Thermodynamic Analysis of Coking in the Steam Reforming of Hydrocarbons

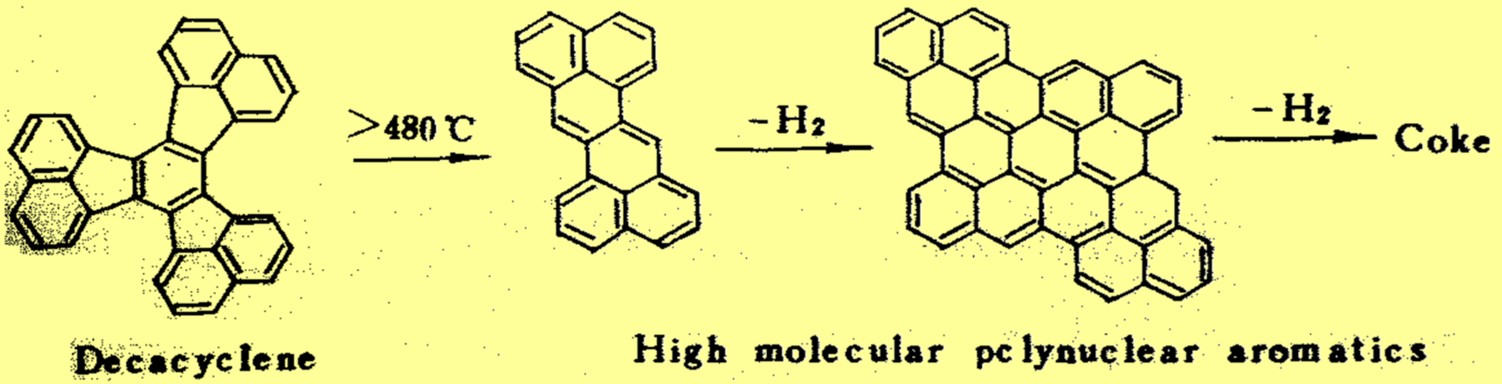
Ju Ho Lee and Chul Soo Lee
Dept. of Chemical Engineering
Korea University

Coke formation in steam reforming and steam cracking

1. The high-temperature pyrolysis of HC
   Acetylenic intermediate stage

$CH2{=}CH2 \rightarrow CH2{=}CH \rightarrow CH{\equiv}CH \rightarrow CH{\equiv}C \rightarrow C{\equiv}C \rightarrow C_n$

2. Aromatics intermediate stage(Low T)



Suppression of Coke Deposition

Effect of Carbon Deposition

- Pressure drop in the coil
- Corrosion of the coil

Method of suppression of Coke deposition

- By diluent or gasifying agents(He, H_2, CO,steam)
- By Changing surface conditions of coil
- By Additives like Sulfur, Phosphate

Gasification of coke mechanism

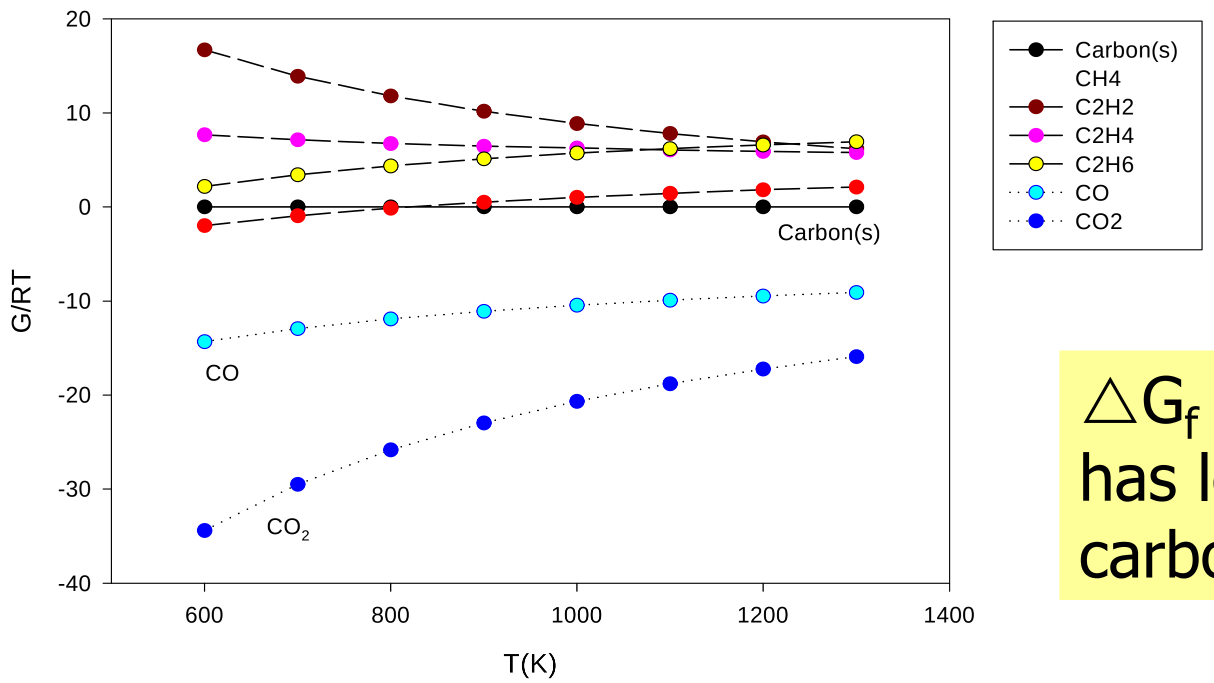
$$C + H_2O = CO + H_2$$
$$CO + H_2O = CO_2 + H_2$$
$$C + CO_2 = 2CO$$
$$C + 2H_2 = CH_4$$

