Hydrogen Enrichment Via Chemical Recuperation to Increase Efficiency and Reduce Emissions in Engines

David Vernon

Introduction:

With internal combustion engines the majority of the chemical energy held in the original fuel is exhausted as waste heat rather than being converted to useable work. This represents a significant potential source of energy if this currently wasted energy can be harvested effectively. One method of harvesting this energy is using it as a thermal source of energy to upgrade the original fuel. Hydrogen rich gas can be produced from this exhaust heat and such an upgraded fuel can be burned in the cylinder with simultaneous benefits of increasing efficiency as well as reducing emissions by enabling low temperature combustion regimes.

Hydrogen Enriched Compressed Natural Gas (HCNG) has recently attracted attention as a fuel for internal combustion engines enabling extremely low NOx emissions without exhaust aftertreatment. HCNG allows engines to utilize high charge dilution (air rich operation or EGR) which can significantly increase engine efficiency with the simultaneous benefit of low NOx operation. Recent results using HCNG have been promising showing large efficiency increases (>15%) over stoichiometric CNG operation while enabling low NOx levels [1, 2, 3, 4]. Current liabilities of the HCNG system are the onboard storage of the fuel mixture and the lack of current facilities and infrastructure to deliver such a mixture.

The impediments to HCNG use can be overcome and the benefits of HCNG and waste heat recovery can be achieved by chemically recuperating the exhaust of the internal combustion engine to upgrade CNG to a HCNG mixture. Demonstration of this concept using the chemical recuperation system in a heavy duty internal combustion engine has taken place at Collier Technologies. However, the characteristics of the hydrogen producing chemical recuperator using the exhaust heat are not well understood and this currently prohibits high throughput operation [5]. There is an obvious need for further characterization of the hydrogen producing device.

We plan to characterize the hydrogen generation process utilizing waste heat from exhaust gases. In addition we plan to explore the application of the chemical recuperation process to internal combustion engines using liquid fuels with an initial focus on ethanol. This work aims to increase fundamental understanding regarding chemical recuperation and the effects of hydrogen on combustion processes. This knowledge can enable future development of chemical recuperation technologies. In cooperation with the Challenge X team it may be possible to demonstrate this technology in conjunction with the hybrid concepts currently being investigated. This fundamental scientific research coupled with applications focused vehicle research programs offers a unique opportunity to both advance the state of knowledge surrounding hydrogen production as well as educate industry and the public about near term application for hydrogen in transportation.

Research Questions:

- Can hydrogen enrichment be applied to liquid hydrocarbon fuels in internal combustion engines?
- What is the most effective pathway for generating hydrogen for hydrogen enrichment?
- What are the synergies between hydrogen enrichment and chemical recuperation?

Overall Research Goal:

Increase fundamental understanding regarding chemical recuperation and the effects of hydrogen on combustion processes. This fundamental investigation will be carried out keeping in mind its value to future development of chemical recuperation technologies.

The addition of applications driven systems engineering/research to validate the modeling and fundamental parametric experiments will add significant value to this effort and help to ensure it's applicability to real world vehicles.

Expected Contributions:

Contributions from any research work come in the context of surrounding efforts. This work constitutes completely original research building upon past work in reformation and hydrogen enrichment both here at UC Davis as well as at partner universities and private companies.

Reformation technologies including both steam reformation and autothermal reformation have a rich literature. Reformation using heat from exhaust gases and or directly mixing exhaust gases in the reformer have been investigated to a much more limited extent. Previous and current work in this area has been spearheaded by Professor Wyszynski at the University of Birmingham. In Wyszynski's seminal papers natural gas and gasoline reformation have been explored theoretically with some fundamental experimental work [6,7,8]. No fully operational system has been investigated utilizing the waste heat from the engine being supplied with enriched fuel. In contrast Collier Technologies have demonstrated a closed-loop system but has done so with a focus on development as opposed to garnering fundamental understanding of the process [5]. The gap between the early fundamental work and the technology demonstration leaves a rich area of research to be explored here at UC Davis in cooperation with both of these partners. The Hydrogen Production and Utilization Laboratory is uniquely suited to investigate the effects of scale and geometry on the chemical recuperation process. Utilizing the extensive reactor and data acquisition infrastructure many investigations can be carried out with minimal further investment in equipment.

