RGC Ref.: M-PolyU509/13

The Research Grants Council of Hong Kong
SRFDP & RGC ERG Joint Research Scheme
Completion Report

(Please attach a copy of the completion report submitted to the Ministry of Education by the Mainland researcher)

Part A: The Project and Investigator(s)

1. Project Title

Theoretical Chemical Kinetics for Pyrolysis and Oxidation of Large Biodiesel Molecules

2. Investigator(s) and Academic Department/Units Involved

	Hong Kong Team	Mainland Team
Name of Principal Investigator *(with title)*	Dr. Zhang Peng	Prof. Law Chung K.
Post	Associate Professor	Professor
Unit / Department / Institution	Department of Mechanical Engineering / The Hong Kong Polytechnic University	Center for Combustion Energy / Tsinghua University
Contact Information	Tel: (852) 2766 6664 pengzhang.zhang@polyu.edu.hk	Tel: (86) 010-62798267 cklaw@tsinghua.edu.cn
Co-investigator(s) *(with title and institution)*	N.A.	Prof. You Xiaoqing Tsinghua University
PhD student(s) (with period of involvement)	Name: Ms. Qinxue Chen Institution: ME/HKPolyU Period from 01-Sep-2013 to 31-Aug-2015 Name: Mr. Xuren Zhu Institution: ME/HKPolyU Period from 28-Apr-2014 to the present Name: Mr. Dehai Yu Institution: ME/HKPolyU Period from 15-Aug-2014 to the present	Name: Ms. Xiaoyu Li Institution: CCE/Tsinghua Period from 1-Jan-2014 to the present

Note: The Hong Kong project team must involve at least one research postgraduate student pursuing a Doctor of Philosophy degree at the UGC-funded university (PhD student) at any time throughout the project period.

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted*)
Project Start date	1 January 2014	N/A	N/A
Project Completion date	31 December 2016	30 April 2017	18 January 2017
Duration *(in month)*	36	40	
Deadline for Submission of Completion Report	31 December 2017	30 April 2018	

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. To obtain bench mark reaction rate constants, by using the theoretical chemical kinetics, for the key reactions in the pyrolysis and oxidation of methyl oleate ($C_{19}H_{36}O_2$) and methyl linolate ($C_{19}H_{34}O_2$), which are the most important biodiesel component molecules. The key reactions include the decomposition reactions of the weakest bonds in the molecules and the hydrogen abstraction reactions by H (HK Team), OH and HO_2 (China Team) as well as the decomposition and isomerization reactions of the product radicals.
2. To obtain understanding on the influence of C=C double bond on the rate constants through comparing the monounsaturated methyl oleate and the polyunsaturated methyl linolate.
3. To explore theoretical methodology for high-accuracy quantum chemistry calculation of thermochemical and kinetic data for large methyl ester molecules.
4. To examine and update the previous reaction mechanisms for large biodiesel molecules.
5. To fulfill all the objectives from 1) to 4), relatively frequent visits between the Hong Kong team and the Mainland China team are necessary to effectively exchange research progress.

5.2 Revised Objectives

N/A

6. Research Outcome

Major findings and research outcome
(maximum 1 page; please make reference to Part C where necessary)

1. A two-layer ONIOM[QCISD(T)/CBS:DFT] method

Biodiesel combustion urges the need for the theoretical chemical kinetics of large biodiesel molecule. This is computationally challenging for prevalent high-level electronic structure theory based methods. The ONIOM method employed a QCISD(T)/CBS method for the high layer and a DFT method for the low layer. The calculated thermochemical results, energy barriers and heats of reaction, are in excellent agreement with those obtained using the widely accepted high-level method. The ONIOM[QCISD(T)/CBS:DFT] method provides a computationally accurate and affordable approach to the high-level theoretical chemical kinetics of large fuel molecules.

