

Dear ENFL Members,

Welcome to the ACS ENFL's fall 2020 newsletter. We hope you are managing to cope through the COVID-19 pandemic. The Fall 2020 ACS National Meeting, scheduled to be held at San Francisco, CA on August 17-20, was completely virtual for the first time. This newsletter contains news from the conference, including symposia and events held by ENFL, information about awards and honors received by our members, announcement of new division officers elected for 2021, and the symposia planned for next year. At the end of this issue is an article by Eric Sheu on the 10 year anniversary in memory of Prof. Teh-Fu Yen, reminding us of his outstanding contributions and lifetime accomplishments in petroleum science and environmental chemistry.

This newsletter is brought to you by the ENFL communication and technology committee. Please check out more news and update on our website at https://enfl.aps.anl.gov/ or social media. If you have any comments or suggestions, please feel free to email us at ENFLDivision@gmail.com.



From the Desk of ENFL Chair, Prof. J. Louise Liu

Dear ENFL Colleagues,

It has been my great honor to serve as the Energy and Fuels Division (ENFL) Chair during 2020. This special year evidenced the ENFL's resilience, openness, tolerance and progress due to the contributions by our members and division leaders. I would like to name a couple:

- Senior researchers from the academia and industry received Outstanding national awards (George A. Olah: Dr. H. Kung, Northwestern Univ.; Henry H. Storch: Dr. S Islam, Univ. of Bath), ENFL Distinguished Researcher award (Dr. J. Brazdil, Archer Daniels Midland Company), and the R.A. Glenn award (Dr. E Rogel, Chevron Energy Technology Co.)
- Junior faculty and researchers received the ENFL Emerging Researcher award (Dr. O. Farha, Northwestern Univ.) and the R. A. Glenn award (Dr. Y. Zhang, ExxonMobil Research Engineering Company)
- Lisa Houston and Yun Hang Hu were recognized for the ENFL Distinguished Service Award for their continuous and outstanding services
- Our immediate past Chair, Dr. D. Heldebrant (Pacific Northwest National Laboratory) was invited to deliver a TED-talk as one of the Four heroes at the "Opening Session: We Are All Heroes in Moving Chemistry from Bench to Market"
- Dr. Alissa Park was recognized as a fellow by both Royal Society of Chemistry and American Chemical Society (the first double fellow, 2020); and Dr. Yun Hang Hu also received his double fellowship from both the ACS and the ASM in 2020
- ENFL students presented their posters virtually and 8 received awards of Student Poster Award Competition (SPAC).

In order to further advance the contribution to the Science, Technology and Engineering (STE), ENFL will launch "Monthly Invited Talk series (*MITs*)" via <u>zoom virtual meeting</u> to promote and disseminate the research discoveries by our members. Our officers, committee members, and volunteers have been contributing to the Division and ACS community for the betterment of STE, with a focus on energy and fuels. The precious time and gracious support from all are the cornerstones for the division to move forward.

Respectfully,

Jingbo Louise Liu, Ph.D., CSci., CChem., FRSC Professor of Chemistry, JSPS Invitation Fellow and US Air Force DEBI Fellow Texas A&M Energy Institute and Texas A&M University-Kingsville





News from the 2020 ACS Fall Virtual Meeting & ENFL Division

The Fall 2020 ACS National Meeting in San Francisco was held virtually for the first time during Aug 17-20, 2020 due to the COVID-19 pandemic. The conference featured over 250 Live and Broadcast sessions, interactive video Q&A, and over 6000 on-demand oral and poster presentations, plus many networking and social events. The theme of the meeting was "Moving Chemistry From Bench to Market," and the meeting kicked off on Monday, Aug 17 with a Live

Events session on We Are All Heroes in Moving Chemistry from Bench to Market. One of the four keynote speakers in the opening session were our very own ENFL immediate past chair Dr. David Heldebrant from Pacific Northwest National Labs. Other speakers in the following days including Dr. David Berkowitz, the Director of the National Science Foundation's Chemistry Division who spoke on the current and future path of energy technologies. Thanks to them for sharing their insights on the impact of Energy on chemistry and the world, and highlighting contributions by our members and ENFL division.