Hydrogen enrichment of gaseous and liquid fuels has become a topic of particular interest. Fundamental chemistry investigations of the effect of hydrogen enrichment on flame characteristics and internal combustion processes have shown that hydrogen enrichment can greatly extend the lean limit and dilution limit of many different fuel mixtures [9]. This extension of the lean and dilution limits enables advanced combustion regimes with low combustion temperatures [1, 2, 3, 5, 10]. In actual applications of HCNG these advanced combustion regimes with low combustion temperatures produce much lower NOx emissions, as much as a 90 to 98% reduction, and can increase the thermal efficiency of the engine by 10 to 20% [1,2,3,4,5]. UC Davis is at the forefront of research in HCNG applications through the active research program under Marshall Miller investigating the benefits of HCNG in transit buses. This HCNG program is also in cooperation with Collier Technologies who have expertise in developing engines for HCNG applications. Much less work has been done investigating the use of hydrogen rich gases or reformate streams to enrich fuel mixtures for internal combustion engines. Leveraging our expertise in reformation process testing and our developed infrastructure for engine testing in the Hybrid Electric Vehicle Center we have a unique opportunity to further this diverse area of study with minimal expense. There are virtually no other laboratory groups world-wide who have the necessary combination of fundamental reformer expertise and engine expertise to approach this topic. Combining this fact with our active Challenge X program where it may be possible to demonstrate early stages of the chemical recuperation technology we have a historic opportunity to bring hydrogen into vehicle application in the near term, paving the way for future hydrogen applications in transportation.

Support of FCH2V Center Goals:

This work directly supports the broad vision of the FCH2V Center by enhancing the thermodynamic efficiency of internal combustion engines including those used in hybrids. Furthermore hydrogen enrichment has the capacity to enable power capability under all environmental conditions with ultra-low emissions. This technology is an important step on the path to increasing internal combustion engine efficiency up to 45 percent or higher. This technology can be used in hybrid or conventional vehicles and may eventually be used with advanced combustion technologies such as Homogeneous Charge Combustion (HCCI) or to supply hydrogen for fuel cell vehicles.

By leveraging the well developed infrastructure of the HyPAUL, HEVC, the well established network of hydrogen researchers and the close cooperation of industrial partners this project can make significant contributions with the relatively low cost student support. By funding current efforts in this area a larger program of research is being initiated that will continue to produce not only gains in fundamental knowledge but well trained, creative engineers with a thorough understanding of both fundamental science as well as the process of applying this knowledge to vehicle applications. Producing leaders for the broad application of hydrogen to transportation will be one of the largest impacts of this work.

By supporting near term applications of hydrogen in existing vehicles this work may help to provide a bridge to hydrogen based transportation. In the long run the hydrogen production devices developed in this project will help to reduce costs, reduce complexity and increase reliability of hydrogen production devices that could be used to supply hydrogen for the hydrogen economy and fuel cell vehicles. This early stage niche of supplying hydrogen for combustion processes allows development of these technologies in a much more forgiving area where critical parts of the technology can be brought to maturity before making the further refinements necessary to supply hydrogen for fuel cells. The daunting complexity of systems to supply hydrogen for fuel cells has been a major deterrent to continued inclusion of reformer systems in fuel cell vehicle demonstrations. By developing the base systems in this niche we can lay the groundwork for future applications with more stringent requirements.

Research Methodology:

Thermodynamic modeling of both the hydrogen production process and the enriched combustion process as well as a systems level modeling approach will provide insight into the research and development path for this technology. Modeling will be accomplished using a combination of MATLAB/Simulink, LabVIEW, Motohawk motor controller software packages and may utilize specialized thermodynamic modeling software including CATT2 and ChemWorks.