2. High-level theoretical studies of the reactions between unsaturated methyl esters, $C_nH_{2n-1}COOCH_3$ (n=2-5, 17), and hydrogen radical

We comprehensively investigated the unsaturated alkyl esters, particularly the influence of mono- and multi- C=C bonds on combustion characteristics. Because of the conjugation effect of the C=C double bond, we further developed the ONIOM method to extend its applicability. The predicted energy barriers and heat of reactions by using the ONIOM method are in excellent agreement with the results by using QCISD(T)/CBS method, as validated by that the computational differences are less than 0.15 kcal/mol, for almost all the reaction pathways under consideration and investigation. **A paper based on the work is under the second review of Journal of Physical Chemistry A.**

3. Theoretical kinetics study on unimolecular reaction of methyl decanoate radicals

We calculated for the first time the accurate rate constant of the unimolecular reactions of methyl decanoate radicals. High-level quantum chemical calculation methods based on a two-layer ONIOM method were employed to predict single point energies of all the species considered. Compared with available literature data of the MB, n-decane and MD, satisfactory agreement between MB and MD was found. In addition to provide highly reliable rate constants for the kinetics modeling of practical biodiesel combustion, the explored reactivity-structure relationships for the thermal decompositions of MD radicals can be applied to realistic biodiesel combustion chemistry. **A paper based on the work is under review of Proceedings of the Combustion Institute.**

4. Spin-off projects

During the study of the pyrolysis reaction of MO ($C_{19}H_{36}O_2$), we encountered a problem of adopting appropriate theoretical methodology for studying radical-radical fission reactions. We overcame the problem in cooperation with Dr. Klippenstein and Dr. Harding. This learning and collaborative activity has resulted in a peer-reviewed publication. **(P. Zhang*, S. J. Klippenstein*, L. B. Harding, H. Sun, C. K. Law, RSC Advances, 2014, 4, 62951).**

As an attempt to apply the project results to real-world applications, we successfully conducted related work has resulted in three peer-reviewed publications. **(K. Sun, T. Wang, P Zhang*, C. K. Law, Physical Review E., 2015, 91 023009; K. Sun, P Zhang*, C. K. Law*, T. Wang, Physical Review Applied, 2015, 4, 054013; C. Tang, J. Zhao, P. Zhang*, C. K. Law*, Z. Huang, Journal of Fluid Mechanics, 2016, 795, 671-689).**

Potential for further development of the research and the proposed course of action *(maximum half a page)*

In the present project, we developed, applied and improved the ONIOM method for studying chemical kinetics of large biodiesel molecules. Apparently, the same methodology can be applied to other large fuel molecules. Large hydrocarbon molecules containing more than ten carbon atoms are the primary components of aviation kerosene and its surrogates. High-level ab initio chemical kinetics of large hydrocarbon is crucial to establish the chemical reaction mechanisms of aviation kerosene combustion. Potential difficulties associated with this further development are those originating from the high-accuracy calculation of partition functions of anharmonic torsional modes and the rate coefficient calculation from interconnected multiple-well master equation analysis. The success of the present project has paved the road for studying large hydrocarbon molecules in aviation kerosene.

7. The Layman's Summary

(describe in layman's language the nature, significance and value of the research project, in no more than 200 words)

Utilization of non-petroleum-based alternative fuels was proposed as practical solution for the increasing concerns about energy sustainability, energy security and climate change. Biodiesels are among various alternative fuels and have these merits, renewability, low pollution and low emission. The biodiesel is the most widely used biofuels all over the world and it can replace or blend with petroleum-based diesel for direct utilization in diesel engine without or with only minor modification. Biodiesel is a mixture of fatty acid alkyl ester with varying molecular structure and physiochemical properties, and the molecules often contain 12-19 carbon atoms and the combustion results in extremely complex pyrolysis and oxidation chemistry with thousands of intermediate chemical species and ten thousands of reaction pathways. The project aims to study the key reactions in the pyrolysis and oxidation of large biodiesel molecules by using the theoretical chemical kinetics. Establishing detailed and comprehensive chemical reaction mechanisms of large biodiesel molecules requires accurate and efficient theoretical chemical kinetics calculation. High-accuracy quantum chemistry method (ONIOM) for large biodiesel molecules has also been systematically investigated and validated. It provides a computationally accurate and affordable approach to study the large biodiesel molecules that are of interest to combustion chemistry.

Part C: Research Output

8. Peer-reviewed journal publication(s) arising directly from this research project

(Please attach a copy of each publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.)

