

Effect of Steam on Coking in the Non-catalytic Pyrolysis of Naphtha Components

Ju Ho Lee, Kwan Moon Kim, Sung Hyun Kim and Chul Soo Lee*

Department of Chemical and Biological Engineering, Korea University, 5-Ga Anam-Dong, Sungbuk-Ku, Seoul 136-701, Korea
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Abstract—Coking has presented difficulties in reactions including pyrolysis and steam has been added to reduce coking. In this study, the effect of steam on coking in the pyrolysis of naphtha components was studied thermodynamically and experimentally for non-catalytic tubular reactor systems. The qualitative relations between these two thermodynamic and experimental studies were established. In both studies coking was reduced as the steam ratio increased. However, experimental studies indicated that the reduction was more effective for smaller values of the ratio, leading to an effective ratio of about 0.5, and that weak coking still occurred for the ratio greater than the thermodynamic zero-coke ratio.

Key words: Coking, Reaction Equilibrium, Naphtha, Steam

INTRODUCTION

The deposition of carbonaceous materials on reactor walls, or coking, has presented difficulties in hydrocarbon processing. Coking reduces the effective volume of reactor and heat transfer from or to walls. It is also known to induce corrosion of reactor walls [Tsai and Albright, 1983] and to deactivate catalysts [Song and Ihm, 2003]. Various measures have been taken to prevent or to reduce coking, or periodic decoking of reactor walls was needed. Steam is reported to react with graphite by diffusion to coke layer and reaction to produce carbon monoxide, carbon dioxide and hydrogen [Riede and Hanesian, 1975]. In real processes steam is charged into pyrolysis reactors with raw materials [Van Damme et al., 1975].

Typical naphtha is a mixture of normal and iso-paraffins, naphthenes and aromatics, in which c5 and c6 paraffin compounds dominate as shown in Table 1. Ethylene, propylene, butane, butylene and aromatics are produced in the pyrolysis of naphtha. Olefins and diolefins produced in the pyrolysis are known to act as precursors to

coke [Albright and Marek, 1988; Poutsma, 1988]. At temperatures 900-1,000 °C precursors are transformed to acetylene by dehydrogenation, to poly-acetylene by polymerization and then to coke by dehydrogenation [Zou Renjun, 1993]. In another pathway, precursors are transformed to mononuclear aromatics by cyclization, to poly-aromatics, and then to coke by dehydrogenation and condensation [Trimm, 1983]. Coke is not pure graphite but contains varying amounts of hydrogen [Trimm, 1983].

Cokes produced in these mechanisms are of two structures: amorphous and filamentous [Albert and John, 1982; Crynes and Crynes, 1987]. Amorphous structure is believed to form by deposition of tar-like products on the reactor wall and the subsequent dehydrogenation. Thus, a relatively large amount of hydrogen is expected to remain in the structure [Valerio, 1997]. Catalytic effects of metal particles in gas phase produce filamentous structure. This process is expected to continue until the metal particles are completely covered by coke [Baker and Yates, 1982]. Kinetics of cracking was simulated for a quasi-steady state process of the coke deposition from gas phase to reactor walls [Sundaram and Froment, 1979; Sundaram et al., 1981]. The studies showed that the carbon concentration, and coking per reactor volume, increased along a tubular reactor. By assuming carbon-steam reaction in the propane pyrolysis simulation, it is shown that steam could reduce the amount of coke deposited [Sundaram and Froment, 1979]. Since reaction equilibrium is approached as the reaction mixture proceeds to the exit, the thermodynamic analysis on the effect of steam in coking is expected to give some insights for preventing coking.

In this study two major components of naphtha, n-pentane and n-hexane, were selected and effects of steam on coking were studied experimentally. Methane, ethane, propane, butane and pentane were selected for thermodynamic analysis to determine the steam ratio above which coking can be prevented. By comparing both results, the relations are to be studied.