These modeling efforts will be validated empirically using Statistical analysis of factorial experiments. These experiments will investigate the effects of the factorial inputs upon the metrics of performance in both the reformation process as well as the internal combustion process.

Factorial Experiments		
	Autothermal Reformation	Reformate Enrichment
Metrics for Comparison	Efficiency	Flame stability
	Hydrogen production rate	Efficiency
		Emissions
Factorial Inputs	Temperature	Hydrogen concentration
	Steam to carbon ratio	Air to fuel ratio
	Oxygen to carbon ratio	Speed (RPM)
	Flow rate	Torque
		Spark Timing

As our understanding of the fundamental processes develops the feasibility of a closed loop system will be investigated with a view towards future applications. This systems level research can help to bridge the gas between university fundamental research and applied research in the private sector.

With the unique opportunity to take advantage of ITS expertise we will be able to incorporate an understanding of both the regulatory environment surrounding these technologies as well as pay attention to the economic potential of these ideas. As part of the literature search I plan to stay current on developing regulations that affect the demand for NOx reduction technologies. I also plan to develop a preliminary economic model looking at the cost of materials for the system versus the expected fuel savings.

Literature Review:

I have already done a significant review of the literature surrounding reformation technologies as well as hydrogen enrichment in internal combustion engines. I plan to continue this review over the course of this project. The following section is taken directly from a paper that Professor Erickson and I prepared for the 2005 NHA conference. Please see the bibliography at the end of this document for reference papers.

With internal combustion engines the majority of the chemical energy held in the original fuel is exhausted as waste heat from the cylinders rather than being converted to useable work. This represents a significant potential source of energy if this currently wasted energy can be harvested effectively. One method of harvesting this energy is using it as a thermal source of energy to upgrade the original fuel [11]. Hydrogen rich gas can be produced from this exhaust heat and such an upgraded fuel can be recirculated to the cylinders with simultaneous benefits regarding efficiency, low temperature combustion and lower emissions. Potentially, closed-loop chemical recuperation technologies could be implemented on a wide range of internal combustion engine sizes, applications, and fuel types.

For example, Hydrogen Enriched Compressed Natural Gas (HCNG) has recently attracted attention as a fuel for internal combustion engines enabling extremely low NOx emissions without after-treatment. Because of the favorable combustion characteristics of hydrogen, HCNG allows engines to utilize high charge dilution (fuel lean or high exhaust gas recirculation operation) which can significantly increase engine efficiency with the simultaneous benefit of low NOx operation [1, 2, 3, 9, 10, 12, 13]. Recent results using HCNG have been promising showing large efficiency increases (>15%) over stoichiometric CNG operation while enabling low NOx levels. Figure 1 representing the level of NOx output for hydrogen concentration and equivalence ratio is shown below [1,2]. Optimal concentrations of hydrogen seem to be near 30% [1]. Higher concentrations allow further reductions in NOx but diminishing overall benefits because of the difficulties of storing the hydrogen fuel.