Thermodynamics and Properties Lab.

Korea University

Why steam is used in reforming and cracking process for gasification ?

Gibbs Energy of components in pyrolysis



$\triangle G_f$ of CO and CO_2 has lower value than carbon(graphite)

Critical Steam Ratio

- At equilibrium states,

  There is steam/feed ratio which makes no carbon deposition in process

- Critical steam ratio

  Steam/feed ratio which which makes no carbon deposition in process

The Equilibrium Model

- **Minimization of the total Gibbs energy**

$(dG_{system})_{T,P} = 0$

$G_{system} = \sum n_j G_j$

$G_j = G_j^o + RT\ln(a_j)$

for ideal gas phase. $a_j = y_i P$

for solid phase(C), $a_j = 1$

- **Minimization routine : DLCONF(IMSL)**

Species

- **Feed : CH_4,C_2H_6,C_3H_8,C_4H_{10},C_5H_{12}**
- **Product :**

H_2O, H_2, CO_2, CO, C(s)

CH_4,C_2H_2,C_2H_4,C_2H_6,C_3H_4,C_3H_6,C_3H_8(For CH_4)

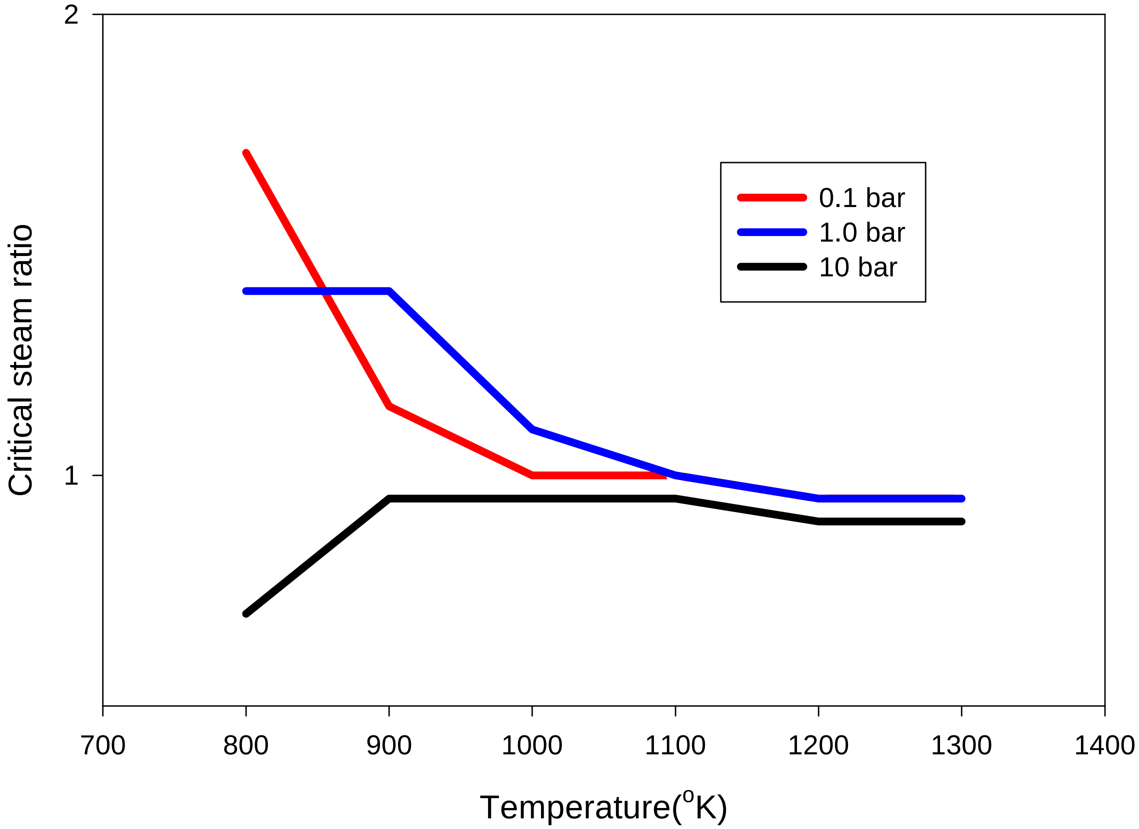
C_4H_6,C_4H_8,C_4H_{10},C_6H_6 (For higher alkane)