The Latest Status of Publications				Author(s)	Title and Journal/ Book	Submitted to RGC	Attached to this report	Acknowledged the support of this Joint Research Scheme	Accessible from the institutional repository
Year of publication	Year of Acceptance *(For paper accepted but not yet published)*	Under Review	Under Preparation *(optional)*	***(bold** the authors belonging to the project teams and denote the corresponding author with an asterisk*)*	*(with the volume, pages and other necessary publishing details specified)*	*(indicate the year ending of the relevant progress report)*	*(Yes or No)*	*(Yes or No)*	*(Yes or No)*
2014	2014	N/A	N/A	**Peng Zhang***, Stephen J. Klippenstein*, Lawrence B. Harding, Hongyan Sun and **Chung K. Law**	Secondary channels in the thermal decomposition of monomethylhydrazine (CH3NHNH2), RSC Advances, 2014, **4**, 62951 (IF=3.84)	N/A	Yes	Yes	Yes
2015	2015	N/A	N/A	Kai Sun, Tianyou Wang, **Peng Zhang,* and Chung K. Law**	Non-Newtonian flow effects on the coalescence and mixing of initially stationary droplets of shear-thinning fluids, PHYSICAL REVIEW E **91**, 023009 (2015) (IF=2.29)	N/A	Yes	Yes	Yes
2015	2015	N/A	N/A	Kai Sun, **Peng Zhang***, **Chung K. Law*** and Tian you Wang	Collision Dynamics and Internal Mixing of Droplets of Non-Newtonian Liquids, PHYSICAL REVIEW APPLIED, **4**, 054013 (2015) (IF=4.808)	N/A	Yes	Yes	Yes
2016	2016	N/A	N/A	Chenglong Tang, Jiaquan Zhao, **Peng Zhang***, **Chung K. Law*** and Zuohua Huang	Dynamics of internal jets in the merging of two droplets of unequal sizes, Journal of Fluid Mechanics, 2016, 795, 671-689 (IF=2.821)	N/A	Yes	Yes	Yes

		Yes	N/A	Lidong Zhang, Qinghui Meng, Yicheng Chi and **Peng Zhang***	Towards high-level Theoretical Studies of Large Biodiesel Molecules: An ONIOM [QCISD(T)/CBS:DFT] Study of the Reactions between Unsaturated Methyl Esters (CnH2n-1COOCH3) and Hydrogen Radical, Journal Physical Chemistry A (IF=2.847)	N/A	Yes	Yes	Yes
		Yes	N/A	Qinghui Meng, Yicheng Chi, Lidong Zhang*, **Peng Zhang***, and Liusi Sheng	A theoretical kinetics study on unimolecular reactions of methyl decanoate radicals, Proceedings of the Combustion Institute. (IF=3.2)	N/A	Yes	Yes	Yes

9. Recognized international conference(s) in which paper(s) related to this research project was/were delivered *(Please attach a copy of each delivered paper. All listed papers must acknowledge RGC's funding support by quoting the specific grant reference.)*

Month/Year/ Place	Title	Conference Name	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*	Accessible from the institutional repository *(Yes or No)*
N/A						

10. Student(s) trained *(Please attach a copy of the title page of the thesis.)*

Name	Degree registered for	Date of registration	Date of thesis submission/ graduation
Qinxue Chen	Master of Science	01-Sep-2013	31-Aug-2015

11. Other impact *(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, etc.)*

Excellent Poster Award.

Yicheng Chi, Yajie Zhu, Qinghui Meng, Lidong Zhang and **Peng Zhang***. An ONIOM-method-based High-level Theoretical Study on Hydrogen Abstraction

Reactions of Large Straight-chain Alkanes Molecules by Hydrogen Radical. China National Symposium on Combustion [C]. 2017.

Collaborations have been made with the following research personnel/institutions.

1. Dr. Stephen J. Klippenstein, Argonne Distinguished Fellow, Argonne National Laboratory, Department of Energy, USA
2. Dr. Lawrence B. Harding, Argonne Distinguished Fellow, Argonne National Laboratory, Department of Energy, USA
3. Dr. Hongyan Sun, Air Force Res Lab Edwards Air Force Base, USA
4. Prof. Tianyou Wang, State Key Laboratory of Engines, Tianjin University, PRC
5. Prof. Chenglong Tang and Prof. Zuohua Huang, Xi'an Jiaotong University, PRC