

氏名	まつかわよしや 松川 嘉也		
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指導教員	東北大学教授 青木 秀之		
論文審査委員	主査	東北大学教授 青木 秀之	東北大学教授 猪股 宏
		東北大学教授 塚田 隆夫	

論文内容要旨

Chapter 1: Introduction

In the industrial process with pyrolysis of hydrocarbon, coke on the wall in the tube often causes problems. Inhibition of coke production is important because coke fouls the catalyst, and reduces heat transfer rate in the tube. In this study, focusing on Polycyclic Aromatic Hydrocarbon (PAH), which is thought to be one of the precursors, the reaction mechanism for precursors was investigated experimentally and theoretically. In addition, two types of reaction model were constructed for hydrocarbon pyrolysis, and the hydrocarbon concentrations near wall were investigated. One is the detailed kinetic mechanism, and the other is modeled by some representative variables.

Chapter 2: Experimental investigation of formation mechanism of polycyclic aromatic hydrocarbon

The Hydrogen-Abstraction/Carbon-Addition (HACA) mechanism has been broadly thought to be dominant on the formation of PAH. However, some experimental studies suggested that Phenyl Addition Cyclization (PAC) or Methyl Addition Cyclization (MAC) might be dominant on the PAH formation during thermal pyrolysis at 1100–1373 K [1, 2]. To establish operation condition of olefin plant to reduce PAH formation, the dominant mechanism of PAHs in pyrolysis tube needs to be clarified. In this chapter, the formation mechanism of PAH during pyrolysis were investigated using Gas Chromatograph (GC). The intermediate products of

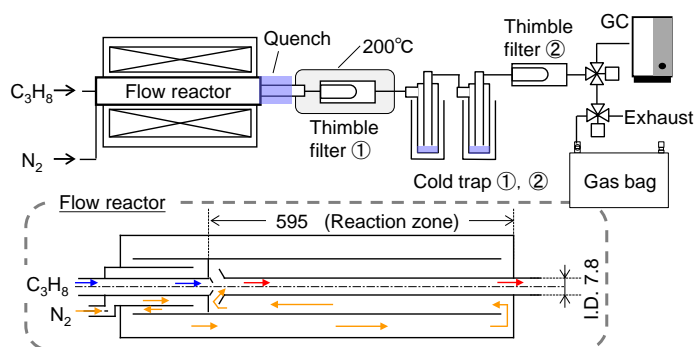


Fig. 1 Schematic diagram of experimental apparatus

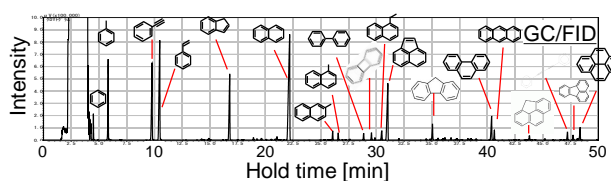


Fig. 2 Chromatogram of product, $T = 1273$ K, elapsed time: 0.3 s

HACA, PAC, and MAC were detected at some level.

Chapter 3: Theoretical investigation of reaction rate of polycyclic aromatic hydrocarbon based on quantum chemistry

Both the stacking of PAHs and oligomer formation reactions from PAHs should cause soot nucleation. In the previous study, the oligomer formation reaction was studied by the pyrolysis of feedstock which contains benzene and a small amount of PAHs. Both the addition of pyrene or anthracene promoted soot formation more than that of phenanthrene. This difference was suggested to be due to the difference of types of site on PAHs because pyrene and anthracene do not have armchair site whereas phenanthrene has the one. However, this discussion was speculation from experimental result, and it has never been studied theoretically. In this study, the effect of the difference of site on the oligomer formation reaction was studied by density functional calculation. By comparing the reaction rate constants calculated from transition state theory, the reactions to the radical on armchair site is energetically-unfavorable, and the reaction rate constants are similar in case the combination of site types is the same.

Next, the effect of addition reaction of CH_3 , C_2H_2 or phenyl radical on the growth of PAHs is evaluated. The reaction rate constants of elementary reaction are calculated by density functional theory and transitional state theory. The effect of CH_3 addition was very limited compared to that of C_2H_2 or phenyl radical. In addition, the C_2H_2 addition reaction was faster than the phenyl addition reaction, and they competed against each other for the consumption of radical of PAHs.

Chapter 4: Efficient algorithm on kinetic Monte Carlo simulation for methyl addition to aromatic hydrocarbon

In Chapter 3, the MAC mechanism suggested not to be important mechanism for growth of small molecular weight PAH. In this chapter, the effect of the MAC on the growth of large molecular weight PAH was investigated. Although the detailed kinetic mechanism is powerful tool to simulate vapor reaction, its weak point is huge computational cost and considerable labor required for construction for large molecule or molecule with branching like PAH with some sidechains. On the other hand, kinetic Monte Carlo (KMC) simulation is relatively easy to construct. However, previous KMC models cannot overcome the problem of computational cost for molecule with branching. In this chapter, a new algorithm to solve this problem was proposed, and it enabled to simulate the MAC reaction on PAHs.