- **Calculation Conditions:**

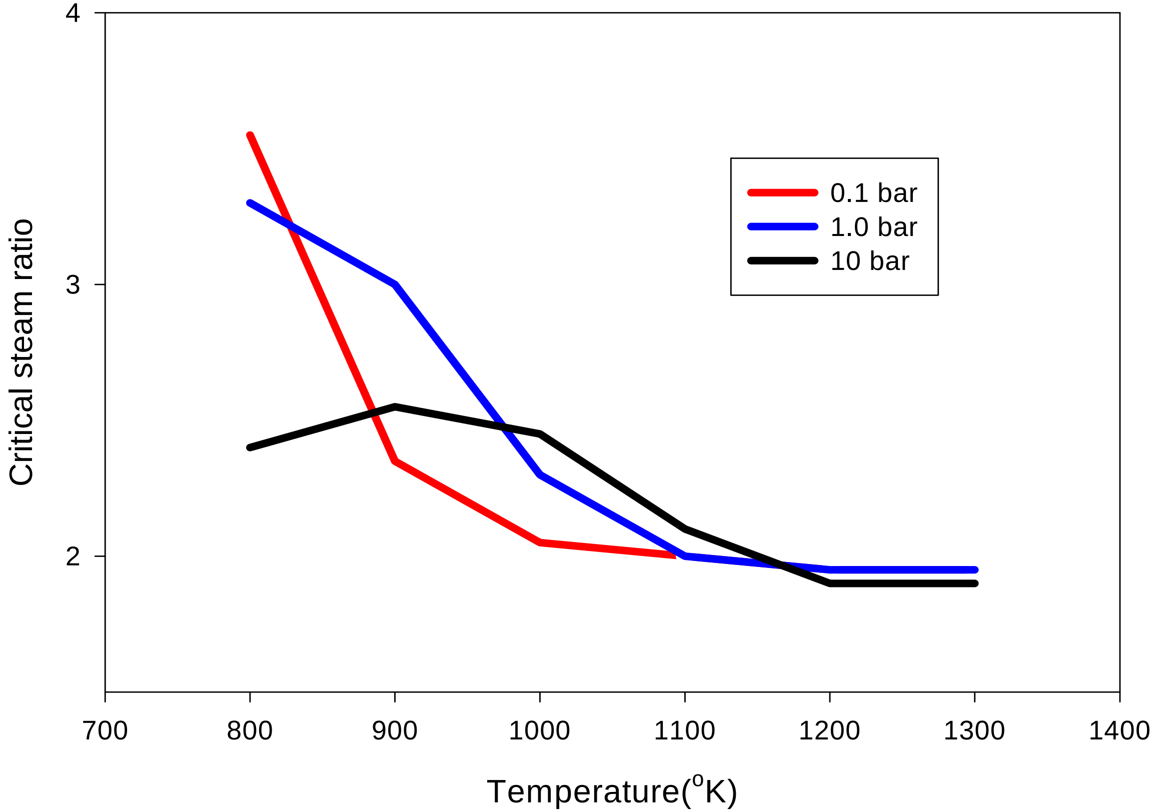
T = 800~1300

P = 0.1, 1, 10bar

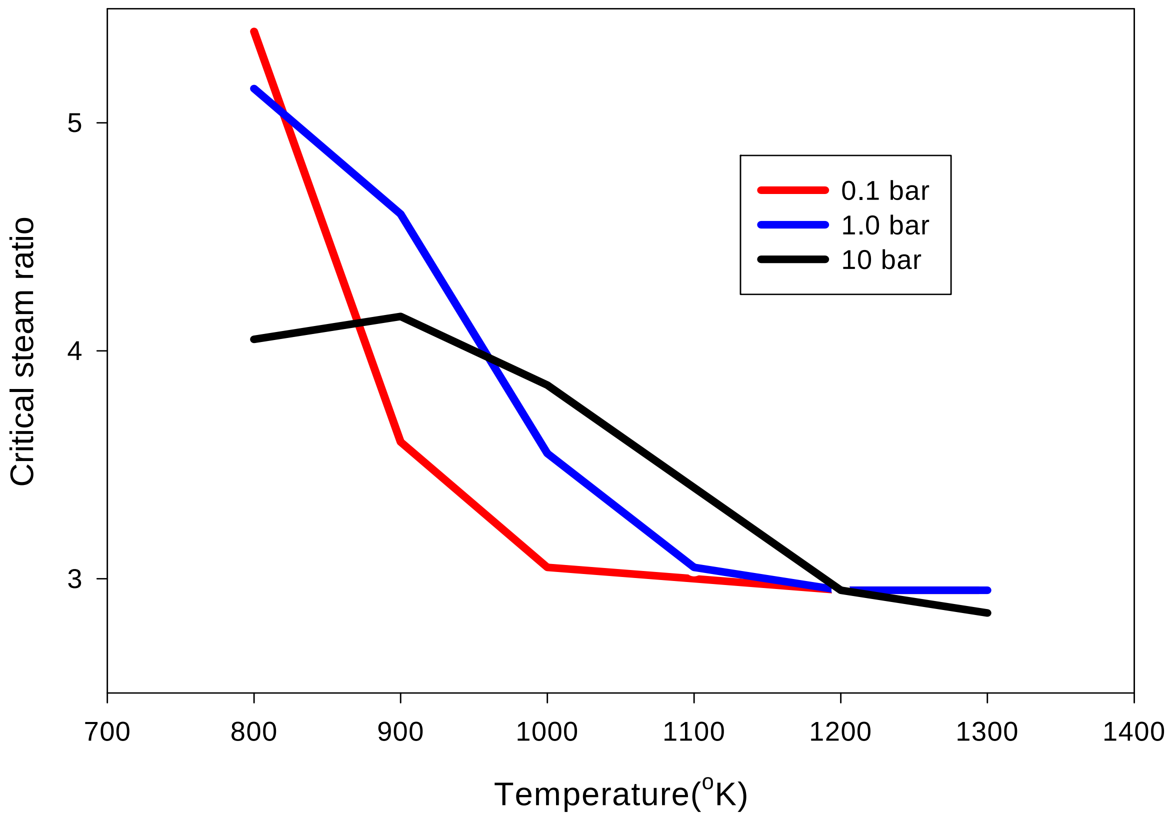
❑ Methane


2
1
Critical steam ratio
0.1 bar
1.0 bar
10 bar
