

Texas A&M AgriLife Research Air Quality Research Program FY 2014-2015

Title: Photo-catalytic destruction of Methane (and Volatile Organic Compounds) at Room Temperature

Principal Investigator: Sandun Fernando, Ph.D., P.E.

Amount Requested per year: \$92,176 FY 2014; \$95,841 FY 2015

Executive Summary

Identified Need in Texas Agriculture: According to US-EPA, methane (CH₄) is a highly potent greenhouse gas with a comparative impact on climate change over 20 times greater than CO₂. In Texas, livestock feedlots and chicken farming operations contribute significantly to methane emissions. Due to the nature of the spatial distribution of generating sources (surfaces of feedlots, open manure storage ponds, etc.) a significant fraction of this methane is directly released into the atmosphere. Methane emissions are mandated to be reported to monitoring agencies and due to the highly destructive potential to the environment, there is a high probability for this gas to be regulated in the future. Therefore, it is of paramount importance to develop techniques to mitigate (non-point source) methane emissions.

One of the most significant challenges when developing an abatement strategy is the inability to activate methane at low temperature. Due to its high thermodynamic stability, methane needs temperatures in excess of 400°C to overcome the activation energy barrier to initiate a reaction. Providing such a high-temperature environment is impractical when the (methane) sources are physically spread out. **Accordingly, the overall goal of this seed proposal is to develop a catalytic process that can oxidize and disintegrate methane (including reactive and odor-producing volatile organic compounds (VOCs)) at room temperature using sunlight (instead of heat) as the energy source.**

A catalyst is a material that significantly increases the rate of a particular chemical reaction by re-routing the reaction via a less energy-intensive pathway (A good example is the three-way catalytic converter in an automobile which disintegrates harmful NO_x, CO and unburned hydrocarbons to N₂, O₂, CO₂ and H₂O with a fraction of the energy required if these reactions were carried out without a catalyst). Photo-catalysts (that include TiO₂ and numerous metal sulfides) can perform such reactions using light as the energy source (instead of heat energy) and drive these kinetically “unfavorable” reactions at low temperature. Proposed research will attempt developing a catalytic material (in powder or granular form) once spread over methane sources (such as surfaces of manure collection areas or open ponds etc.), will oxidize and disintegrate methane into less harmful forms (like methanol or CO₂).

Research Approach and Expected Deliverables: With the intention of developing a scalable and farm-adoptable technology, following specific Objectives will be pursued:

1. Rapid Screening of photo-active materials for catalyzing methane activation/oxidation using sunlight.
2. Optimizing the performance of select catalysts for agricultural use.

It is expected that this work will result in a potent catalyst that can activate and disintegrate methane at room temperature. Studies will reveal the level of activity of the catalyst(s) toward methane conversion and selectivity toward specific product species (i.e., methanol, other oxygenates or CO₂) as a function of numerous system variables. The attractiveness of this technology is that with relative ease, the catalysts can be modified to react and oxidize other select organics from reactive and odor-producing volatile organic compounds (VOCs). This is because once the technology to activate/oxidize methane (the most thermodynamically stable and thus unreactive) is perfected; the knowhow will be available to handle the more reactive forms. With the seed funds, it is anticipated to collect proof-of-concept data that will be leveraged to attract competitive funding from EPA, USDA (NIFA) or NSF (Environmental Engineering or Catalysis and Biocatalysis Program). PI has already an ongoing methane activation project funded by NSF (Energy for Sustainability Program) using high-temperature (non-photocatalytic) catalysts.

Proposal narrative:

Overview and objectives:

Methane (CH_4) is a highly potent greenhouse gas with a comparative impact on climate change over 20 times greater than CO_2 (on a weight basis)¹. The major sources of methane in the US include industrial, agriculture and waste disposal

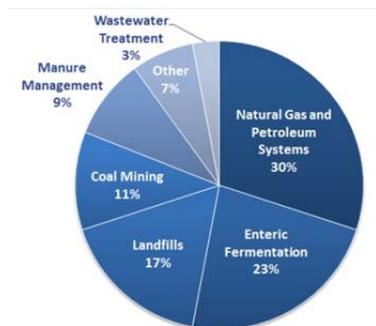


Figure 1: Methane emission estimates from the [Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2011](#).