Table 1. Composition of a typical naphtha

Composition (wt%)	n-Paraffin	i-Paraffin	Naphthene	Aromatics
C4	1-3	0.5-0.7	0	0
C5	16-20	12-16	1-1.5	0
C6	11-12	11-13	5-7	1.2-2.0
C7	4-6	5-6	5-8	1.2-2.0
C8	1-2	2-3		0.5-2.0
C9	0.5-1.5	1-1.5		0.2-1.0
C10	0.2-0.5	0.5-0.7		0.1
Final boiling point (°C)	140-160			
Total sulfur (wt. ppm)	200-500			

*To whom correspondence should be addressed.

E-mail: cslee@korea.ac.kr

*This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

EQUILIBRIUM CONSIDERATIONS

Desirable conditions for hydrocarbon pyrolysis are optimized for conversion and the yield of valuable products. Hydrocarbon py-

rolysis reactions generally do not go to completion to maximize the ethylene yield, but the exit condition can be close to equilibrium states if the residence time of the reaction mixture is sufficient. If coke produced per volume increases along the reactor, then the coke concentration will be the maximum at the reactor exit. This behavior is shown in the pyrolysis simulation of Froment and Sundaram [Sundaram and Froment, 1979]. In some pyrolysis studies, steam is regarded as an inert diluent in spite of gasifying reaction of carbon deposited in the reaction [Goossens and Ranzi, 1970]. Standard reaction Gibbs free energy from graphite to carbon monoxide or dioxide is negative in reactions with water and the products are favored in the reaction. Thus water can participate in converting carbon to gaseous components. If there is a steam to hydrocarbon ratio at which coke deposition stops, the use of more steam will result in no coking.

Given the initial composition of reactants, the global minimization of the total Gibbs free energy at a temperature and pressure yields the equilibrium composition. This method is well documented [Smith and Missen, 1982] and has been applied for the computation of methane pyrolysis [Gueret et al., 1997; Rokstad et al., 1992].

$$G^{Total} = \sum_{gas} n_i G_i + \sum_{condensed} n_i G_i$$

$$= \sum_{gas} n_i \left(\Delta G_{f,i}^o + RT \ln \left(\frac{f_i}{P^o} \right) \right) + \sum_{condensed} n_i \Delta G_{f,i}^o$$

where $\Delta G_{f,i}^o$ denotes the free energy of formation of component i at the standard pressure. We also assumed that carbon is graphite, exists as condensed phase and the pressure is low. Furthermore, the gas phase may be assumed ideal at high reaction temperatures. Then for a component in condensed phase [Koh et al., 2001],

$$\Delta G_{f,i}^o = 0$$

for a component in gas phase,

$$f_i = y_i P$$

The required information is the Gibbs free energy of formation that is obtained from Barin [Barin and Plazki, 1995], Reid et al. [1988] and NIST's web site. The species present in the reacting mixture are selected from the literature and kinetic study [Back and Back, 1983; Sundaram and Froment, 1978] and listed in Table 2. The radicals higher than C4 are not considered in the present calculation since they are isomerized and directly decomposed in pyrolysis [Ranzi, 1982]. By extrapolating the calculated amount of coke versus the initial amount of steam to the zero-coke condition the zero-coke steam ratio can be obtained as shown in Fig. 1.