700
800
900
1000
1100
1200
1300
1400
Temperature(°K)

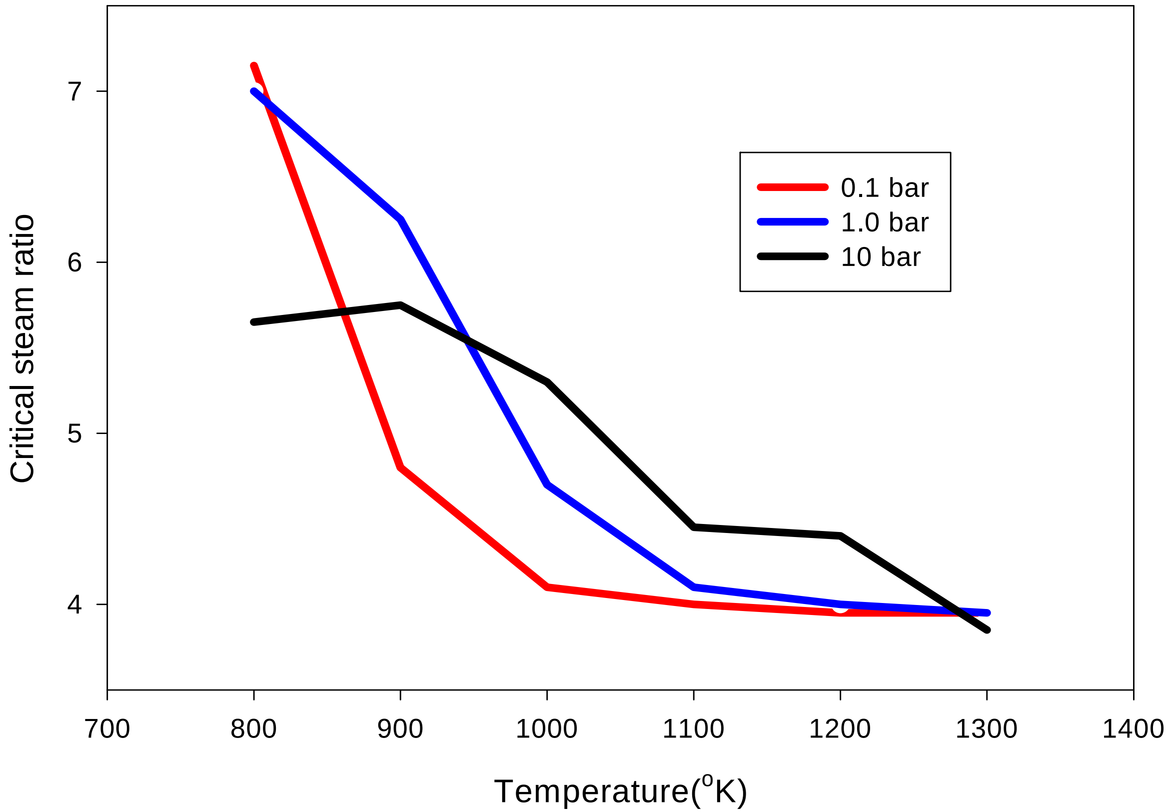
Ethane


4
3
2
Critical steam ratio
700
800
900
1000
1100
1200
1300
1400
Temperature(°K)
0.1 bar
1.0 bar
10 bar