(Figure 1). Inventory of U.S. Greenhouse Gas Emissions and Sinks (1990-2011)² estimates that 60% of the methane emissions are due to human activities of which agriculture sector is the largest contributor³. It is unfortunate that while emissions from industrial sector (from the exploration and production of natural gas and petroleum products) decreased during this time period, those associated with agricultural activities increased⁴ – and this is a significant problem!

If effectively collected, methane can be easily oxidized at high temperature to carbon dioxide (while indeed using the exothermic energy for energetic purposes)^{5,6}. However, due to the non-point nature of the sources in a typical farm setting (such as manure scattered across ground surfaces or accumulated in large-surface-area storage ponds), it is impractical or too expensive to capture a large portion of the released methane⁷⁻⁹. Moreover, dilute methane is not suitable as a combustion fuel and needs to be destructed via catalytic means

– using high temperature.^{10,11} Methane, due to its high thermodynamic stability, needs temperatures well over 400°C to become activated. It is obvious that providing such temperatures over scattered areas are impractical in a farm setting. Sunlight, on the other hand, is a form of energy that is amply available throughout Texas. A chemical process that can activate and destruct methane using solar energy is much pragmatic in a farm setting as compared to using heat energy. Accordingly, **the overall goal of this seed proposal is to develop a catalytic process that can oxidize and disintegrate methane at room temperature using sunlight (instead of heat) as the sole energy source needed to drive the reaction forward.**

A catalyst is a material that significantly increases the rate of a particular chemical reaction by re-routing the reaction via a less energy-intensive pathway. A reaction that usually requires a significant amount of energy and time can progress rapidly with only a fraction of this energy in the presence of a catalyst. Photo-catalysts (that include TiO_2 and numerous metal sulfides) can perform such reactions using light as the energy source (instead of heat) and drive these kinetically “unfavorable” reactions at low temperature. *This research will attempt developing a catalytic material (in powder or granular form) once spread over methane sources (such as surfaces of manure collection areas or open ponds etc.), will oxidize and disintegrate methane into less harmful forms (like methanol or CO_2).*

The **specific objectives** are as follows:

1. Rapid Screening of photo-active materials for catalyzing methane activation/oxidation using sunlight.
Possible catalysts for methane activation will be rapidly screened in a photo-reactor. The initial candidates include dye-sensitized titania and select metal sulfides (i.e., Cd, Co and Ni sulfides)^{12,13} that can absorb the sun’s full spectrum.
2. Optimizing the performance of select catalysts for agricultural use.
Select catalysts from Specific Objective 1 will be evaluated for their performance under various simulated environmental conditions.

The **novelty** of this research is usage of photo-responsive materials that are known to utilize the full spectrum of sunlight (as opposed to only the ultraviolet (UV) spectrum) but have never been tested for practical methane activation/destruction.

Strategies and Methodology

Methane is the most thermodynamically stable hydrocarbon available. The C-H bond requires 439 kJ/mole to break apart and even in the presence of catalysts, requires temperatures well over 400°C to activate. So, in light of these energy requirements, is it possible to activate methane at low temperature? Interestingly, the answer is yes – it is possible to activate methane at room temperature if the catalyst has the ability to provide necessary activation energy in a way alternative to heat. For example, biocatalysts are able to activate methane at much milder conditions using biochemical pathways using ATP as the energy provider. Alternatively, the ability of methanotrophic microorganisms to oxidize methane (initially to methanol using methane-monooxygenase and then all the way to CO₂ using dehydrogenases) is well known in biology.^{14, 15} Similarly, photo-catalysts use light as the energy source to drive the reactions forward and will be the approach attempted in this proposed work.