The ACS ENFL program contained 58 broadcast talks and 29 on-demand talks and several poster presentations. The symposia organized by ENFL include: ACS George A. Olah Award in Hydrocarbon or Petroleum Chemistry in Honor of Professor Harold Kung, ACS Henry H. Storch Award in Energy Chemistry in Honor of Professor Saiful Islam, Energy Technologies: From Concept to Commercialization: Advances in Hydrocracking and Hydrotreating; Routes to Sustainable Aviation Fuels; Bioderived and Waste Feedstocks to Energy and Chemicals; Utilization and Storage of CO₂ in the Subsurface; Gas Separations, Storage and Utilization; and Chemistry of Fuel Properties, Combustion, and Fuel-Engine Interactions.

ENFL Events kicked off with the Student Poster Award Competition (SPAC) on Sunday. Students presented their research remotely from different places in the world, ranging from early morning to midnight in their local time zones. Nine students were selected to receive their poster awards for their excellent research. Congratulations to them and thanks to all students for their participation and hard work!

ENFL programing and business meetings were also held on Sunday to discuss plans and preparations for the virtual meeting, symposia, and various reports. This was followed by division banquet which has been traditionally held on Tuesday evenings to recognize winners of awards. The virtual banquet was joined by many friends and colleagues. Great to see many familiar faces and catch up with friends on zoom!

Opening Session We are All Heroes in Moving Chemistry from Bench to Market







est National Labs











Awards and Honors

We are pleased to announce that the awards and honors received by our members. Congratulations to all of them!

2020 ENFL Emerging Researcher Award: Prof. Omar K. Farha

Prof. Omar K. Farha is professor of chemistry at Northwestern University and an Associate Editor for ACS Applied Materials & Interfaces. His current research spans diverse areas of chemistry and materials science ranging from energy to defense-related challenges. Specifically, his research focuses on the rational design of metal–organic frameworks (MOFs) for applications sensing, catalysis, storage, separations and water purification. His research accomplishments have been recognized by several awards and honors including fellowship in the European Academy of Sciences, Kuwait Prize, Japanese Society of Coordination Chemistry "International award for creative work"; the Royal Society of Chemistry "Environment, Sustainability and Energy Division Early Career" Award; the American Chemical Society "The Satinder Ahuja Award for Young Investigators in Separation Science; and an award established by the Department of Chemistry at Northwestern University in his honor: the Omar Farha Award for



Research Leadership "awarded for stewardship, cooperation and leadership in the finest pursuit of research in chemistry" and given annually to an outstanding research scientist working in the department. Prof. Farha has more than 450 peerreviewed publications, holds 16 patents, 53,000 citation and h-index of 110 (google Scholar), and has been named a "Highly Cited Researcher" in 2014 to 2019. Omar is the co-founder of NuMat Technologies, the first company to commercialized an engineered system level product enabled by Metal-Organic Framework Materials.

2020 Class of ACS Fellow: Prof. Alissa Park



Prof. A.-H. Alissa Park is the Lenfest Chair in Applied Climate Science of Earth and Environmental Engineering & Chemical Engineering at Columbia University. She is also the Director of the Lenfest Center for Sustainable Energy. Her research focuses on sustainable energy and materials conversion pathways with emphasis on integrated Carbon Capture, Utilization and Storage (CCUS) technologies. Park's group is also

working on Direct Air Capture of CO₂ and Negative Emission Technologies including BioEnergy with Carbon Capture and Storage (BECCS). Park has received a number of professional awards and honors including the U.S. C3E Research Award (2018), PSRI Lectureship Award in Fluidization from the American Institute of Chemical Engineers (2018), American Chemical Society Energy and Fuels Division - Emerging Researcher Award (2018), International Partnership Award for Young Scientists from the Chinese Academy of Sciences (2018), Janette and Armen Avanessians Diversity Award at Columbia University (2017), American Chemical Society WCC Rising Star Award (2017), and the National Science Foundation CAREER Award (2009). She continues to lead important global and national discussions on CCUS including the Mission Innovation Workshop (2017) and the National Petroleum Council CCUS Report (2019). She is a fellow of the American Chemical Society and the Royal Society of Chemistry.