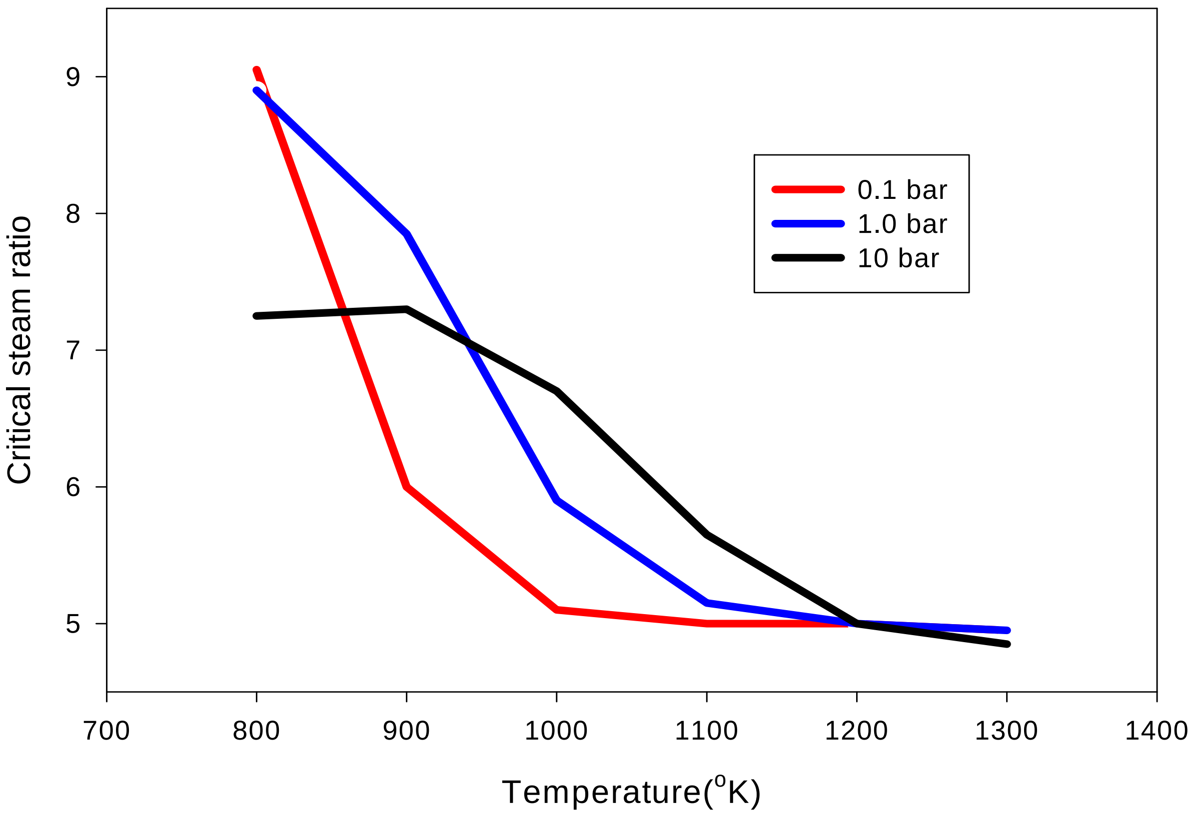
Propane


Critical steam ratio
Temperature(°K)
0.1 bar
1.0 bar
10 bar
3
4
5
700
800
900
1000
1100
1200
1300
1400

