Research Activity Report **2013.10.31**

Research title		Combustion Chemistry and Its Experimental Validation for Biofuels and Surrogate Fuels -Collaboration between Quantum Chemistry and Combustion Engineering-
Visiting researcher	**Name**	Hisashi Nakamura
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	Title	Assistant Professor
Visiting institution		Combustion Chemistry Centre, National University of Ireland, Galway, Ireland
Visiting period		September 2011 - September 2012
Host researcher	**Name**	Henry Curran
	Affiliation	Combustion Chemistry Centre, National University of Ireland, Galway, Ireland
	Title	Professor

Summary of Collaborative Research Activities

Combustion is a complicated phenomenon of chemical kinetics and flame dynamics. Since physical backgrounds of these two phenomena are significantly different each other (electron transfer based on quantum chemistry for chemical kinetics; molecular and heat transfer based on continuum mechanics for flame dynamics), corroborative researches must be conducted to develop effective combustion devices. I joined Combustion Chemistry Centre (Director: Prof. Henry Curran), National University of Ireland, Galway (NUIG) for a year, and development and validation of chemical kinetics of biofuels and surrogate fuels were conducted. I was mainly involved to projects for two fuels: alkylbenzene and diethyl carbonate (DEC).

- Oxidation of alkylbenzene [1-3]

Alkylbenzene is an important component of diesel surrogates and its oxidation process must be investigated to develop higher-efficiency diesel engines. We focused on *n*–proplybenzene and *n*–butylbenzene in this project because these oxidation processes were not fully understood. The most difficult point for development and validation of gas-phase chemical kinetics of these fuels is that vapor pressures of the fuels are extremely low. Fuel condensation must not occur to obtain well-defined ignition data. For homogeneous initial temperature in a rapid compression machine and a shock tube, heating system was improved and validation of initial temperature was conducted, to which my experience of combustion engineering contributed. As a result, ignition data for these fuels and air mixtures in wide ranges of temperature, pressure and fuel concentration were obtained and chemical kinetics was validated.

- Oxidation of DEC [4]

DEC is an oxygenated fuel that can be produced from sugar from plants. It is expected that the

replacement of petroleum fuel by bio-derived DEC will lead to reductions in CO_2 and soot emission, especially from diesel engines. A detailed chemical kinetic mechanism for the oxidation of DEC is needed to simulate its combustion in engines; however no experimental data is currently available for validation purposes. Ignition delay times were obtained using a shock tube and a rapid compression machine and showed near negative temperature coefficient, although DEC has no ROO<=>QOOH isomerization of 6– and 7–membered ring structures. Rate constants of the isomerizations were estimated using quantum chemistry computation (Fig. 1) and chemical reaction mechanism of DEC including the low-temperature oxidation was developed.

Through these projects, I had a chance to collaborate with many excellent researchers not only in NUIG but also in other institutes: Dr. P. Dagaut and Dr. C. Togbé (CNRS-INSIS, France), Dr. W.J. Pitz, Dr. M. Mehl and C.K. Westbrook (Lawrence Livermore National Laboratory, USA); Prof. S.M. Sarathy (King Abdullah University of Science and Technology, Saudi Arabia). This program finished but collaboration with them as well as Prof. Henry Curran continues.

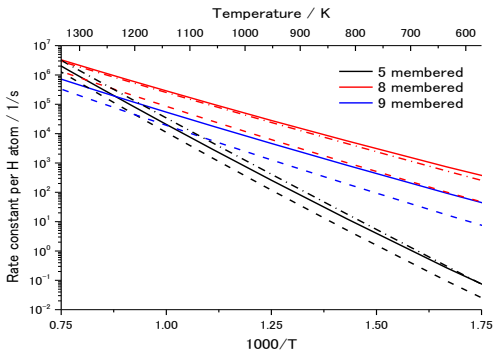

Figure 1 Computed rate constant of ROO<=>QOOH isomerization; solid lines: CBS-QB3; dashed lines: CCSD(T)/cc-pVTZ; dashed-dotted lines: Dean's alkane rate rule

Publications

1) Journal or conference papers with full paper review (including review papers, invited papers, etc.)

[1] H. Nakamura, D. Darcy, M. Mehl, C.J. Tobin, W.K. Metcalfe, W.J. Pitz, C.K. Westbrook, H.J. Curran: An experimental and modeling study of shock tube and rapid compression machine ignition of n-butylbenzene/air mixtures, *Combust. Flame*, in press. IF2011: 3.585

[2] D. Darcy, H. Hakamura, C.J. Tobin, M. Mehl, W.K. Metcalfe, W.J. Pitz, C.K. Westbrook, H.J. Curran: A high-pressure rapid compression machine study of n-propylbenzene ignition, *Combust. Flame*, in press. IF2011: 3.585

2) Conference papers or presentation without full paper review

[3] H. Nakamura, D. Darcy, M. Mehl, C. Tobin, K. Yasunaga, J. Simmie, J. Wurmel, W. Metcalfe, W.J. Pitz, C.K. Westbrook, H. Curran: n-Butylbenzene Oxidation in the Low-Temperature Region and its Comparison with n-Propylbenzene, *34th International Symposium on Combustion*, WiPP, W5P086, Aug. 2012, Warsaw.

[4] H. Nakamura, H. Curran, A.P. Cordoba, W.J. Pitz, P. Dagaut, C. Togbe, M. Sarathy, M. Mehl: Experimental and kinetic modeling study of oxidation of diethyl carbonate, *34th International Symposium on Combustion*, WiPP, W5P087, Aug. 2012, Warsaw.

3) Patent, award, press release etc.

Not applicable