EXPERIMENTAL

Table 2. Components present in reacting mixtures

Feed	Present components
CH ₄	H, CH ₃ , CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₄ , C ₃ H ₆ , C ₃ H ₈ , C ₄ H ₆ , C ₄ H ₈ , C ₆ H ₆ , H ₂ O, CO ₂ , CO, C
C ₂ H ₆	H, CH ₃ , CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₄ , C ₃ H ₆ , C ₃ H ₈ , C ₄ H ₆ , C ₄ H ₈ , C ₆ H ₆ , H ₂ O, CO ₂ , CO, C
C ₃ H ₈	H, CH ₃ , CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₄ , C ₃ H ₆ , C ₃ H ₈ , C ₄ H ₆ , C ₄ H ₈ , C ₆ H ₆ , H ₂ O, CO ₂ , CO, C
C ₄ H ₁₀	H, CH ₃ , CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₄ , C ₃ H ₆ , C ₃ H ₈ , C ₄ H ₆ , C ₄ H ₈ , C ₄ H ₁₀ , C ₆ H ₆ , H ₂ O, CO ₂ , CO, C
C ₅ H ₁₂	H, CH ₃ , CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₄ , C ₃ H ₆ , C ₃ H ₈ , C ₄ H ₆ , C ₄ H ₈ , C ₆ H ₆ , C ₅ H ₁₂ , H ₂ O, CO ₂ , CO, C

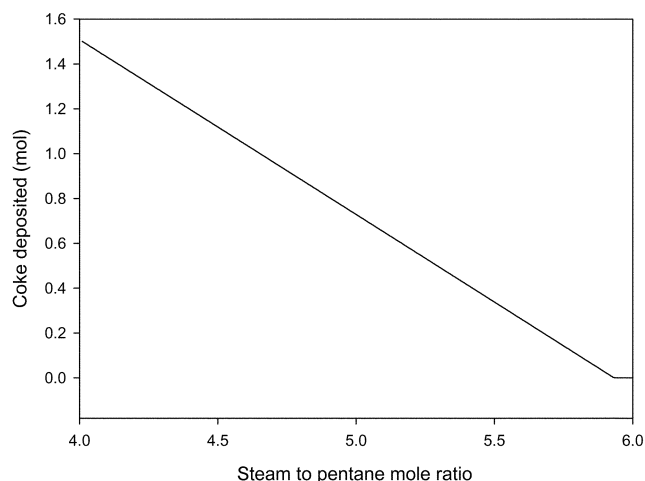


Fig. 1. Effect of steam to hydrocarbon ratio on the amount of coke deposited for 1 mol of pentane at 1,000 K and 1 bar.

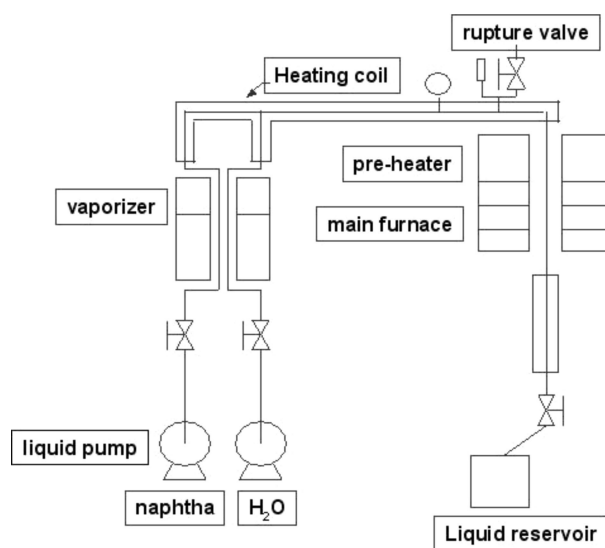


Fig. 2. Schematic diagram of pyrolysis reaction system.

Reactants were n-pentane and n-hexane from Kanto Chemical Co. with 99% purity. A schematic diagram of the experimental apparatus is shown in Fig. 2. A reactant and distilled water were separately fed from reservoirs by Hitachi pumps (model L-7110) through a vaporizer into the reactor after being preheated at 300 °C. The tubular reactor was made of Inconel Alloy 600 to prevent corrosion. The reactor was 0.995 cm in inside diameter, 1.285 cm in outside diameter and 100.0 cm in length. The reaction mixture was dis-

charged after being cooled through a heat exchanger. The reactor pressure was maintained at atmospheric pressure by a valve installed after the heat exchanger. The reactor is divided into four heating zones to maintain the reaction temperature constant at 900 °C. A temperature probe was installed on the outside wall of the furnace. A rupture valve was used to cope with unexpected pressure buildups. Connecting line between vaporizer and heating zone was heated to prevent reactant vapor mixtures from condensation. The product is condensed in a condenser and transformed into liquid phase. The difference in the mass of the reactor before and after reactions for varying reaction time was taken as the amount of coke deposited.