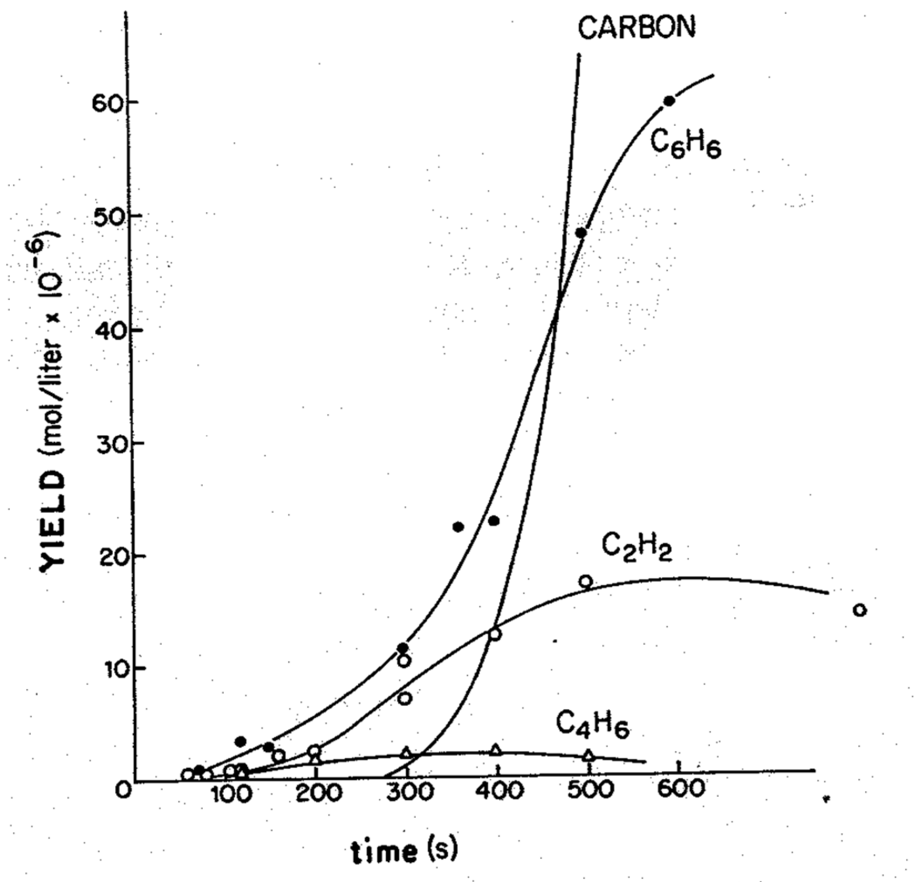
Butane


0.1 bar
1.0 bar
10 bar
Critical steam ratio
7
6
5
4
700
800
900
1000
1100
1200
1300
1400
Temperature(oK)

Pentane


0.1 bar
1.0 bar
10 bar
Critical steam ratio
9
8
7
6
5
700
800
900
1000
1100
1200
1300
1400
Temperature(°K)

How this result be used in cracking process?

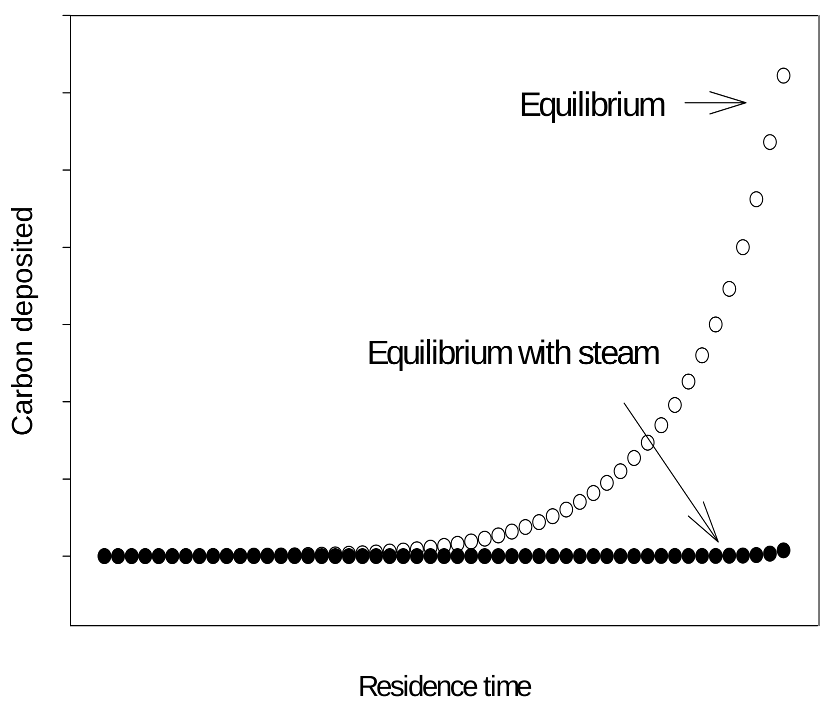


At equilibrium conditions, (High residence time) The amount of carbon deposited has maximum value

Yields of later products from the pyrolysis of methane in static system at 1181°C and 307 torr(Chen and Back, 1979)

How this result be used in cracking process?

Effect of steam to Coke deposition



By reducing the coke in equilibrium state, the coke in the entire reactor length would not be precipitated

Steam reforming is regarded as the state of steam cracking when residence time prolongs

The Kinetic Model

Reaction Model – Ethane Pyrolysis

Radical mechanisms of Sundaram and Froment(1978)

22 species and 49 radical reactions

→ 17 species and 28 radical reactions

Coke formation Model

$C_2H_2 \rightarrow 2C(s) + H_2$ (Sundaram and Froment(1978))

Caron-steam reaction Model

$C(s) + 2H_2O(g) \rightarrow CO_2 + 2H_2$

Simulation results.