2020 Class of ACS Fellow Prof. Yun Hang Hu



Prof. Yun Hang Hu is the Charles and Carroll McArthur Endowed Chair Professor at Department of Materials Science and Engineering, Michigan Technological University. He is an elected fellow of American Association for the Advancement of Science (AAAS), American Chemical Society (ACS), American Institute of Chemical Engineers (AIChE), American Society of Metals (ASM), and Royal Society of Chemistry (RSC). He was the chair

of the ACS Energy and Fuels Division in 2015. He has been the president of the Hydrogen Storage Division of International Association of Hydrogen Energy since 2015. He is the editor-inchief of "Energy Science & Engineering" (Wiley journal) and an editorial board member for 8 international journals published by Nature group, ACS, RSC, Elsevier, and Springe, such as ACS Energy Letters, Catalysis Today, Scientific Report, and International Journal of Energy. He has made pioneering contributions to various areas, such as nanomaterials, catalysis/photocatalysis/electrocatalysis, clean fuels, solar energy, batteries, supercapacitors, fuel cells, hydrogen storage materials, and CO₂ conversion. He published more than 250 papers in prestigious journals and delivered more than 160 invited presentations, including 43 plenary/keynote talks to national and international conferences, such as the very prestigious plenary talk for the opening session of the ACS National Meeting.



ACS Division of Energy & Fuels Fall 2020 Newsletter

2020 ENFL Distinguished Service Award: Lisa Houston



Lisa Houston is Vice President at PAC. LP. an analvtical instrumentation company, where she is responsible for the financial success of the Process Analytics segment. She received her bachelor's degree in biochemistry from the University of North Texas in 1986. Lisa has been an active Chemical American Society volunteer at all levels including Local Section, Division, Regional, and

National since becoming a member in 1990. She has been a major contributor to the success of ENFL. Lisa has organized the long range planning effort and has been involved in many aspects of the Division and has served as a Councilor.

2020 ENFL Distinguished Service Award: Yun Hang Hu



Prof Yun Hang Hu is the Charles and Carroll McArthur Endowed Chair Professor at Department of Materials Science and Engineering, Michigan Technological University. He is an elected fellow of American Association for the Advancement of Science (AAAS), American Chemical Society (ACS), American Institute of Chemical Engineers (AIChE), American Society of Metals (ASM), and Royal Society of Chemistry (RSC). He was the chair

of the ACS Energy and Fuels Division in 2015. Yun was a program chair and is the chair of the selection committee for the ENLF Emerging researcher Award. Currently Yun is a Director at Large for ENFL

The following 2021 ACS national award recipients have been announced in the August 13th issue of <u>*C&EN*</u>. Symposia in honor of these awardees will be hosted by ENFL or co-hosted with ORGN at the 2021 ACS Spring National Meeting in San Antonio, Texas.

2021 ACS Award in the Chemistry of Materials, Yury Gogotsi, Drexel University 2021 ACS Henry H. Storch Award in Energy Chemistry: Harry W. Deckman, ExxonMobil Research & Engineering. 2021 ACS George A. Olah Award in Hydrocarbon or Petroleum Chemistry: Michael M. Haley, University of Oregon

Call for Nominations

The following 2021 ENFL awards or ACS national awards are open for nominations:

- 2021 ENFL Distinguished Researcher Award (contact: Dr. Chunshan Song, <u>cxs23@psu.edu</u>), deadline: September 15, 2020
- 2021 ENFL Emerging Researcher Award (contact: Dr. Yun Hang Hu, <u>yunhangh@mtu.edu</u>), deadline: April 01, 2021
- 2021 ENFL R. A. Glenn Award (contact: Dr. Alan Chaffee, <u>alan.chaffee@monash.edu</u>), deadline: April 01, 2021
- 2021 ENFL Distinguished Service Award (contact: Dr. Alan Chaffee, <u>alan.chaffee@monash.edu</u>) deadline: May 15, 2021
- 2022 ACS Henry H. Storch Award in Energy Chemistry, due to the ACS by November 1, 2020

Have a Story to Tell?