RESULTS AND DISCUSSION

For the thermodynamic analysis, three different values of pressure were selected (0.1, 1, 10 bar) and temperature ranges were from 800 K to 1,300 K. The pressure and the temperature dependence of the zero-coke steam ratio were calculated and presented in Figs. 3-7 for methane, ethane, propane, butane, and pentane. The computation indicated that the steam ratio exists in all conditions. As shown by Fig. 1, the reduction in coking is proportional to the steam

ratio up to the zero-coke ratio. For methane the zero-coke steam ratio ranged from 0.7 to 1.7 at 800 K for the pressures selected but approaches to 1 above 1,200 K regardless of pressure. Similar convergence at high temperatures was obtained for ethane, propane,

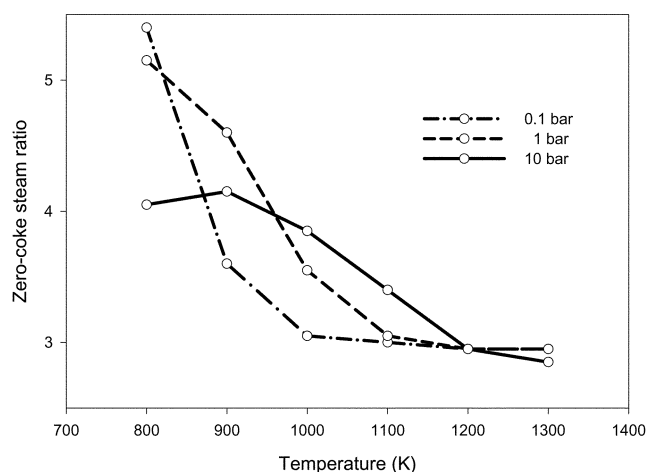


Fig. 5. Zero-coke steam ratio of propane pyrolysis.

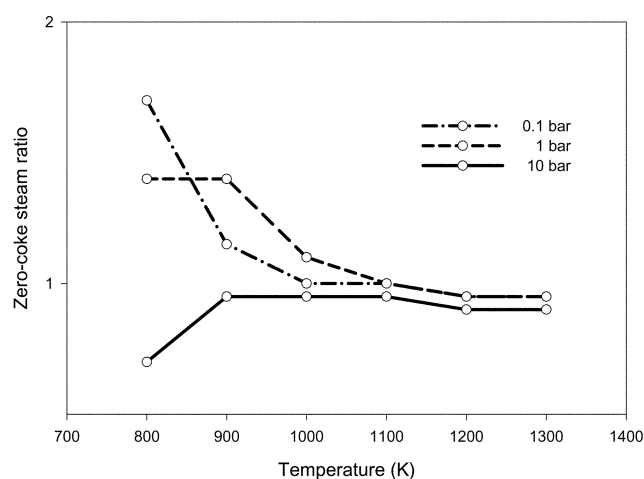


Fig. 3. Equilibrium zero-coke steam to alkane ratio for methane.