T_{inlet}=900K

P_{inlet}=304kPa

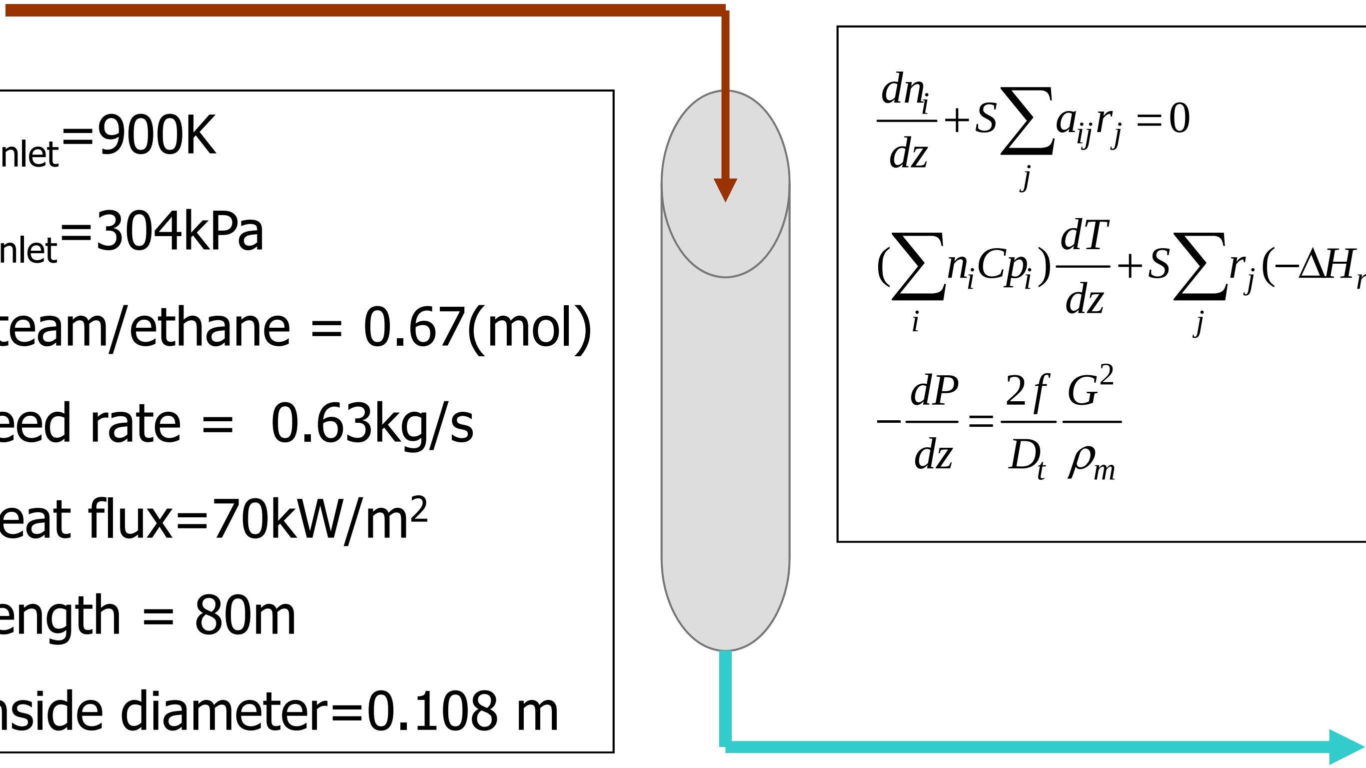
Steam/ethane = 0.67(mol)