Chapter 5: Construction of detailed kinetic mechanism and simplified mechanism

Detailed kinetic mechanisms are widely used as kinetic models for the reaction about aromatic hydrocarbons and light aliphatic hydrocarbons. Especially, the detailed kinetic mechanism proposed by Wang et al. [3] (KM2), which is one of the most highly accurate mechanisms for PAHs, is widely used for various

simulations considering PAH formation. In contrast, few detailed kinetic mechanisms for heavier aliphatic hydrocarbons were proposed. The number of species and elementary reactions of detailed kinetic mechanisms exponentially increase with an increase of the number of carbon atoms in aliphatic hydrocarbon molecule. Because of this, the detailed kinetic mechanism which can consider any hydrocarbons is not realistic. Generally, the detailed kinetic mechanism constructed by rule-based mechanism generator is used as the detailed kinetic mechanism for such an aliphatic hydrocarbon pyrolysis or combustion. Basically, mechanism generator is based on group additive theory for reaction and thermodynamic property.

Even if constructing the detailed kinetic mechanism by rule-based mechanism generator as much as needed, the mechanism should be too huge to keep CFD with the mechanism hard because of calculation cost. In this chapter, mechanism reduction was also investigated. Importance of the method to determine interaction coefficient to the directed relation graph with error propagation (DRGEP) method [4] is explored by considering the pyrolysis reaction with time variation of temperature. In order to taking into account time dependency of skeletal mechanism, interaction coefficients were determined using four different methods: one commonly-used method and three alternative methods. The conventional method uses the overall interaction coefficient (OIC) from direct interaction coefficient (DIC) determined by ratio of time averaged production rate. Two of the three alternative methods use the OIC computed from DIC determined by maximum value of ratio of production rate in each time, and the OIC computed from DIC determined by the averaged value of ratio of production rate in each time, respectively. The other method considers OIC computed from time-dependent direct interaction coefficient. Dijkstra's algorithm is used for graph search algorithm to generate skeletal mechanisms for detailed kinetic mechanism for prediction of PAH formation during C2 pyrolysis [5]. The concentration of benzene by the reduced mechanism was compared with the original mechanism. In the conventional method, the smallest skeletal mechanism with accuracy has 60 species. Trying further reduction of species using the conventional method, the important species near chemical equilibrium were reduced. In contrast, the skeletal mechanisms constructed by the DRGEP with new methods accurately predict the concentration with only 45 species. In addition, the logarithm of the error was decreasing roughly in proportion to the number of species. The DRGEP and new methods are suggested to be suited for skeletal mechanism of reduction with time variation of temperature.

Chapter 6: Chemical reaction model and turbulence model at coupled analysis with computational fluid dynamics
Correction of reaction rate for analytical Jacobian with preventing the harmful effect of negative value of species concentration during time integration of detailed kinetic reaction with VODE was proposed. In the case of reacting flow calculation with detailed kinetic reaction, the computational cost of the calculation is increasing with increasing of the number of species considered. When using the implicit ordinary equation

solver, VODE, the calculation of Jacobian is the bottleneck for computational cost. In this study, analytical Jacobian was introduced to reduce whole the computational cost for computing reacting flow. Negative values of concentration of chemical species prevent the calculation of analytical Jacobian because of the lack of differentiability in reaction rate around zero of the concentration. The corrections of reaction rate with cubic function enabled the evaluation of analytical Jacobian.

The technique to estimate the distance from wall based on Finite Volume Method (FVM) in unstructured grid was also investigated to realize damping function near wall in LES simulation and low-Re $k-\varepsilon$ model. In addition, the recycle inflow boundary was also introduced to overcome large aspect ratio of reaction tube. Several RANS (Reynolds-averaged Navier–Stokes) models were assessed for flow behavior in reaction tube.

Chapter 7: The reaction rate model with Progress Variables of enthalpy, and species concentrations

Despite the effort of reducing of the detailed kinetic mechanism and acceleration of the time integration of the reaction, the computational cost is still high. In this chapter, the novel approach to model the reaction with enthalpy and species concentrations was proposed. The reaction property (for example, temperature and species concentration) during pyrolysis is suggested to be representative with enthalpy and C_2H_4 concentration and other species concentration.

Chapter8: Effect of transport phenomena on distribution of species concentration in pyrolysis tube of olefin plant

The technique developed in Chapter 7 was applied to the simulation of pyrolysis reactor of olefin plant. The species concentrations near wall were investigated. The thickness of boundary layer of PAHs near wall is smaller with an increase in the molecular weight of PAHs.