Although photo-activation studies specifically directed at pure methane at room temperature limited, fundamental studies have shown that C-H bond, in fact, can be disintegrated using photocatalysts at low temperatures using light energy of specific wavelengths (specifically the UV range)¹⁶⁻¹⁸. *In retrospect, this project aims to build on these fundamental studies and engineer a practical and scalable technique to disintegrate methane using visible light as opposed to only the UV range.*

Although many metal oxides that possess semi-conductor properties have photocatalytic effects, the most widely investigated material that can dissociate C-H bonds is titania (i.e., anatase and rutile forms of TiO₂). Semi-conductive materials possess a void energy region (called the band-gap) where no energy levels are available to promote

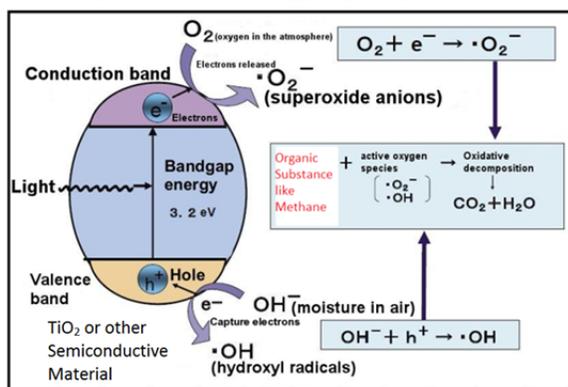


Figure 2: Photocatalysis process in more detail.

recombination of an electron and hole produced by photoactivation. When light falls on these semiconductors, the electron present in the valence band jumps to the conduction band, a result of which is the generation of a positive hole (Figure 2). The excited electrons can react with oxygen in the atmosphere forming superoxide anions (•O₂⁻), and the holes react with moisture in the atmosphere producing hydroxyl radicals (•OH). These active oxygen species are extremely reactive, and oxidize and decompose organic substances. The approach in this instance is to use these highly oxidative hydroxyl radicals to oxidize methane.

What are the gaps in knowledge: In developing a practical strategy to photocatalytically disintegrate methane, several knowledge gaps still exist:

1. It is yet unknown whether readily available photocatalysts (such as dye-sensitized titania, other metal oxides and sulfides that are sensitive to sun's full spectrum) can be engineered to perform the proposed methane disintegration chemistry using visible sunlight (as opposed to ultraviolet light).
2. How can the catalyst and conditions be optimized to render maximum methane activation in a practical agricultural setting?
 - a. What type, form (powder, granules or coatings) and concentrations of catalysts will be the most effective for methane activation in a farm setting?
 - b. What will be the impact of varying conditions (such as light intensity and temperature) on the catalytic performance?

The intent of this proposal to answer above research questions by conducting studies described below:

Specific Objective 1: Screening for photo-active catalysts that can activate and oxidize methane

The objective here is to rapidly screen potential catalysts that are highly selective for methane activation using the visible spectrum of sunlight (Note: photocatalysts that are sensitive only to ultraviolet portion of sunlight has little value for practical applications). Critical variables associated with this process are given in Table 1. To assist rapid screening in this initial study, the variables will be kept to a minimum by via conducting a 2ⁿ factor preliminary study (where select independent variables will be kept only at two levels, i.e., high and low) and others constant.

Table 1: Variables associated with photo-catalytic methane activation.

Variable	Levels	Sp. Objective 1	Sp. Objective 2
Catalyst Type Form Concentration	<ul style="list-style-type: none">Dye-sensitized TiO₂ (anatase, rutile and mixtures), other metal oxides, and metal sulfides.Powder or granular.To be determined (TBD) based on preliminary studies.	<ul style="list-style-type: none">A larger array of catalystsPowerHigh and low	<ul style="list-style-type: none">Select high-performing fewPowder and pelletsA range of levels
Substrate (methane) Concentration Space velocity	<ul style="list-style-type: none">Methane concentrations will be determined based on field data and simulated in the laboratory by mixing pure methane with air.Stagnant and flowing (based on typical field air velocities)	<ul style="list-style-type: none">One select concentration and flow rateConstant flow	<ul style="list-style-type: none">A range of levels based on preliminary dataA range of levels
Conditions Light Wavelength Intensity Temperature	<ul style="list-style-type: none">UV, visible, and UV-vis.To be determined (TBD) based on field dataSelect temperatures based on seasonal and daily variation.	<ul style="list-style-type: none">UV and visible rangeConstantConstant (room)	<ul style="list-style-type: none">UV-visible complete rangeA range of levelsA range of levels