Feed rate = 0.63kg/s

Heat flux=70kW/m^2

Length = 80m

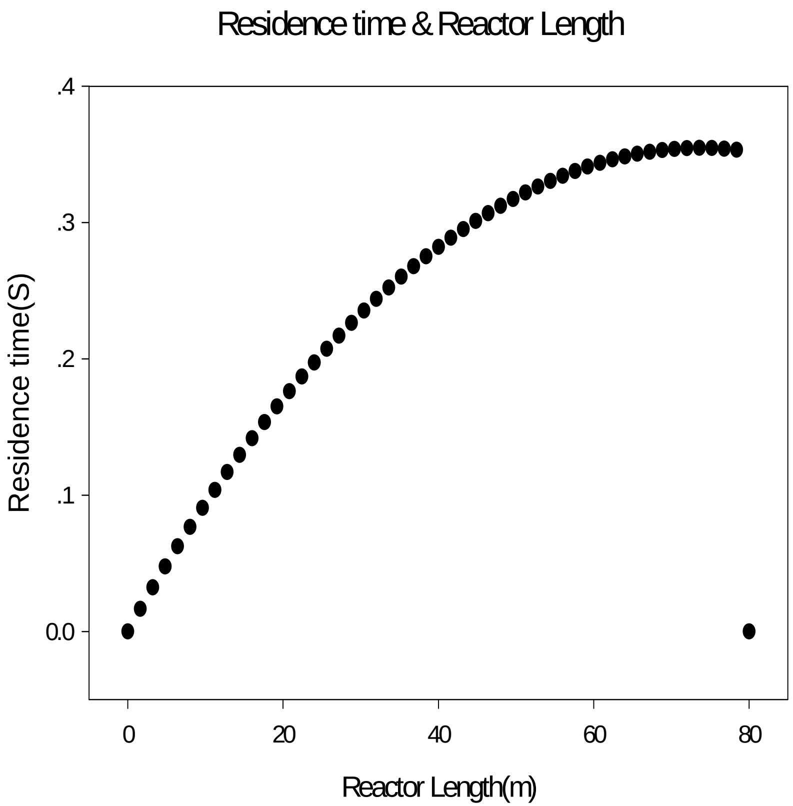
Inside diameter=0.108 m

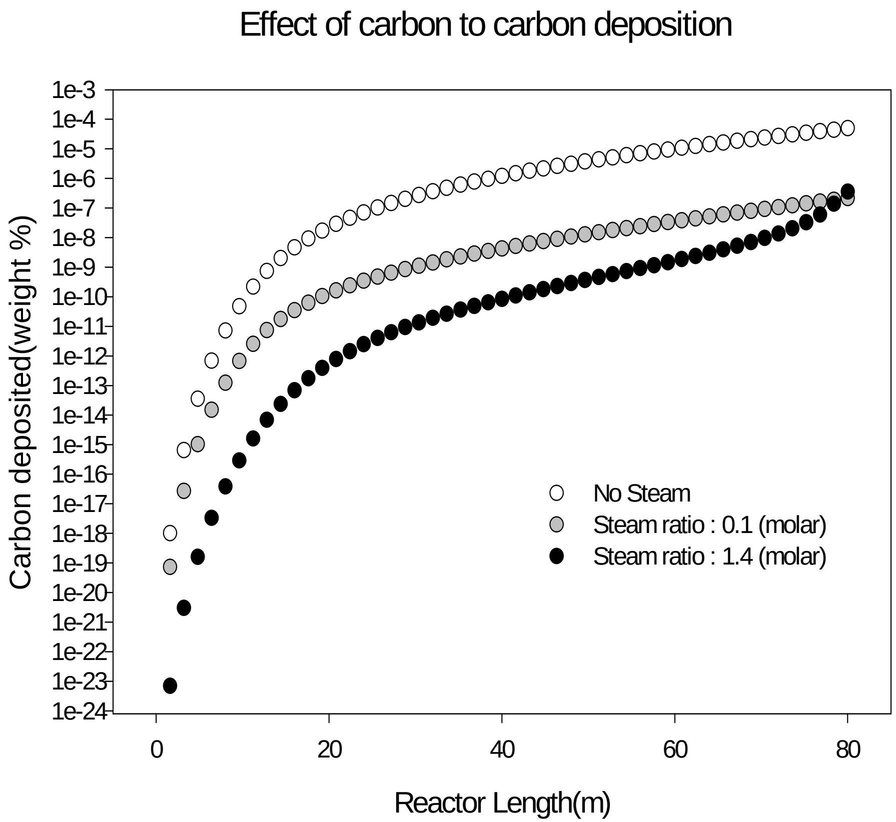


$$\frac{dn_i}{dz} + S\sum_j a_{ij} r_j = 0$$

$$(\sum_i n_i Cp_i)\frac{dT}{dz} + S\sum_j r_j(-\Delta H_r)_j - Q(z)\pi D_t = 0$$

$$-\frac{dP}{dz} = \frac{2f}{D_t}\frac{G^2}{\rho_m}$$


Residence time & Reactor Length
Residence time(S)
.4
.3
.2
.1
0.0
0
20
40
60
80
Reactor Length(m)


Effect of carbon to carbon deposition
Carbon deposited(weight %)
1e-3
1e-4
1e-5
1e-6
1e-7
1e-8
1e-9
1e-10
1e-11
1e-12
1e-13
1e-14
1e-15
1e-16
1e-17
1e-18
1e-19
1e-20
1e-21
1e-22
1e-23
1e-24
0
20
40
60
80
Reactor Length(m)
No Steam
Steam ratio : 0.1 (molar)
Steam ratio : 1.4 (molar)

Conclusion

- Coking in steam-reforming reactions was studied to find the critical steam ratio above which coking does not occur as a function of temperature and pressure at the reaction equilibrium. And this results is shown to used for carbon-free deposition conditions of steam cracking process
- The critical steam ratio is strongly dependent on pressure at lower temperatures.
- By simulation based on kinetic modeling, deposited carbon is affected by steam ratio to HC