Do you, your organization, or someone you know have something to celebrate? Send email us at <u>ENFLDivision@Gmail.com</u>.



Announcements

Monthly invited talk series (MITs)

ENFL will kick off the monthly invited talk series starting September, 2020. The seminars will be held on one of the Fridays of each month, 7-8 pm at the speaker's local time. The speaker, titles and dates are listed below. Please contact Prof. J. Louise Liu if you are interested in giving talks or nominating speakers. The same hyperlink <u>zoom</u> address will be used as provided below.

Speaker: Prof. Omar Farha, Northwestern University

Time: September 18, 2020, 19:00-20:00 (EST)

Title: Programmable and Smart Sponges for Energy Relevant Applications

<u>zoom</u>

Abstract: Metal–organic frameworks (MOFs) are a class of solid-state materials built up from metal-based nodes and organic linkers. They exhibit permanent porosity and unprecedented surface areas which can be readily tuned through coordination chemistry at the inorganic node and/or organic chemistry at the linkers. The high porosities, tunability, and stability are highly attractive in the context of gas storage and catalysis applications. This talk will address new advances in the synthesis of new MOF materials developed at Northwestern University.

Speaker: *Prof. Veronica Augustyn*, Materials Science & Engineering, University Faculty Scholar at North Carolina State University

Time: October 02, 2020, 19:00-20:00 (EST)

Title: Electrochemical Charge Storage and Reactivity under Confinement in Layered Materials <u>zoom</u>

Abstract: Many layered materials of interest for electrochemical energy storage and conversion applications are flexible hosts whose interlayers can be expanded to accommodate not just ions but also solvents, organic molecules, polymers, and organometallics. When these "hybrid" materials are placed into an electrochemical environment, the distinction between surface and bulk becomes blurred since the electrochemical interface can now be viewed to extend into the interlayer. During this seminar, I will discuss fundamental aspects of charge storage at electrochemical interfaces and how

extend into the interlayer. During this seminar, I will discuss fundamental aspects of charge storage at electrochemical interfaces and how interfacial charge storage and reactivity change under confinement. I will also describe synthesis of hybrid layered materials and the use of in situ and operando characterization to understand the relationships between structure and composition and the resulting electrochemical reactivity.

S Speaker: *Prof. Feng Jiao*, Chemical and Biomolecular Engineering, University of Delaware Time: Nov 06, 2020, 19:00-20:00 (EST)

Title: Electrochemical conversion of carbon dioxide to valuable chemicals

zoom



Abstract: Electrochemical conversion of carbon dioxide (CO_2) using renewable electricity is an attractive means for sustainable production of fuels and chemicals. Copper (Cu) has a unique capability of catalyzing carbon-carbon (C-C) bond formation to form high-value multi-carbon (C2+) products. While highly alkaline electrolytes are often used to enhance C2+ selectivity, the inevitable reaction of hydroxide ions with CO₂ to form undesired carbonates at the

electrode-electrolyte interface disrupts the electrolysis process. This fundamental challenge can be solved by decoupling the CO_2 electrolysis into a two-step process, where CO_2 is first electrochemically reduced to carbon monoxide (CO) at neutral conditions, followed by CO electroreduction to produce C2+ chemicals in alkaline environments. Nonetheless, only four major C2+ products, i.e., ethylene, acetate, ethanol, and n-propanol, have been reported for CO_2/CO electrolysis in aqueous electrolytes. In this talk, we will present a new study to expand beyond this limited range of simple C-C coupling by demonstrating electrochemical production of acetamide with nearly