The response variables would be:

- Selectivity of the catalyst toward different oxidized products (primarily methanol and/or CO₂)
- Methane conversion

A typical experiment would consist of following steps:

Step 1: Development of catalytic material:

Catalytic material required for screening study will be directly purchased from chemical vendors (in powder form) and sensitized to sunlight by staining with select dyes (e.g. ruthenium dye^{19,20} and organic dyes²¹). Catalyst pellets for experiments associated with Specific Objective 2 will be formed using the manual mini-pelletizing unit present in PI's laboratory. Also, oxide thin films on less costly supports (such as silica or alumina) will be formed by wet impregnation method perfected in our laboratory. Different forms of catalysts are depicted in Figure 3 for illustrative purposes.



Figure 3: Various forms of catalysts (Source: Statoil)

In wet impregnation, water or alcohol-soluble metal salts will be injected onto the select support. These supports may be in powder form or pre-fabricated pellets. Salts are loaded and dried until the required composition is achieved. Then, the salt-loaded supports are calcined so that the anion is decomposed/oxidized and removed. Once oxidized, nanoscale islands of loaded photo-active metal oxides will remain on the support surface.

Step 2: Catalyst Testing in the photoreactor:

All experiments will be carried out in an assembled photo chemical reactor as depicted in Figure 4. Prepared catalytic material will be placed in the Borosilicate reactor and the lamp illuminated. Methane/inert gas mixture will be metered (using a gas controller) through the reactor vessel. The exit gas will be directly routed to an inline gas chromatograph to analyze product composition. The reactor has provisions to cool the system via a removable inner cooling tube placed in a quartz immersion well along with joints for fixing sparger tube, condenser, and thermometer (as necessary).

This set up is ideal not only for conducting continuous flow experiments with gaseous substrates (such as methane) but also for batch-mode experiments where the volatile matter is emitted from a solid or liquid source (such as manure in liquid, semi-solid or solid phase). In batch mode experiments, the catalyst material will be suspended (in case of a liquid source) or sprinkled (in case of solid) on top of the surface(s) and the emissions profile will be analyzed in the GC.



Figure 4: Photoreactor where the experiments will be carried out.

Catalyst Characterization

It is necessary to characterize catalysts for verification of their physical and chemical properties before and after testing. The types of characterization techniques that will be adopted during this study are as follows:

Property	Characterization method	Rationale
Metal loading	X-ray Diffraction (XRD)	Necessary to explain differences in catalyst performance by normalizing results to a consistent metal loading.
Surface area of the support and surface area of the catalyst after metal loading	Brunauer, Emmett and Teller (BET) method	Similar to above. Performance results should be normalized for differences in surface area.
Catalyst particle size and dispersion	Temperature Programmed Reduction (TPR) and Scanning Electron Microscopy / Energy Dissipative X-ray (EDX)	Even at the same meal loading, differences in metal dispersion and particle size affect changes in performance. Thus, results should be normalized taking into account these effects.

PI's laboratory and central user facilities at Texas A&M University are equipped with the necessary equipment needed for proposed characterizations.

Specific Objective 2: Optimizing the performance of select catalysts for agricultural use

Once the most active catalysts are identified, optimization studies will be conducted. The goal here is to expand the levels of variables so that the most optimal performance parameters are identified.

The levels used here (as given in Table 1) will be dictated by results obtained during Sp. Objective 1. The variables that will be expanded during this phase will include: catalyst form (including pellets – since pellets are more manageable to be used in a farm setting than a powder); catalyst concentration; methane concentration (to identify the upper limit that a particular catalyst concentration could effectively handle); light wavelength (to include the entire visible spectrum); absorption enhancers (to broaden the spectrum that the catalyst can respond to); light intensity (to discern effect of diurnal light intensity variations on the effectiveness of the catalyst) and temperature (to discern the effect of diurnal and seasonal temperature variations on the effectiveness of the catalyst).