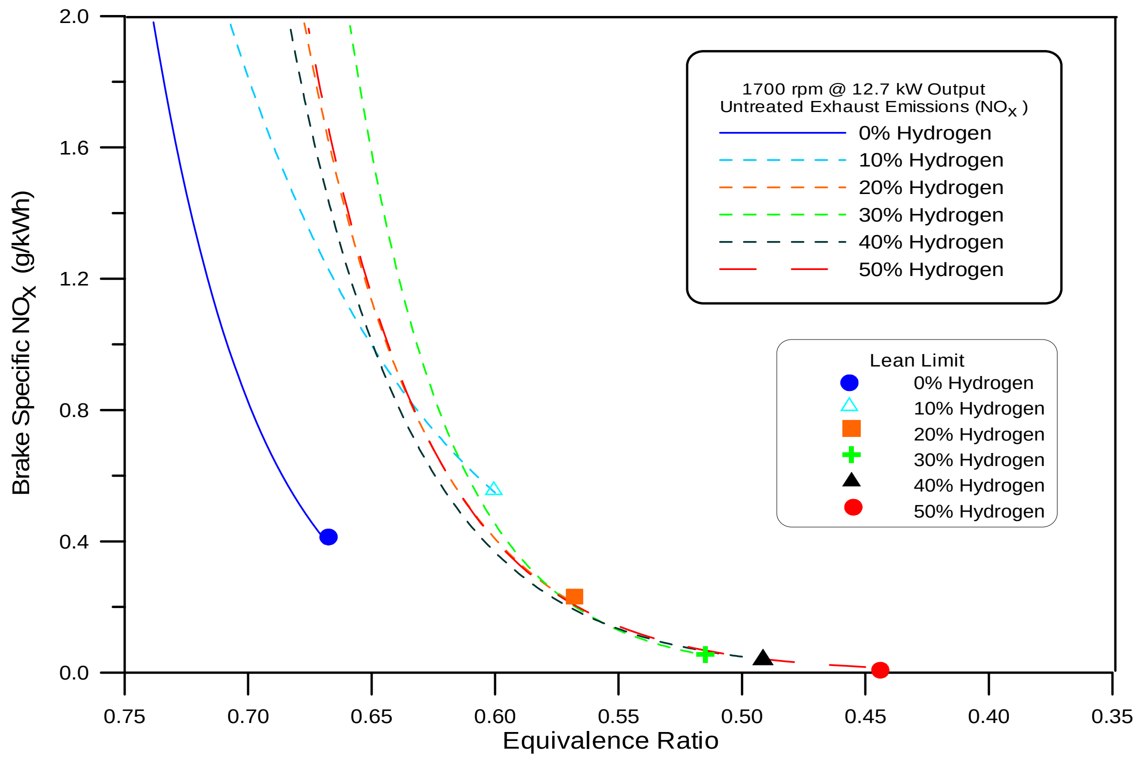

Figure 1 NOx emissions as a function of Equivalence Ratio with lean limits for various CNG H2 mixtures [1]

Current difficulties with the HCNG system are the onboard storage of the fuel mixture and the lack of current facilities and infrastructure to deliver such a mixture. The difficulties of HCNG can be overcome and the benefits of HCNG and waste heat recovery can be joined by chemically recuperating the exhaust of the internal combustion engine to upgrade CNG to a HCNG mixture on-board as the mixture is needed.

A schematic of the process is shown in Figure 2 below.