40% Faradaic efficiency at a current density of 300 mA/cm², where the carbon-nitrogen (C-N) bond is formed through CO electroreduction in the presence of ammonia. Full solvent quantum mechanical calculations showed earlier that the under neutral or basic conditions the reaction mechanism involves CO dimerization and sequential transfer of H from two surface waters to form the (HO)C*-C*OH intermediate that subsequently leads through two separate pathways to form C₂H₄ (90%) and ethanol (10%). We show now that (HO)C*-C*OH is also hydrolyzed to *C=C=O, which in turn reacts with NH₃ to form intermediates leading to acetamide while suppressing formation of other C2 products. Our results provide useful mechanistic insights into Cu-catalyzed CO₂/CO electroreduction and demonstrate the construction of carbon-heteroatom bonds in CO₂/CO electrolysis. This largely expands the scope of electrocatalytic CO2 utilization pathways for sustainable chemical production.







Speaker: Prof. Ying Li, Texas A&M University Time: Dec. 04, 2020, 19:00-20:00 (CST) zoom

Title: conversion of carbon dioxide to value-added products via photocatalytic, electrocatalytic, and photo-thermochemical approaches

Abstract: O_2 is a major greenhouse gas resulting from fossil fuel consumption. An ideal strategy to mitigate the global climate change is to convert O_2 emissions back into fuels and useful chemicals. Photochemical and electrochemical reduction of O_2 are promising approaches because renewable energy (e.g. solar and wind) can be used to produce sustainable fuel and solve the energy storage challenge simultaneously. However, the biggest challenge is the design of a high-performance and low-cost catalyst. In this seminar, I will summarize the recent progress in our research group in the development of cost-effective photocatalysts and electrocatalysts for O_2



reduction to CO, photo-thermo-chemical catalysts for CO₂ reforming of methane to produce syngas, as well as mechanistic studies on the reaction mechanisms and pathways with the assistance of various in situ spectroscopy analyses.

From the Editor-in-Chief of ACS Energy & Fuels, Prof. Hongwei Wu

Owing to the outstanding services of Prof. Mike Klein as the former EIC and his editorial team from 2002 to 2019, *Energy & Fuels* sustained a ten-fold growth and earned its highly acclaimed reputation globally in the domain of traditional fossil fuel research. Looking forward, the field of energy and fuels research has undergone significant transitions, with growing attentions and research efforts on renewable and unconventional energy sources, sustainable development and carbon dioxide issues. Innovations in energy conversion and storage are increasingly critical to our sustainable future. As the new EIC, I am eternally grateful to the ACS Division of Energy and Fuels for the opportunity of sharing my vision for the journal with the broader research community.



My vision for *Energy & Fuels* is to implement an integrated strategy to seize this unique opportunity to grow the journal to the next level. We are rapidly expanding into broader domains of alternative

energy research (notably energy storage, energy materials and solar energy conversion). *Energy & Fuels* continues publishing research on conventional fossil fuels but with an increasing emphasis on sustainable development. The journal will focus on publishing original research that leads to the discovery of new fundamental knowledge and/or advancements in technologies. As an international journal, *Energy & Fuels* has also set the priority to develop further into emerging geological regions. We are looking forward to your continuous support and contributions as authors, reviewers and readers, for sharing and disseminating many exciting works in addressing the grand energy challenges.

Prof Hongwei Wu received his Bachelor and Master of Engineering in 1993 and 1996, respectively, both in Thermal Power Engineering, from Huazhong University of Science and Technology, China. He then pursued his Ph.D. in Chemical Engineering at the University of Newcastle, Australia, and received his Ph.D. degree in August 2000. After a two-year postdoctoral fellowship at Monash University, Australia, Prof Wu was appointed as a junior lecturer in the Department of Chemical Engineering at Curtin University, Australia, in August 2002. He was then promoted to Senior Lecturer in 2006 and Associate Professor in 2008. Since 2010, he has been made as a full professor of chemical engineering at Curtin University. Prof Wu's research interests span a broad number of topics, including bioenergy science and engineering, coal science and engineering, production of green chemicals from biomass, thermochemical processing of solid fuels, production and applications of slurry fuels, transformation of impurities in fuels, and life cycle analysis. Prof Wu has authored ~200 peer-reviewed publications in international journals. He has won the 2010 Curtin Commercial Innovation Award and 2011 Western Australia Innovator of the Year Woodside Encouragement Award. He was also the recipient of the inaugural 2018 Curtin Awards for Excellence in Higher Degree by Research Supervision. He is a fellow of the Combustion Institute (2019). After served as Associate Editor (2008-2019), Prof Wu has then been appointed as the new Editor-in-Chief of *Energy & Fuels* (http://pubs.acs.org/ef) by the American Chemical Society since Jan 2020.