Deliverables with timelines:

Description/Milestone/Deliverable	Timeline
<p>Specific Objective 1:</p> <ol style="list-style-type: none"> 1. Setting up the photoreactor 2. Catalyst screening 3. Catalyst characterization 4. Identification of the best catalysts (milestone) <p>Specific Objective 2:</p> <ol style="list-style-type: none"> 1. Optimization studies 2. Identification of the best catalyst under simulated field conditions (deliverable) 3. Preparation of reports 	<p>'13 A S O D '14 J F M A M J J A S O N D '15 J F M A M J J A</p> <p>*****</p> <p>*****</p> <p>*****</p> <p>§</p> <p>*****</p> <p>Đ</p> <p>***</p> <p>***</p>

Key: ***** - progress; §- milestone; Đ - deliverable

Potential for Leveraging Resources:

It is anticipated that these photo-catalysts, in addition to methane, can oxidize other organic compounds. Consequently, such photocatalytic effects can be extended for air quality applications including deodorization and elimination of volatile organic compounds (VOCs). Our goal is to evaluate the applicability of this concept for VOC reduction and odor elimination. Findings from this study will be leveraged to obtain funding from federal granting agencies including the National Science Foundation (NSF), United States Environmental Protection Agency (US-EPA), and United States Department of Agriculture (USDA - AFRI program). Preliminary data collected will help strengthen such proposals. PI has consistently participated in proposal review panels in USDA and NSF and it is clear that panels increasingly rely on convincing preliminary data before recommending proposals for funding. If successful, the knowledge acquired while working with a difficult-to-activate product will help making a convincing case on our ability to tackle more complex (but easy-to-activate) organic compounds such as VOCs and those contributing to odor.

Proof-of-concept data gathered under State of Texas initiatives' support has already resulted in two federally funded research projects:

1. Fernando, S. (PI), Towards Sustainable Hydrocarbon Biorefineries: Deoxygenation of Biomass Oxygenates to HCs via Methane. National Science Foundation, Total Award - \$320,000, PI's contribution \$320,000. Ending December 2013 .
2. Fernando, S. (co-PI) with a consortium of researchers across the nation, National Alliance for Advanced Biofuels and Bioproducts (NAABB). US Department of Energy. Total Award - \$40 million. PI's allocation \$200,000. Ending summer 2013.

PI, Dr. San Fernando: Dr. Fernando has worked in the catalysis area for over ten years. His primary focus has been development of catalytic processes for energetic and environmental applications. His research program has been supported by federal agencies including NSF (four grants as PI), DOE (seven grants) and USDA (two grants) (and other regional/local entities). Of the aforementioned projects, only two are ongoing and in line to be completed by the end of this year. His work (51 articles in total) has been published in high-impact peer reviewed journals including Energy and Environmental Science (Impact Factor 9.4), Bioresource Technology (4.4), Biomass and Bioenergy (3.6), Catalysis Today (3.6), Fuel (3.2) and the premier publication of our professional society, Transactions of ASABE. His work has been cited 2294 times to date.

Budget:

Name	Role	Year 1	Year 2	TOTAL
Senior/Key Person				
San Fernando	Co-PI	12,176	12,918	25,094
Other Personnel				
To Be Named	Post Doc	48,000	50,923	98,923
Student Workers	Hourly As Needed	8,000	8,000	16,000
Total Salaries and Wages		68,176	71,841	140,017
Total Personnel Costs		68,176	71,841	140,017
Travel				
Domestic Travel		4,000	4,000	8,000
Other Direct Costs				
Materials & Supplies		12,000	12,000	24,000
Publication Costs		1,000	1,000	2,000
Contractual (laboratory analysis and service contracts)		7,000	7,000	14,000
Modified Total Direct Costs (MTDC)		92,176	95,841	188,017
Total Direct Costs		92,176	95,841	188,017
TOTAL PROJECT COSTS		\$92,176	\$95,841	188,017

Biographical Sketch, Sandun D Fernando Ph.D., P.E.

(a) Professional Preparation:

PhD 2003. **University of Nebraska-Lincoln**

Major: Biological Systems Engineering

Dissertation: (Advisor – Dr. Milford Hanna). The dissertation research was centered on catalytic production of fatty acid methyl esters (FAMES) and the ability of FAMES to stabilize immiscible ternary liquid systems.