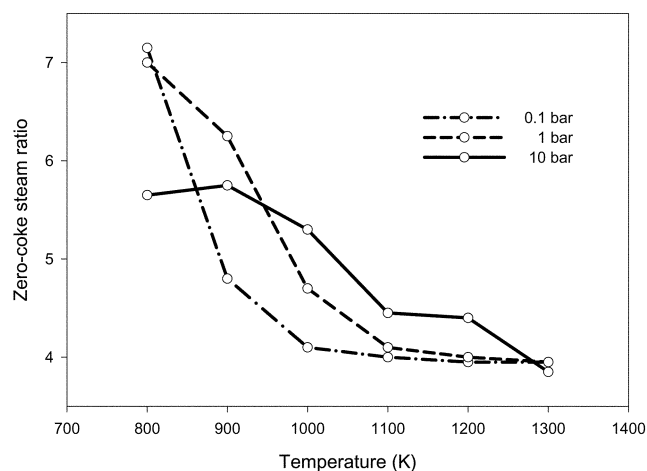


Fig. 6. Zero-coke steam ratio of butane pyrolysis.

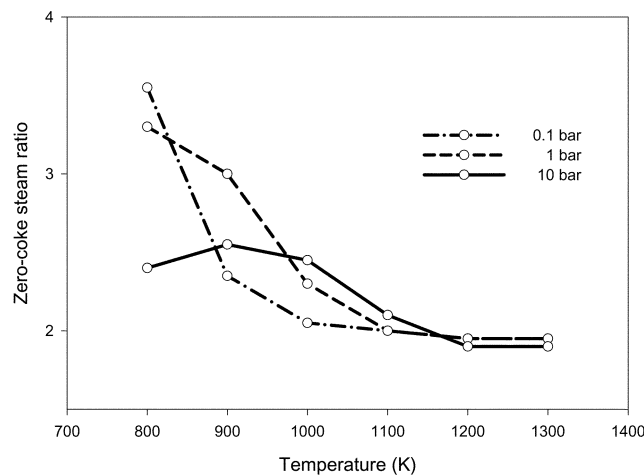


Fig. 4. Zero-coke steam ratio of ethane pyrolysis.

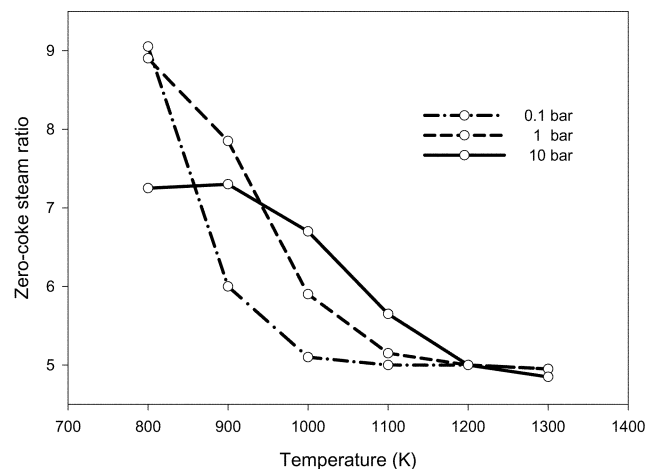


Fig. 7. Zero-coke steam ratio of pentane pyrolysis.

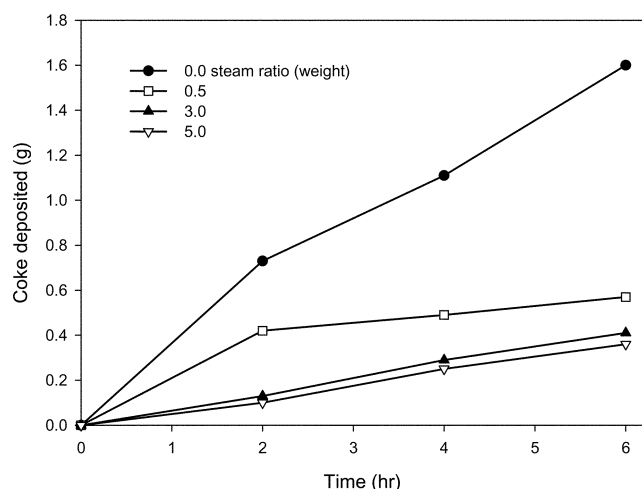


Fig. 8. The effect of steam ratios on coke formation for n-pentane at 1,173.15 K.