New Officers for ENFL 2021

2021 Division Chair: Dr. Alan Chaffee

Dr. Alan Chaffee works in the School of Chemistry at Monash University as a Professor. Before becoming an academic, he worked for a number of years in Australia's national research laboratory (CSIRO) and in private industry (BHP). His group undertakes applied chemistry research on topics that are related to biomass and fossil fuel utilization. For example, new approaches to the preparation of industrial chemicals, specialty liquid fuels, road bitumen, coke for steel making, carbon fibers and specialist (monolithic) high surface area active carbons are being developed that utilize low cost precursors and minimize energy losses (and, hence, CO_2 emissions). The group also investigates the capture of CO_2 emissions by adsorption and, once captured, its transformation back into useful products by heterogeneous catalysis. In doing so, innovative new materials such as mesoporous silica, metal-organic frameworks (MOFs) and ionic liquids (ILs) are employed as adsorbents, catalysts and/or solvents. These novel materials are often sourced from other research groups within the School. Molecular modeling tools are also frequently applied, so that experiment and theory inform each other. In addition to journal contributions, he holds a number of patents and, with his team, is endeavoring to commercialize some of these opportunities.

2021 ENFL Program Co-Chair: Dr. Yuyan Shao

Dr. Yuyan Shao is a Senior Scientist and Team Lead for Fundamental Battery Research at the US Department of Energy (DOE) Pacific Northwest National Laboratory (PNNL). He received his B.S. (2001) and Ph.D. (2006) in Applied Chemistry from Harbin Institute of Technology. His research focus has been on fundamental materials chemistry, electrochemical energy materials, and devices, including batteries, fuel cells, hydrogen production, and biomass upgrading. He has authored some 150 scientific papers (H-Index = 65). He is also an inventor of about 50 patents/patent applications. He has been selected as Thomson Reuters/Clarivate Analytics "Highly Cited Researcher" (2014, 2017-2019). He has served as a Guest Editor for the journals *Advanced Materials* (Special Issue: Materials Electrochemistry for Chemical Transformation - 2019) and *Nano Energy* (Special Issue: Electrocatalysis - 2016).

2021 ENFL Program Co-Chair: Dr. Jun Lu

Dr. Jun Lu is a Chemist at Argonne National Laboratory. His research interests focus on the electrochemical energy storage and conversion technology, with focus on beyond Li-ion battery technology. Dr. Lu earned his bachelor's degree in chemistry physics from University of Science and Technology of China (USTC) in 2000. He completed his Ph.D. from the Department of Metallurgical Engineering at University of Utah in 2009 with major research on metal hydrides for reversible hydrogen storage applications. He is the awardee of the first DOE-EERE postdoctoral fellow under Vehicles Technology Program from 2011-2013. He serves as the associate editor of ACS Applied Materials and Interfaces. He was elected as associate president and board committee member of the International Academy of Electrochemical Energy Science (IAOEES). He is also the first awardee of IAOEES Award for Research Excellence in Electrochemistry Energy in 2016. Dr. Lu has authored/co-authored more than 300 peer-reviewed research articles, including *Nature; Nature Energy, Nature Nanotechnology; Chem. Rev.; Nature Commun.; JACS*; and has filed over 20 patents and patent applications.