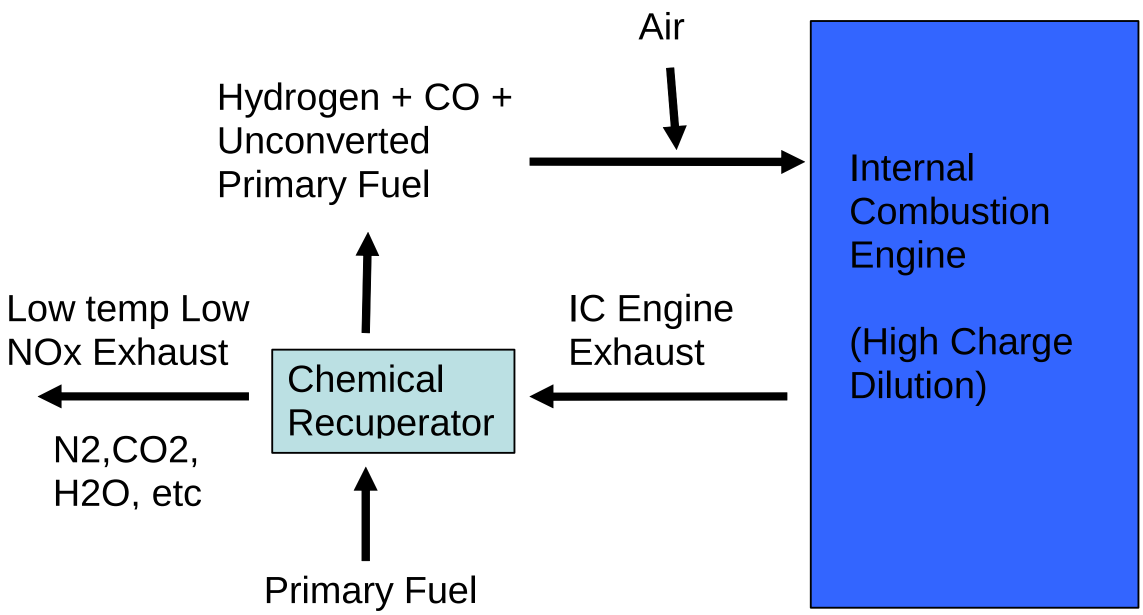

Figure 2 Schematic of a chemical recuperation process.

Note that the system is effectively a typical internal combustion engine yet creates a hydrogen rich gas mixture from the exhaust heat and exhaust products which is then burned. The generated hydrogen enables high charge dilution operation which results in lower emissions for the internal combustion engine in a similar way to the previously discussed HCNG operation. The following examples represent the current state of the art regarding this concept.

Demonstration of efficient operation using the chemical recuperation system in a heavy duty internal combustion engine has taken place at Collier Technologies. However, the characteristics of the hydrogen production device using the exhaust heat are not well understood and this currently prohibits high throughput operation. Preliminary testing has been performed on an 11L Daewoo natural gas engine at Collier Technologies. The catalyst in the chemical recuperator is a Johnson Matthey Autothermal Reformation (ATR) catalyst of proprietary formulation. A single exhaust port is dedicated to the recuperation process which simultaneously generates hydrogen and provides exhaust gas recirculation. This configuration, in combination with the EGR results in less than 10ppm exhaust gas NOx emissions. At low power settings, the resultant fuel composition is approximately 60% H_2, 11% CO, and 29% CH_4 by volume. As engine output power increases, the ratio of hydrogen to methane decreases. At 100 kW output, the composition changes to approximately 28% H_2, 8% CO, and 66% CH_4 by volume. At power levels above 100 kW, the hydrogen content falls below the concentration necessary to support the level of charge dilution required for low NOx operation. This example provides two vital pieces of information.

1. The proposed cycle is technically viable.
2. The chemical recuperation process needs to be further understood before high throughput can be expected.

Other types of fuels are also similarly affected by the use of hydrogen in the internal combustion process. The following examples are those of using hydrogen enriched combustion with liquid fuels without generating the hydrogen from the exhaust energy in the "closed loop" as described above.

A research group at the University of Birmingham in the United Kingdom has demonstrated the hydrogen-enrichment concept using a variety of gasoline and diesel fuels. Their experiments have shown a significant increase in efficiency along with a great reduction in both NOx and Hydrocarbon emissions. They have also assembled a system that utilizes the exhaust gases to help reform the fuel. However, they have not been able to overcome the losses associated with the reformation process. Therefore, they have not been able to demonstrate a closed loop system. In their experiments with hydrogen enriched gasoline, tests have shown as much as a 20% increase in thermal efficiency for the internal combustion engine. Other results show a 10 % reduction in fuel consumption combined with large reductions in NOx emissions [6].

Many questions concerning the viability of the concepts have been answered by these preliminary tests. First with the closed loop system by Collier, it has been shown that exhaust gas compositions and temperatures commensurate with extremely low NOx operation will produce sufficient hydrogen to support continuous closed loop operation. Secondly, the system is stable. Perturbations in the normal operation of the engine under load do not create changes in fuel composition that upset that balance. In regards to open-loop liquid fuel systems, hydrogen-enrichment with various liquid fuels is proven and practical. These are important results. Now, the major practical question is: How does one increase the power output of the engine to its full rated output without the hydrogen content of the reactor falling too low? The goal of this project is to answer that question and also how the closed–loop concept might be applied to liquid hydrocarbon fuels including alcohol mixtures.