Certificate. MIT Professional Education Institute. **Massachusetts Institute of Technology**

Nanomaterials for Biological and Pharmaceutical Technologies (Summer 2009)

MS 2001 Biological Systems Engineering, **University of Nebraska-Lincoln**

BSc 1995 Agricultural Engineering (major), Honors, University of Peradeniya, Sri-Lanka

(b) Appointments:

- Associate Professor, Biological and Agricultural Engineering (BAEN) Department , Texas A&M University (September 2011- date)
- Assistant Professor, BAEN Department, Texas A&M University (May 2008-2011)
- Assistant Professor in Bioenergy, Department of Ag and Biological Engineering, Mississippi State University (October 2003 to April 2008)

(c) Publications and Products:

Five Selected Publications Closely Related to the Proposed Research (out of 51)

(* indicates MS, Ph.D., Post Doc, or Research Scientist directly supervised by Dr. Fernando. Principle author underlined)

1. Nawaratna*, G., Capareda, S., and S. Fernando. 2013. Effect of metal groups in transition metal alkoxide catalysts on transesterification. *Advances in Materials*. 2012; 1(1). 1-8.
2. Gunawardena*, A., and S. Fernando. 2012. Thermodynamic Equilibrium Analysis of Methanol Conversion to Aromatic Hydrocarbons using SAS: A prelude to Biomass Deoxygenation. *Trans. of ASABE*. 55 (3), 1025-1031.
3. Gunawardena*, D.A. and S. D. Fernando. 2012. Thermodynamic Equilibrium Analysis of Methanol Conversion to Hydrocarbons Using Cantera Methodology. *Journal of Thermodynamics*, vol. 2012, Article ID 125460, 7 pages.
4. Gunawardena*, D. A. and S. Fernando. 2011. Deoxygenation of methanol over ZSM-5 in a high pressure catalytic pyroprobe. *Chemical Engineering and Technology*. 34 (2). 173–178.
5. Singh*, A. and S. Fernando. 2009. Preparation and Reaction Kinetics Studies of Na-based Mixed Metal Oxide for Transesterification. *Energy and Fuels*. 23. 5160–5164.

Five Other Significant Publications:

1. Liu*, S., Musuku*, S.R., Adhikari*, S., and S. Fernando. 2009. Adsorption of Glycerol from Biodiesel Washwaters. *Environmental Technology*. 30 (5). 505-510.
2. Fernando, S., Hall*, C., and S. Jha*. 2006. NOx Reduction from Biodiesel Fuels. *Energy & Fuels*. 20(1). 376-382.
3. Haryanto*, A., Fernando, S., N. Murali*, and S. Adhikari*. 2005. Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: A Review. *Energy & Fuels*. 19(5), 2098-2106.
4. Fernando, S., Bhushan, S. and M. Naveen*. 2005. Agricultural Engineering Education in Developing Countries. *Int. J. o.f Eng. Edu. Dublin Institute of Tech. Dublin, Ireland*. 22 (1).
5. Fernando, S., Adhikari*, S., Chandrapal*, C., and N. Murali*. 2006. Biorefineries: Current Status, Challenges, and Future Direction. *Energy & Fuels*. 20(4). 1727-1737.

(d) Synergistic Activities:

- Development of a new graduate level course in introduction to Nanoscience and Engineering and an undergraduate course in Biological and Ag. Eng. Fundamentals.
- **Training minority and under-represented students:** The PI has consistently provided research and education experience to minority and under-represented students in his laboratory. Women engineering undergraduate students trained in his lab include, Christina Leonhardt ('12), Taylor Kastensmidt ('12), Janise Anderson ('11), Mina Tahai ('06), Chelsea Tilley ('06) and Latoya Allan ('06 African American), K-12 students that were trained in his laboratory include Kim Petite ('07), Anna Campbell ('06), Stephanie Doty ('06), Emily Smith ('06), Ranjitha Bandi ('05-'07), Nitin Mantena ('05); Brandi Smith ('04); and Jeremy Seymour ('04). Also, during the summers of 2004, 2006, and 2007, Dr. Fernando conducted a laboratory workshop for 11, 36, and 38 African American students, respectively, on production of biodiesel, the use of basic laboratory equipment, and the importance of bioenergy research for a cleaner environment.