Tentative ENFL Program for 2021 Spring ACS Meeting

ENFL is now calling for symposium proposals for Fall 2021 ACS meeting. Please send your symposium proposals directly to program chairs (Yuyan Shao, <u>yuyan.shao@pnnl.gov</u> and Jun Lu, <u>junlu@anl.gov</u>). The tentative list of symposia for Spring 2021 ACS Meeting are shown below (Award symposia pending further review):

- Advances in Materials Synthesis & Characterization of Li-ion, Na-ion & Multi-Valent Batteries
- Innovative Chemistry and Materials for Electrochemical Energy Storage
- Electrochemistry-enabled catalysis for energy, chemicals, and materials
- Energy-efficient Chemical Separations through 21st Century Scientific Capabilities
- Engineered Materials Chemistry at the Oil/Gas/Water Interfaces: From Ions to Macromolecules
- Recent Advancements in Lignin Valorization Strategies for Fuels and Chemicals
- Catalytic and Non-catalytic Upgrading of Heavy Oils and Vegetable Oils: Hydrodesulfurization, Hydrodenitrogenation, Hydrodeoxygenation, and Oxidative Desulfurization
- Chemistry of Fuel Properties, Combustion, and Fuel-Engine Interactions
- Fuel Characterization by Multidimensional Gas Chromatography
- Engineered Interfaces for Energy and Fuels
- ACS-GCI Green Chemistry Opportunities for Oilfield Applications









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- Advances in Hydrocracking and Hydrotreating
- Macromolecular and Structured Electrolytes for Energy and Related Applications
- Renewable plastics: Conversion of waste plastic to fuels and chemicals
- Progress in macromolecular chemistry for advanced fuels formulation
- Materials for Energy and Environmental Sustainability
- Energy and Fuels: The Driving Force for The Second Century
- MPPG Macromolecular Chemistry in Energy and Fuels: Design, Application, and Challenges

ENFL Periodic Table 2020



Volunteers and New Members Welcome

ENFL is looking for volunteers to help with Division activities and business. These will only take 5-10 hours/month and will provide leadership and functional skills as well as excellent networking opportunities with Division leaders and members. We particularly need help with the following but also have opening on all committees. Please email us at <u>enfldivision@gmail.com</u> if you are interested.

- Area Representatives
- Elected ENFL officers: Chair-elect 2022, Councilor, Alternate Councilor, Director-at-large
- Appointed ENFL positions: Program Secretary, and Program Chair (2023)



10 Year Anniversary in Memory of Professor Teh-Fu Yen

Teh-Fu Yen (宴德福) (1927-2010)



Teh-Fu ("Dave") Yen received his B.S. in chemistry in 1947 from Huachung University in China. Then he came to the US in 1949 and obtained a M.S. in chemistry and chemical engineering from West Virginia University in 1953, and a Ph.D. in organic chemistry and biochemistry from Virginia Polytechnic Institute in 1956. After working on polymer sciences in Goodyear and Rubber Co. for a few years, he joined the Mellon Institute (Pittsburg, PA) in 1959, where he worked on fossil fuels and geochemistry and made many contributions, including the famous Yen model of asphaltenes. When the Mellon Institute was dissolved and merged into Carnegie Mellon University in 1967, Yen moved to academia. After a short stay in California State University, he joined the University of Southern California (USC) in 1969 as a professor of the department of civil and environmental engineering, and remained there over 40 years until his passing on Jan. 12, 2010. Over his career, he established an international reputation for his works in petroleum chemistry, geochemistry and environmental chemistry. Yen published more than 500 papers and authored 26 books. He was a founder of the geochemistry division of the American Chemical Society, and he was elected as a fellow of both the American Institute of Chemists and the Institute of

Petroleum.

Asphaltene Physics and Chemistry – A Passion of Professor Teh-Fu Yen

Eric Sheu

Vanton Research Laboratory, LLC, 3355 Clayton Road, Concord, CA 9419 (ericsheu@vantonlab.com)

Asphaltene is a fascinating scientific topic even though its hindrance on production frequently gives field engineers headaches. It has held mystery that often created dilemmas and conflicts ever since field engineers first encountered its impact on production more than a century ago¹. Asphaltene is a generic name defined as the petroleum material fraction within a solvent cut (e.g., the fraction between pentane or heptane, and toluene). As a result, it contains over a million components that are dissimilar, yet close enough behave in similar ways. Asphaltene exhibits solution-like behavior, colloidal properties, polymeric-like morphology, and even liquid crystal-like structure; all are an indication of its complex and rich physical and chemical nature. Defining such a multi-character material is a daunting job. Good understanding of the molecular structures (the microscopic view), as well as the thermodynamic behaviors (macroscopic view) are the basics to learn about this mysterious material under different conditions.

