Biologically derived diesel fuels and NO formation

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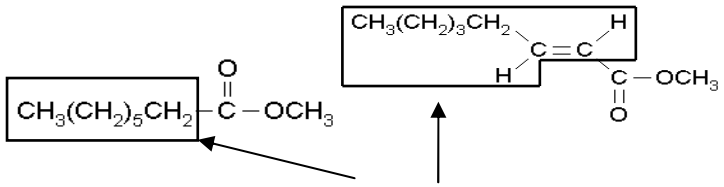
Pyrolysis experiments on n-heptane, 1-heptene and 1,6-heptadiene have been performed using the UIC High Pressure Shock tube (HPST) at pressures relevant to diesel combustion systems in order to examine the correlation between an increase in the degree of unsaturation in biologically derived diesel fuels and an increase in NO formation through acetylene and the Fenimore mechanism. Complementary fuel-rich oxidation experiments were then conducted at nominal reaction pressures of 10 atm using the Jet Stirred Reactor (JSR) facility at CNRS in Orleans, France. The oxidation studies were made possible by the NSF International Research & Education in Engineering (IREE) program for collaborative research. Through cooperation, originally fostered by the NSF-IREE award, an international and inter-institution collaboration and exchanged has been initiated that advances the international scientific community through both cultural and scientific exploration.

INTRODUCTION

A grant to study the oxidation of biologically derived diesel fuels has been awarded to the High Pressure Shock Tube (HPST) Laboratory at the University of Illinois at Chicago (UIC). The aim of this high temperature (T > 1000K), high pressure (P > 25 atm) study is to determine the effect of an increase in the degree of unsaturated in the alkyl side chain of methyl ester biodiesel surrogates on acetylene formation and prompt NO. The biodiesel surrogates selected for this study are methyl octenoate and methyl octanoate. Methyl octenoate and methyl octanoate were chosen because the eight carbon chain (including the carbon with the double bonded oxygen atom) has the length long enough to be representative of the methyl esters present in biodiesels[1] and also reflects the fact that all naturally occurring fatty acids from which the ester is made are of even carbon number, in this case 8. These two methyl esters also have long enough hydrocarbon tails to influence NO production in the way observed in engines yet short enough to have significant vapor pressure (about 20 torr at approximately 100ºC[2]) at the operating temperatures of the heated shock tube.

Pyrolysis studies on n-heptane, 1-heptene, and 1,6-heptadiene, akin to the saturated and unsaturated C_7 alkyl side chain, have been conducted on the UIC high pressure shock tube at nominal reaction pressures of both 25 atm and 50 atm and nominal reaction times of 2.2 milliseconds.



Methyl Octanoate ($C_9H_{18}O_2$) Methyl *trans*-2-octenoate ($C_9H_{16}O_2$)

Figure 1: Surrogate Fatty Acid Methyl Esters

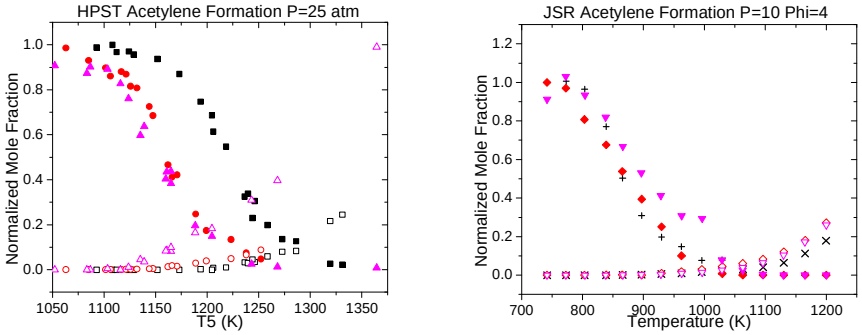
These experiments have, thus far, have illustrated 2 main points: an increase in the degree of unsaturation corresponds to an increase in the acetylene formation and the reaction high pressure limit has been reached by 25 atm since there is no appreciable difference in the experimental data experimental data gathered at nominal reaction pressures of 25 atm and 50 atm. Oxidation experiments have also been performed with the same C_7 fuels on a Jet Stirred Reactor to compare with the data gathered from the HPST.

