 °C						
CH_4	12 11	19 86	19 16	20 54	20 04	21 12
C_2H_4	35 86	46 21	39 37	44 31	40 19	42 71
C_3H_6	8 57	1 95	7 53	1 70	8 02	1 50
$1\text{-}C_4H_8$	0 82	0 20	0 42	0 15	1 16	0 13
$1,3\text{-}C_4H_6$	2 22	1 37	1 51	1 28	1 92	1 18

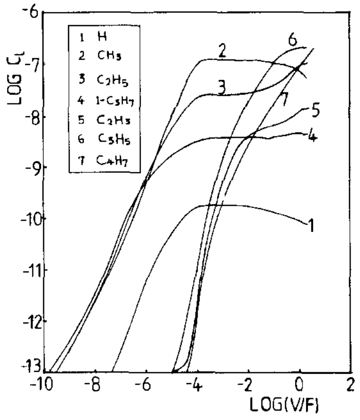


Fig 1 Simulated radical concentrations in n-heptane pyrolysis at 700 ° C

Figures 1–3 show the variations of the radical concentrations with reaction time $CH_3^\cdot$, $C_2H_5^\cdot$, $C_3H_5^\cdot$ and $C_4H_7^\cdot$ predominate in n-heptane pyrolysis The initial rapid increase in the concentrations of $H^\cdot$, $CH_3^\cdot$, $C_2H_5^\cdot$ and $1\text{-}C_3H_7^\cdot$ with reaction time is due to the initiation reactions of n-heptane Also, $C_3H_5^\cdot$, $C_4H_7^\cdot$ and $C_2H_3^\cdot$ appear in the pyrolysis system much later than other radicals, their appearance marks the onset of secondary reactions of the primary products and hence of inhibition and self-inhibition in the pyrolysis of n-heptane Some of the key reactions responsible for inhibitions

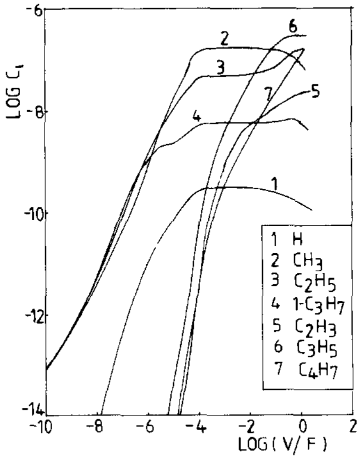


Fig 2 Simulated radical concentrations in n-heptane pyrolysis at 720 ° C

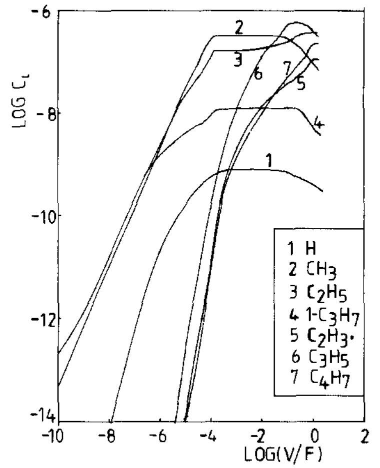


Fig 3 Simulated radical concentrations in n-heptane pyrolysis at 760 °C

are the H-abstractions from primary olefinic products (C_3H_6, 1-C_4H_8, etc) by light reactive radicals to form relatively more stable allylic radicals

$$R^{\bullet} + C_3H_6 \rightarrow RH + C_3H_5^{\bullet}$$

$$R^{\bullet} + 1\text{-}C_4H_8 \rightarrow RH + C_4H_7^{\bullet}$$

$$(R^{\bullet} = H^{\bullet}, CH_3^{\bullet}, C_2H_5^{\bullet})$$

Furthermore, it is clear (Figs 1–3) that radical concentrations in hydrocarbon pyrolysis never really attain true steady states However, a few radicals ($H^{\bullet}$, $CH_3^{\bullet}$, $C_2H_5^{\bullet}$ and 1-$C_3H_7^{\bullet}$) appear to go into steady states during part of the reaction time regime, immediately after the initial rapid increase in their concentrations Consequently, the PSSA approach is not appropriate, the availability of fast computers and highly efficient numerical techniques for handling stiff ODEs makes its use unnecessary Hindmarsh's [36] "GEARS" and Deuflhard and coworkers' [27] "LARKIN" are two of the currently available program packages that contain very fast stiff integrators which are very well suited for handling stiff ODEs arising from complex chemical reaction systems.

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