Further development is limited by this lack of understanding regarding chemical recuperation using exhaust heat. The proposed project directly addresses this need for greater understanding of the hydrogen production step and the implications of using exhaust heat in such a system. Furthermore, the team will work toward optimizing the design of the hydrogen production device and integrate it into an internal combustion engine system. The proposed project intends to fill the basic and fundamental knowledge gaps regarding the technology and to assist in further proving the technology at the required throughputs. In the proposed project several fuels will be researched through literature review including CNG, Gasoline, Diesel and Alcohol Fuels. Experimental work will focus on understanding the process using liquid fuel mixtures.

Timeline and Deliverables:

Please see the attached GANNT chart for an overview of the project timeline. Deliverables, including the quarterly reports, are described in the GANNT chart.

Interim Publications:

Professor Erickson and I in cooperation with Kirk Collier and Neal Mulligan from Collier Technologies, have already presented a paper outlining this project titled "LOW NOx OPERATION AND RECUPERATION OF THERMAL AND CHEMICAL ENERGY THROUGH HYDROGEN IN INTERNAL COMBUSTION ENGINES" for the 2004 NHA conference [5]. I plan to publish two papers related to this work in the near future "Heat Transfer Limitations in Steam Reformation of Methanol for Hydrogen Production" and "Control of Steam Reformer Systems for Hydrogen Production". In continuation of this project

I plan to publish three background review papers, a review of chemical recuperation technologies for small scale applications, a review of hydrogen enrichment for internal combustion engines and a discussion of near term applications for hydrogen on-board vehicles. As this project progresses I plan to publish papers describing the thermodynamic and systems modeling results and then publishes papers describing the experimental results and their relationship to the model predictions. There are many different journals and conferences where these papers could be published including the Society of Automotive Engineering, National Hydrogen Association Conference, the International Journal of Hydrogen Energy, the Journal of Power Systems, The Journal of Applied Energy, and The Journal of Energy Conversion and Management.

Interaction with other researchers:

Due to the diverse nature of this investigation interaction with many different researchers will be very valuable. Below is a brief list of researchers that I expect to interact with in the course of this work.

Professor Erickson – Oversees HyPAUL as well as faculty advisor for Challenge X team
Eddy Jordan – Cooperating on the hydrogen enrichment in engines work
Mat Caldwell – Currently investigating Autothermal reformation of Ethanol
Kurt Kornbluth – Investigating use of hydrogen production from landfill gas (LFG) with possibility of utilizing the hydrogen for LFG enrichment in engines
Marshall Miller – Leading current HCNG transit bus studies
Kirk Collier and Neal Mulligan – Collier Technologies managers overseeing HCNG engine development and chemical recuperation project
Professor Dwyer – Developing advanced combustion models
Professor Andy Frank – Faculty advisor to the Challenge X team, working to understand the possible benefits of hydrogen enrichment and chemical recuperation in hybrid vehicles
Andy Burke – interested in the potential efficiency increases for ICEs
Professor Wyszynski – Primary investigator for exhaust gas reformation and hydrogen enrichment work at the University of Birmingham, Future Transportation Laboratory
Jay Keller – Sandia National Laboratories Group Leader, working in hydrogen combustion and advanced combustion engines such as HCCI
Dennis Schutzle - Biofuels and bio-alcohols

Possible corporate partners

Hess Microgen – manufacturer of ICE based stationary generators, very interested in chemical recuperation technology due to reduction in emissions and efficiency improvements
TIAX – currently investigating hydrogen enrichment of LFG and LFG reformation

Personal Education Plan:

I am pursuing a Ph.D. in Mechanical Engineering, expected May 2008, Advisor Professor Erickson. This project forms the basis of my dissertation research and will continue for the next two to three years. Over this time period I plan to continue developing my background in thermodynamics, combustion processes and chemical reactor design. In addition to the standard mechanical engineering courses I have taken courses in Chemical Engineering Kinetics to lay the foundation for understanding chemical reactors (ECH 156A and ECH 156B). I have also taken other FCH2V elective courses such as EMS 244, MAE 218, TTP 289B “Hydrogen Economy Journal Review”, TTP 289B “Hydrogen Pathways Research seminar”, and MAE 258.