(e) Collaborations and Other Affiliations

- Training Graduate and Undergraduate Researchers

Postdoctoral Research Associates: Shetian Liu, Xuejun Ye, Aroksami Antonyraj

PhD: Anuradh Gunawardena, Ivantha Bandara, Seaborn Carter, Bjorn Santos, Tahmina Imam (graduated 2012), Agus Haryanto (2008), Sushil Adhikari (2008), and Alok Singh (2008) as major professor
Teiseh Eliasu (2012), Prashanth Buchireddy, Javeed Mohamed as minor professor

MS: Nalin Samarasinghe (graduated '12), Ivantha Bandara ('09), Anuradh Gunawardena ('08), Prashanth Karra ('05), Aishwarya Mahadevan and Sayali Kulkarni as major professor
Mukul Shrekar (2010), C. Chandrapal (2006), Lin Wei as minor professor (2007)

Undergraduate: 35 undergraduate advisees each year (2003-2007), 15 advisees (2008-)

- Co-authors and research collaborators

Dr. Milford Hanna	Graduate Supervisor/coauthor	University of Nebraska-Lincoln
Dr. David Jones	Graduate Supervisor/coauthor	University of Nebraska-Lincoln
Dr. Perla Balbueba	Collaborator	Texas A&M University
Dr. Dan Shantz	Collaborator	Texas A&M University
Dr. Sergio Capareda	Collaborator/coauthor	Texas A&M University
Dr. Sushil Adhikari	Collaborator/coauthor	Auburn University
Dr. Phil Steele	Collaborator/coauthor	Mississippi State University
Dr. Mark White	Collaborator	Mississippi State University

- Other Affiliations:

➤ **Associate Editor in journals of:** Biological Engineering Transactions, Transactions of ASABE, and Applied Engineering in Agriculture; **Review panel member** at NSF – CTS division ('04 – to date); **Review panel member** at USDA – CSREES division (2005-07); **Adhoc Reviewer:** Center for Plant Biotechnology Research (CPBR) 2004, 05, 06, 07, 08 competitions; **Technical**

➤ **Reviewer of Journals:** Industrial and Engineering Chemistry (I&EC) Research; Energy; Fuel; Energy and Fuels; JAOCS, Bioresource Technology, Industrial Crops and Products, Canadian J. of Chem Engineering; Journal of Transactions of ASAE, J. of Applied Eng. in Agriculture

➤ **Registered Professional Engineer (Texas)**

Membership and Services in Professional Associations:

American Society of Agricultural and Biological Engineers (ASABE), American Chemical Society (ACS), Am. Inst. of Chemical Engineering (AIChE), Institute of Biological Engineering (IBE), Sigma Xi.

References:

- (1). Lashof, D. A.; Ahuja, D. R., Relative contributions of greenhouse gas emissions to global warming. *Nature* **1990**, 344, (6266), 529-531.
- (2). EPA Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2010 (April 2012) EPA. EPA 430-R-12-001 <http://www.epa.gov/climatechange/ghgemissions/usinventoryreport/archive.html>
- (3). EPA Overview of Greenhouse Gases. <http://epa.gov/climatechange/ghgemissions/gases/ch4.html>
- (4). State, U. S. D. o., Projected Greenhouse Gas Emissions. In: Fourth Climate Action Report to the UN Framework Convention on Climate Change . U.S. Department of State, Washington, DC, USA. **2007**.
- (5). Schils, R. L. M.; Verhagen, A.; Aarts, H. F. M.; Šebek, L. B. J., A farm level approach to define successful mitigation strategies for GHG emissions from ruminant livestock systems. *Nutrient Cycling in Agroecosystems* **2005**, 71, (2), 163-175.
- (6). Bruhn, A.; Dahl, J.; Nielsen, H. B.; Nikolaisen, L.; Rasmussen, M. B.; Markager, S.; Olesen, B.; Arias, C.; Jensen, P. D., Bioenergy potential of *Ulva lactuca*: Biomass yield, methane production and combustion. *Bioresource Technology* **2011**, 102, (3), 2595-2604.
- (7). Cheng, J., Challenges of CAFO Waste Management. *Journal of Environmental Engineering* **2003**, 129, (5), 391-392.
- (8). Lokey, E., The status and future of methane destruction projects in Mexico. *Renewable Energy* **2009**, 34, (3), 566-569.
- (9). Petersen, S. O.; Sommer, S. G.; Béline, F.; Burton, C.; Dach, J.; Dourmad, J. Y.; Leip, A.; Misselbrook, T.; Nicholson, F.; Poulsen, H. D.; Provolò, G.; Sørensen, P.; Vinnerås, B.; Weiske, A.; Bernal, M. P.; Böhm, R.; Juhász, C.; Mihelic, R., Recycling of livestock manure in a whole-farm perspective. *Livestock Science* **2007**, 112, (3), 180-191.
- (10). Choudhary, V. R.; Uphade, B. S.; Pataskar, S. G., Low temperature complete combustion of dilute methane over Mn-doped ZrO₂ catalysts: factors influencing the reactivity of lattice oxygen and methane combustion activity of the catalyst. *Applied Catalysis A: General* **2002**, 227, (1-2), 29-41.
- (11). Choudhary, V. R.; Uphade, B. S.; Pataskar, S. G., Low temperature complete combustion of methane over Ag-doped LaFeO₃ and LaFe_{0.5}Co_{0.5}O₃ perovskite oxide catalysts. *Fuel* **1999**, 78, (8), 919-921.
- (12). Kapinus, E.; Viktorova, T.; Khalyavka, T., Photocatalytic activity of nanoparticles of metal sulfides in the degradation of organic dyes. *Theoretical and Experimental Chemistry* **2006**, 42, (5), 282-286.
- (13). Navalón, S.; Dhakshinamoorthy, A.; Álvaro, M.; Garcia, H., Photocatalytic CO₂ Reduction using Non-Titanium Metal Oxides and Sulfides. *ChemSusChem* **2013**, 6, (4), 562-577.
- (14). Baik, M.-H.; Newcomb, M.; Friesner, R. A.; Lippard, S. J., Mechanistic Studies on the Hydroxylation of Methane by Methane Monooxygenase. *Journal Name: Chemical Reviews*, 103(6):2385-2419 **2003**, Medium: X.
- (15). Merckx, M.; Kopp, D. A.; Sazinsky, M. H.; Blazyk, J. L.; Müller, J.; Lippard, S. J., Dioxygen Activation and Methane Hydroxylation by Soluble Methane Monooxygenase: A Tale of Two Irons and Three Proteins. *Angewandte Chemie International Edition* **2001**, 40, (15), 2782-2807.
- (16). Wada, K.; Yoshida, K.; Takatani, T.; Watanabe, Y., Selective photo-oxidation of light alkanes using solid metal oxide semiconductors. *Applied Catalysis A: General* **1993**, 99, (1), 21-36.
- (17). Wada, K.; Yoshida, K.; Watanabe, Y.; Suzuki, T., The selective photooxidation of methane and ethane with oxygen over zinc oxide and molybdena-loaded zinc oxide catalysts. *Journal of the Chemical Society, Chemical Communications* **1991**, 0, (10), 726-727.
- (18). Graetzel, M.; Thampi, K. R.; Kiwi, J., Methane oxidation at room temperature and atmospheric pressure activated by light via polytungstate dispersed on titania. *The Journal of Physical Chemistry* **1989**, 93, (10), 4128-4132.
- (19). Adachi, M.; Murata, Y.; Takao, J.; Jiu, J.; Sakamoto, M.; Wang, F., Highly Efficient Dye-Sensitized Solar Cells with a Titania Thin-Film Electrode Composed of a Network Structure of Single-Crystal-like TiO₂ Nanowires Made by the "Oriented Attachment" Mechanism. *Journal of the American Chemical Society* **2004**, 126, (45), 14943-14949.
- (20). Highly efficient photoelectrochemical performance of SrTiO₃/TiO₂ heterojunction nanotube array thin film. *Journal of Nanoparticle Research* **2013**, 15, (6).
- (21). Hara, K.; Koumura, N., *Material Matters* **2009**, 4 (4), 92.