Under the current NSF award and the supplementary NSF-IREE, an award to promote international research cooperatives and expose young researchers to other researching cultures, a PhD student from UIC, Stephen Garner, was sent to a CNRS laboratory in Orleans, France. Under the guidance and sponsorship of Dr. Philippe Dagaut complementary fuel rich oxidation experiments (Φ=4) were conducted in a jet stirred reactor (JSR) at a nominal reaction pressure of 10 atm and at much longer reaction times of 500 milliseconds when compared the HPST experiments. The oxidation experiments conducted at CNRS have served to support the experimental data gathered from the HPST laboratory at the University of Illinois at Chicago which indicate that an increase in the degree of unsaturation can be correlated to an increase in acetylene formation. The ability of the JSR lab at CNRS in Orleans to perform the complementary studies and support the findings from the HPST lab made CNRS a logical choice.

CNRS, Centre National de la Recherche Scientifique is composed of 2 national laboratories and 6 academic departments whose mission is to evaluate and carry out all research capable of advancing knowledge and bringing social, cultural, and economic benefits to society. To that end CNRS actively participates in the analysis of the national and international scientific climate by having 85 exchange agreements with 60 countries, 55 international research groups and 268 international programs for scientific cooperation.

RESEARCH ACTIVITIES AND ACCOMPLISHMENTS OF THE INTERNATIONAL COOPERATION

High pressure shock tube pyrolysis experiments were performed at the UIC High-Pressure Shock Tube (HPST) facility on the pure fuels n-heptane, 1-heptene, and 1,6 heptadiene (P=25-50 atm, t_{rxn} = 1.3-2.7ms). A detailed description of the shock tube apparatus can be found in prior publications[3,4]. Under the current NSF award and the supplementary NSF-IREE award complementary fuel rich oxidation experiments (P=10 atm, $t_{resonance}$ = 500ms, Φ=4) have been conducted on the same fuels utilizing the JSR at CNRS in Orleans, France. A detailed description of the experimental apparatus can be found in a previous publication[5]. The oxidation experiments conducted at CNRS during the IREE exchange have served to support the experimental data gathered from the HPST at the University of Illinois at Chicago that indicate an increase in the degree of unsaturation can be correlated to an increase in acetylene formation. Figures 2a and 2b illustrate this point clearly.



(a) **(b)**

Figure 2

Acetylene formation from C_7 fuels experiments on HPST (pyrolysis) and JSR (oxidation)

■ **n- C_7H_{16}** ● **1-C_7H_{14}** ▲ **1,6-C_7H_{12}** ✚ **n- C7H16** ♦ **1-C7H14** ▼ **96.4% n-C7H16 + 3.6% 1,6-C7H12**

All open symbols represent the acetylene formation from their respective solid symbol fuels

Figure 2a shows that acetylene formation is higher from the diene with n-heptane producing the least amount of acetylene at any given temperature and this same trend was reproduced by the JSR oxidation experiments and can be seen in figure 2b. The results from the JSR experiments will aid in the development and validation of a chemical kinetic model that is to be developed the University of Illinois at Chicago in the HPST lab under the current NSF award.

The JSR experiments, made possible through the international cooperation funded under the NSF-IREE award, enabled the oxidation study of biologically derived diesel fuels at relatively longer resonance times and lower pressures compared with the UIC HPST thus

providing possible insight into chemistry that could not be seen on the time scales of the HPST experiments. This insight will aid in the development and validation of the kinetic model as well as server as an additional constraint. The complementary JRS oxidation studies were made possible through the positive interactions between Stephen and CNRS.

There was much interaction between the researcher, Stephen Garner, and members of ICARE and CNRS laboratories. Regular meetings between Stephen, the project director Dr. Philippe Dagaut and senior research engineer Dr. Sandro Gail served to structure the research path and facilitated the achievement of the research goals. In addition to the planned research that was conducted on the JSR, Stephen was able to have a shared research experience on a shock tube conducting ignition delay studies with a fellow, French, PhD student Thomas Dubois. At the culmination of the exchange program Stephen presented his research to the faculty and students of CNRS as well as visiting faculty from UIC.

In addition to the regular meetings between Stephen and the members of ICARE many meeting were held between his advisor, Prof. K. Brezinsky, and senior research engineer Dr. R. Sivaramakrishnan from UIC. The meetings, which took place at the CNRS laboratory, between Stephen, Prof. Brezinsky, Dr. Sivaramakrishnan, Dr. Gail, and Dr. Dagaut ensured the development of the research methodology, gas chromatographic methods for the separation of stable species, and also provided solutions and educational explanations for the problems that inevitably arise in the course of scientific research. These international collaborative meetings were vital to the success of the IREE exchange and the scientific research.