Over the nine months of this fellowship I plan to take the two MAE combustion courses “Combustion and the Environment” and “Internal Combustion Engines and Future Alternatives”. I am also interested in several of the other FCH2V elective courses including “Fuel Cell and Hydrogen Systems”, “EV Energy Storage and Conversion Technologies”, “Modern Power Systems”, “Engineering of Alt-Fuel Vehicles/Emissions Control”. I look forward to opportunities to help develop the FCH2V center curriculum and plan to take and or help teach these courses when they are offered.

Advisors and Knowledge Contacts:
Professor Erickson – Major advisor and expertise in reformation processes
Eddy Jordan – Expertise in engine control and testing
Mat Caldwell – Autothermal reformation of Ethanol
Marshall Miller – Expertise in HCNG engine performance and regulatory environment
Kirk Collier and Neal Mulligan – Expertise in HCNG engine development
Andy Frank – Expertise in hybrid vehicle design
Andy Burke – interested in the potential efficiency increases for ICEs
Professor Wyszynski – Expertise in exhaust gas reformation and hydrogen enrichment
Jay Keller – Expertise in hydrogen combustion and advanced combustion engines
Dennis Schutzle - Biofuels and bio-alcohols
Frank Lynch – Hydrogen engine developer, Inventor of Hythane
Pacific Northwest National Laboratory – Expertise in compact reformer reactor design

References

1. Collier K., "HCNG, the Proven Low Emissions Technology for Internal Combustion Engines,", 2004 Indian International SAE Conference, New Dehli India, October 2004, paper number 082. 2004
2. Collier, et. al., "Untreated Exhaust Emissions of a Hydrogen-Enriched CNG Production Engine Conversion", SAE 960858, International Congress & Exposition, Detroit MI, February 26-29, 1996.
3. Collier, R.K., Hydrogen Natural Gas Blends, Final Report, U.S. Department of Energy Contract # FC36-966010172.
4. Collier, R.K., Hydrogen Natural Gas Blends, Final Report, U.S. Department of Energy Contract # FC36-966010172
5. Erickson, P., Vernon, D., Jordan, E., Collier K., Mulligan, N., "LOW NOx OPERATION AND RECUPERATION OF THERMAL AND CHEMICAL ENERGY THROUGH HYDROGEN IN INTERNAL COMBUSTION ENGINES", Proceedings of the 16th Annual Hydrogen Conference of the National Hydrogen Association (NHA) April, 2005 Washington, D.C.
6. Jamal, Y., Wyszynski M. L., "On-Board Generation of Hydrogen-Rich Gaseous Fuel – A Review", International Journal of Hydrogen Energy, 19, No. 7, pp. 557-572, 1994.
7. Jamal, Y., Wyszynski M. L., "Exhaust Gas Reforming of Gasoline at Moderate Temperatures", International Journal of Hydrogen Energy, vol. 21, No. 6, pp. 507-519, 1996.
8. Peucheret, S., Wyszynski, M.L., "Use of catalytic reforming to aid natural gas HCCI combustion in engines: experimental and modeling results of open-loop fuel reforming", International Journal of Hydrogen Energy, vol. 30, pp. 1583-154, 2005.
9. Shefer, R.W., "Hydrogen enrichment for improved lean flame stability", International Journal of Hydrogen Energy, 28, (2003), pp. 1131-1141.
10. Shudo, Nakajima, "Combustion and emissions in a methane DI stratified charge engine with hydrogen pre-mixing," Society of Automotive Engineers of Japan, vol. 21, pp3-7, 2000
11. Nakagaki, et. al., "Development of methanol steam reformer for chemical recuperation," presented at the American Society of Mechanical Engineers, Fuels and Combustion Technologies Division (Publication) FACT. v 23 n 1 1999. ASME, Fairfield, NJ, USA. p 569-576
12. Lynch, et. al., U.S. Patent # 5,139,002
13. Collier, et. al., U.S. Patent # 6,508,209
14. Dorr, "ATR Reaction Progression" Masters Thesis UC Davis, 2004