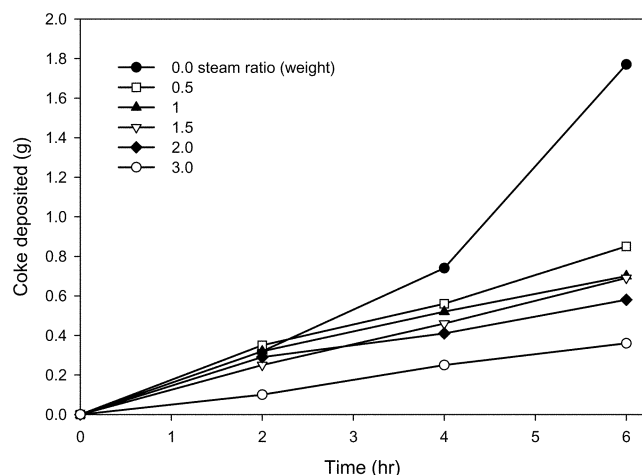


Fig. 9. The effect of steam ratios on coke formation for n-hexane at 1,173.15 K.

butane and pentane. Above 1,200 K, the zero-coke steam ratio on molar basis becomes the number of carbon atoms in feeds, 2 for ethane, 3 for propane and 5 for pentane. These ratios correspond to 1.12 for methane, 1.20 for ethane, 1.23 for propane, 1.24 for butane and 1.25 for pentane on weight basis.

Measured amounts of coke deposited are shown in Figs. 8 and 9 as a function of time for pentane and hexane at different steam to alkane ratios. In all experiments, the coke deposition decreased as the steam ratio increased in qualitative agreements with calculated results. For both substances, measured amounts of coke were found reduced to about a half at the ratio of 0.5 after 6 hours. The reduction in 6 hours was 61.7% for pentane and 52.0% for hexane. These values are also in qualitative agreement with equilibrium values of about 40% based on the linearity as shown by Fig. 1. However, for further increase of the ratio beyond the zero-coke ratio the reduction in coking was insignificant except for pentane with the ratio value of 3. Even at a ratio far greater than the calculated zero-coke steam ratio the coke deposition was still observed contrary to the results of thermodynamic analysis.

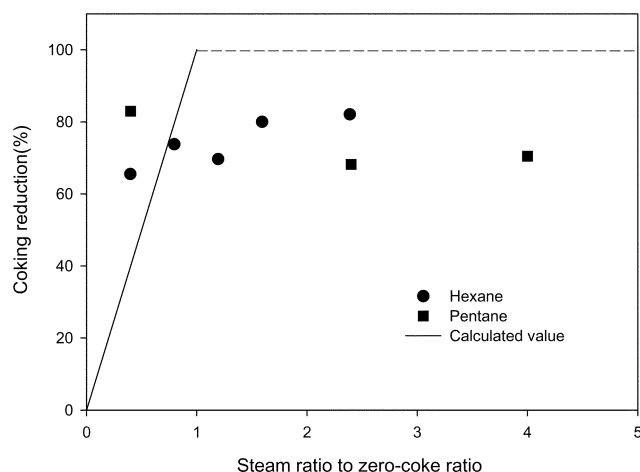


Fig. 10. Comparison of coke reduction at different steam ratio between 2 hr and 6 hr for pentane and hexane at 1,173.15 K and 1 bar.

Further examination of Figs. 8 and 9 indicates that the time behavior is similar to the experimental pyrolysis results for octane [Shah, 1976]. Rate of coking at the initial stage of approximately two hours is different from that in the subsequent stage. Shah suggested that coking begins to cover the surface of reactor during the initial stage. After the surface is covered, coking proceeds due to homogeneous reactions [Shah, 1976]. In the present thermodynamic analysis the initial surface coking was not included. If we concentrate on the later stage, we see that the effect of steam ratio is much more pronounced up to some ratio greater than 0.5 by weight. The reduction in coking from 2 hours to 6 hours is about 82.95% for pentane and 65.5% for hexane for the ratio of 0.5. As discussed in the previous paragraph the equilibrium value was about 40% at the ratio value. For pentane at the ratio 1, the reduction was 76%, which may be compared with equilibrium value of 80%.