BROADER IMPACTS OF THE INTERNATIONAL TRAVEL

Under the IREE travel award Stephen Garner, a PhD student from the University of Illinois at Chicago traveled to the CNRS laboratory in Orleans, France to continue his thesis research on biodiesel surrogates. During his three month visit from May through August 2007 he lived in downtown Orleans not far from the city center. There he was able to experience French culture which aided him in better understanding the differences that exist between the American and French research environments.

While living and working in France, Stephen was able to attend many cultural festivals as well as scientific seminars. All the scientific seminars and thesis defenses attended were conducted in French and at first were difficult comprehend. Prior to arriving at Orleans, Stephen had prepared for his stay by taking a university level course in introductory French. However, when Stephen arrived he spoke little French but during the course of his stay, through help from both friends and cultural immersion, he was able to speak and hold conversations almost entirely in French by the culmination of his stay. This preliminary step of cooperation and cultural exchange between the University of Illinois at Chicago and the CNRS laboratory in Orleans is just the beginning of what hopes to be a long and productive relationship.

The cooperation between Institute for Combustion, Aerothermics, Reactivity, and Environmental sciences, ICARE, at CNRS in Orleans and the HPST laboratory at UIC has a natural synergistic relationship. The capabilities of the individual labs complement each other well in addition to their similar research interests. This synergistic and cooperative relationship can be further illustrated by the UIC HPST laboratory hosting Thomas Dubois, a PhD candidate, from ICARE who is also an employee of the French petroleum company Total.

DISCUSSION AND SUMMARY

The international cooperation and experience awarded by the IREE grant has helped to foster international scientific exchanges as well as inter-institution research collaboration. The international collaboration has yielded many accomplishments. A significant scientific accomplishment, from the point of view of the original NSF biodiesel award, is the further validation of the original hypothesis that an increase in the degree of unsaturation can be correlated to an increase in acetylene formation at practical combustion conditions. The data gathered through the cooperation of ICARE at CNRS will serve to further constrain the chemical kinetic model to be developed under the original grant as well as broaden the experimental spectrum of the project. Through cooperation, originally fostered by the NSF-IREE award, an international and inter-institution scientific and cultural collaboration and exchange has been initiated that advances the international scientific community through both cultural and scientific exploration.

Some recommendations for possible improvements to the current IREE program include providing support for language and culture learning courses both prior to and also during the foreign stay. Part of the cultural learning could stem from interactions between past and current IREE program participants and could be achieved through the creation and dissemination of a database or contact list of other young researchers who had been part of the IREE program. To initiate and maintain a relationship between the host institution and the IREE awarded university, funding should be provided for the faculty advisors to spend sabbatical leave at the institution where students have been and will be spending their IREE stay. Also, one of the goals of the IREE program is to promote an ongoing scientific and cultural collaborative experience and to that end the exchange should not just be a singular experience. Future IREE awards should incorporate financing for short term follow up “booster” visits for both students and faculty advisors.

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BRIEF BIOGRAPHIES OF RESEARCHERS

Kenneth Brezinsky received his B.S. (*magna cum laude*) with honors in Chemistry from City College of C.U.N.Y. He received his Ph.D. in Physical Chemistry, The City University of New York. After completion of his Ph.D, he became a research scientist in the Department of Mechanical and Aerospace Engineering at Princeton University. He then moved to the University of Illinois at Chicago where he is a professor of Mechanical Engineering and studies gas phase shock tube chemical kinetics.

Raghu Sivaramakrishnan received his B.S. with honors in Chemical Engineering from the University of Madras, India. He received his M.S and Ph.D. in Chemical Engineering from the University of Illinois at Chicago. He was recently awarded the Bernard Lewis Fellowship by the Combustion Institute in 2006. His current research focuses on determination of elementary reaction rate coefficient.

Stephen Garner received his BS in Mechanical Engineering from the University of Illinois at Chicago in 2006. He has been a member of the UIC High Pressure Shock Tube group since 2005 and began his thesis research on biodiesel surrogates in 2006.