Chapter9: Conclusion

The kinetic models for precursors of coke were constructed and some novel techniques to implement them in CFD were developed. This thesis contributes to numerical simulation of reacting flow with hydrocarbon reactions.

- [1] B. Shukla *et al.*, *Journal of the American Society for Mass Spectrometry*, **21** (2010) 534-544. [2] B. Shukla *et al.*, *The Journal of Physical Chemistry A*, **115** (2011) 5284-5293. [3] Y. Wang *et al.*, *Combustion and Flame*, **160** (2013) 1667-1676. [4] T. Lu and C. K. Law, *Proceedings of the Combustion Institute*, **30** (2005) 1333 - 1341. [5] J. Appel *et al.*, *Combustion and Flame*, **121** (2000) 122-136.

論文審査結果の要旨

本論文は、反応管内において反応および対流・拡散が多環芳香族炭化水素(PAH)の濃度に及ぼす影響について明らかにしたものである。PAHは、すすやコークの重要な前駆体として知られる。特に、コークは炭化水素の熱分解を伴う装置においては、伝熱を大きく阻害するなど、操業上の大きな問題となりうる。コークの生成という観点から、コーク生成が起こる管壁近傍における PAH 濃度が重要となるが、PAH の生成機構が複雑であり、反応管内の対流・拡散の影響も強く受けるため、その予測は困難である。本博士論文では、PAH の反応機構・反応性について実験的・理論的な検討を行っている。加えて、詳細化学反応機構およびデータベーステーブルに基づくモデルの 2 種類の反応速度モデルを構築して、反応管壁近傍における炭化水素濃度の支配因子を検討している。

論文は全 9 章で構成されている。

第 1 章は総論であり、本研究の背景および目的を述べている。

第 2 章では、熱分解における PAH の生成機構を実験的に検討している。熱分解実験における生成物をガスクロマトグラフィーにより分析することで、様々な反応機構の中間生成物を確認している。

第 3 章では、量子化学計算により、PAH の成長機構に関する反応性の検討を行っている。密度汎関数法により得られた自由エネルギーから遷移状態理論に基づき反応速度定数を算出し、反応性を比較している。PAH 同士の反応によりオリゴマーが生成する反応を検討したところ、Zig-zag サイトや Free-edge サイトにおける反応性が高く、Armchair サイトにおける反応性が小さいことを明らかとしている。また、PAH に対するメチル基、エチニル基、およびフェニル基の付加反応の反応性を検討したところ、エチニル基の付加反応の反応性が著しく大きく、メチル基の付加による反応性が極めて小さいことを明らかにしている。

第 4 章では、動的モンテカルロ法によりメチル基の付加が PAH の成長に及ぼす影響を検討している。PAH の分子量が大きくなるほど、メチル基の付加による PAH の成長速度は小さくなることを明らかとしている。また、動的モンテカルロ法において、高速な構造探索アルゴリズムを提案し、側鎖を持つ PAH の成長反応を考慮できるようにしている。

第 5 章では、詳細化学反応機構を構築している。はじめに、Reaction Mechanism Generator によりナフサの熱分解を考慮可能な詳細化学反応機構を構築している。これを既存の詳細化学反応機構と組み合わせることによって、PAH の成長を考慮可能な詳細化学反応機構を構築している。さらに、既往の熱分解実験における芳香族炭化水素の化学種濃度を再現するためにいくつかの改良を施し、予測精度が大幅に向上させている。構築した詳細化学反応機構は 300 種類以上の化学種を含むものであり、流体計算(CFD)との連成が困難であった。そこで、新規の簡略化手法を提案し、それによって詳細化学反応機構の簡略化を行っている。

第 6 章では、CFD における反応モデルおよび乱流モデルの開発・提案を行った。反応の時間進展において陰解法の連立常微分方程式ソルバーを用いる場合に解析的ヤコビ行列を求めることで、計算コストを大幅に削減する手法を提案している。さらに、非構造格子の有限体積法において、壁面からの距離を短時間で推算する手法を提案している。これにより、壁面の漸近挙動を予測するのに壁面からの距離が必要な乱流モデルを特殊な取り扱いなしに、非構造格子の有限体積法に適用することが可能としている。

第 7 章では、データベーステーブルに基づく反応モデルの提案およびデータベーステーブルの作成を行っている。熱分解においては、エンタルピーと主要生成物の濃度を制御変数とすることで PAH を含めた全体の反応挙動を再現可能であることを見出している。

第 8 章では、これまでの章において構築した反応モデル・乱流モデルを活用して、管壁近傍における化学種濃度を算出している。

第 9 章は総括であり、各章の成果をまとめている。

以上要するに、本論文は PAH の生成機構に関する反応性を検討するとともに、CFD とカップリングさせるための速度モデルを開発・提案し、反応性流体の CFD の研究を大きく発展させた。

よって、本論文は博士(工学)の学位論文として合格と認める。