The relation between equilibrium thermodynamic analysis and the time-dependent experimental coking results is shown graphically in Fig. 10 for the later stage of homogeneous coking. Since experimental results are expected to depend on reaction conditions, only qualitative interpretations are attempted. Thermodynamic analysis for hexane was not computed. It involves other species not listed in Table 2 and the zero-coke ratio by weight was inferred to be 1.26. The figure shows that coking decreases as the steam ratio increases. The effect is more pronounced for smaller values of the steam ratio. The optimal steam ratio to reduce coke is probably around 0.5 by weight, which is the ratio in commercial pyrolysis of ethane [Sundaram et al., 1981]. Froment suggested using a higher steam ratio to reduce coking by analyzing the CO concentration at the reactor exit [Froment, 1990]. However, even with more steam than that the zero-coke ratio coking still proceeds. There could be other mechanisms working that are ignored in the present thermodynamic analysis.

CONCLUSION

The effect of steam on coking in the pyrolysis of naphtha components was studied thermodynamically and experimentally for non-

catalytic tubular reactor systems. Thermodynamic analysis showed that the coking reduced linearly with the steam ratio up to the zero-coke ratio of 1.25 by weight where coking ceased to occur. Experimental results were in qualitative agreement with the thermodynamic analysis. However, they indicated that the reduction was more effective for smaller values of the ratio, leading to an effective ratio of about 0.5, and weak coking still occurred for a ratio greater than the thermodynamic zero-coke ratio.

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NOMENCLATURE

- f_i : fugacity of species j
 G^{total} : total Gibbs energy for the system at T and P
 G_i : the molar Gibbs energy of species j
 $\Delta G_{f,i}^o$: the standard Gibbs free-energy change of formation for species j
 n_i : mole number of species j
 P^o : the standard state pressure, 1 bar
 y_i : mole fraction of species i in gas phase

REFERENCES

- Albert, S. Jr. and John, C. C., "Growth and Initiation Mechanism of Filamentous Coke," Coke Formation on Metal Surfaces, Albright, L. F. and Baker, R. T. K., eds., ACS Symposium Series 202, New York (1982).
- Albright, L. F. and Marek, J. C., "Mechanistic Model for Formation of Coke in Pyrolysis Units Producing Ethylene," *Ind. Eng. Chem. Res.*, **27**, 755 (1988).
- Back, M. H. and Back, R. A., "Thermal Decomposition and Reactions of Methane," Pyrolysis : Theory and Industrial Practice, Albright, L. F., Crynes, B. L. and Cocoran, W. H., eds., Academic Press, New York (1983).
- Baker, R. T. K. and Yates, D. J. C., "Filamentous Carbon Formation over Iron Surfaces," Coke Formation on Metal Surfaces, Albright, L. F. and Baker, R. T. K., eds., ACS Symposium Series 202, New York (1982).
- Barin, I. and Plazki, G., "Thermochemical Data for Pure Substances," VCH, Weinheim (1995).
- Crynes, B. L. and Crynes, L. L., "Coke Formation on Polished and Unpolished Incoloy 800 Coupons during Pyrolysis of Light Hydrocarbons," *Ind. Eng. Chem. Res.*, **26**, 2139 (1987).
- Froment, G. F., "Coke Formation in the Thermal Cracking of Hydrocarbons," *Rev. Chem. Eng.*, **6**, 293 (1990).
- Goossens, A. G., Ranzi, E. and Dente, M., "Optimize Olefin Cracking Coils," *Hydrocarbon process.*, **57**, 227 (1970).
- Gueret, C., Daroux, C. and Billaud, F., "Methane Pyrolysis: Thermodynamics," *Chem. Eng. Sci.*, **52**, 815 (1997).
- Koh, J. H., Kang, B. S., Lim, H. C. and Yoo, Y. S., "Thermodynamic Analysis of Carbon Deposition and Electrochemical Oxidation of Methane for SOFC Anodes," *Electrochem. Solid-state Lett.*, **4**, 12 (2001).
- Ranzi, E., Dente, M., Pierucci, S. and Bardi, G., "Initial Product Distributions from Pyrolysis of Normal and Branched Paraffins," *Ind. Eng. Chem. Fundam.*, **22**, 132 (1982).
- Reid, R. C., Prausnitz, J. M. and Poling, B. E., "The Properties of Gases & Liquids," McGraw-Hill (1988).
- Riede, B. E. and Hanesian, D., "Kinetic Study of Carbon-Steam Reaction," *Ind. Eng. Chem. Process Des. Develop.*, **14**, 70 (1975).
- Rokstad, O. A., Olsvik, O., Jenssen, B. and Holemen, A., "Ethylene, Acetylene, and Benzene From Methane Pyrolysis," Novel Production methods for Ethylene, Light Hydrocarbons, and Aromatics, Albright, L. F., Crynes, B. L. and Nowak, S. M., eds., M. Dekker, New York (1992).
- Poutsma, M. L., "Fundamental Reactions of Free Radical Relevant to Pyrolysis Reactions," *J. Anal. Appl. Pyrolysis*, **54**, 5 (1988).
- Shah, Y. T., Stuart, E. B. and Sheth, K. D., "Coke Formation during Thermal Cracking of n-Octane," *Ind. Eng. Chem. Process Des. Dev.*, **15**, 518 (1976).
- Smith, W. R. and Missen, R. W., "Chemical Reaction Equilibrium Analysis: Theory and Algorithm," Wiley, New York (1982).
- Song, S. K. and Ihm, S. K., "Deactivation Control through Accelerated Precoking for the CoMo/ γ -Al₂O₃ Catalysts in Thiophene Hydrodesulfurization," *Korean J. Chem. Eng.*, **20**, 284 (2003).
- Sundaram, K. M. and Froment, G. F., "Kinetics of Coke Deposition in the Thermal Cracking of Propane," *Chem. Eng. Sci.*, **34**, 635 (1979).
- Sundaram, K. M. and Froment, G. F., "Modeling of Thermal Cracking Kinetics. 3. Radical Mechanisms for the Pyrolysis of Simple Paraffins, Olefins, and Their Mixtures," *Ind. Eng. Chem. Fundam.*, **17**, 174 (1978).
- Sundaram, K. M., Van Damme, P. S. and Froment, G. F., "Coke Deposition in the Thermal Cracking Ethane," *AIChE J.*, **27**, 946 (1981).
- Trimm, D. L., "Fundamental Aspects of the Formation and Gasification of Coke," Pyrolysis: Theory and Industrial Practice, Albright, L. F., Crynes, B. L. and Cocoran, W. H., eds., Academic Press, New York (1983).
- Tsai, C. H. and Albright, L. F., "Importance of Surface Reactions in Pyrolysis Units," Pyrolysis: Theory and Industrial Practice, Albright, L. F., Crynes, B. L. and Cocoran, W. H., eds., Academic Press, New York (1983).
- Valerio, C., "Characterization of Coke Formed in the Pyrolysis of Polyethylene," *Ind. Eng. Chem. Res.*, **36**, 5090 (1997).
- Van Damme, P. S., Narayanan, S. and Froment, G. F., "Thermal Cracking of Propane and Propane-Propylene Mixtures: Pilot Plant Versus Industrial Data," *AIChE J.*, **21**, 1065 (1975).
- Zou Renjun., "Fundamentals of Pyrolysis in Petrochemistry and Technology," CRC Press, 244 (1993).