The scientific route toward defining a system requires several stages of establishment and validation even if this system is already describable by various self-contain physical principles. As the starting point, molecular weight and chemical structure should be determined because they define the system's fundamentals. The next step could be its neat structures and followed by its solution, suspension, or emulsion behaviors. Related to these behaviors are effect of concentration, temperature, and relevant thermodynamic parameters on the system states. Finally, there should be a set of critical parameters to define such systems characterize them unambiguously. These include structural evolution, evolution kinetics, phase behaviors, and critical phenomena related to thermodynamics, kinetics (e.g., under flow, temperature ramping, and quenching), and physical properties (shear, electric, magnetic, dielectric, and gravitational forces). For a system as complex as the asphaltene system, completing all the requirements is certainly very challenging. Yen set the goal to define this complex system and the well-known Yen model was the foundation he proposed to work toward his goal.

At the dawn of microscopic measurement techniques in early 1960's when X-ray scattering, NMR, ESR, and FTIR first emerged in petroleum research, the young Teh-Fu Yen drew a master plan to crack the asphaltene mystery on the molecular scale. He started by gathering as much data as possible in each experiment to reduce the burden of conducting more experiments, which, in the era of nearly no sophisticated microscopic theories, is often a golden rule among experimentalists. Through analysis of massive amounts of experimental data, either collected himself or by others, the well-known Yen asphaltene structure model was born in 1961 (see **Figure 1**)^{[2-}

^{4]}. Yen's colloidal-like structure for asphaltene has since drawn numerous follow-up studies, either designed to validate or invalidate this model. To date, Yen's model continued to be speculated, examined, challenged, validated, and intensively discussed. Under numerous thunders and storms this model stands.



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Zig-zag configurations: saturated carbon chains or loosely net of naphthenic rings Straight lines: the edges of the flat sheet of the condense aromatic rings

Figure 1: Yen's asphaltene structural model derived from the X-ray diffraction data of Gilsonite asphaltene from Baxterville, Mississippi

Yen's model is based on the concept of a "size progressive structure" via aggregation and clustering processes. This is essentially a colloidal view. Yen was not the first to suggest such a view. In 1923, Nellesteyn proposed the colloidal model in his dissertation, 38 years before Yen's proposal.^[5] The next significant contribution after Nellesteyn that led to Yen's view on asphaltene as a colloidal was from Pfeiffer and Saal. They presented a resin peptized asphaltene colloidal model in 1939, which heavily influenced Yen's view.^[6]

Following publication of the now well-known Yen colloidal model, Prof. Yen continued to pursue microscopic characterization of asphaltene for nearly a decade, mostly to validate or confirm the model using different sources of asphaltene and using various measurement techniques.^[7-15] In 1967, Dickie and Yen published a summary, reporting many microscopic techniques they used to confirm the model: X-ray diffraction, mass spectrometer, gel permeation chromatography, ultracentrifugation, and microscopy.^[16] It was in this work where Yen first proposed the size of aromatic core (referred to as disk weight detected in the X-ray scattering) and molecular weight (referred to as "unit" or "sheet" weight) of asphaltene to be between 300-800 Daltons and 800-3500 Daltons, respectively. The molecular weight range was only slightly larger than what is known today, as demonstrated by many recent studies, including the latest direct molecular imaging of asphaltenes by non-contact Atomic Force Microscopy.^[17-26]

Other than the molecular weight determination, Yen tackled two more major research fronts – chemical structures and heterogeneous atoms and complexes. On characterizing the chemical structure, Yen focused on investigating porphyrin structures and the techniques he used included X-ray diffraction, NMR, IR, and ESR.^[27-32] For heterogeneous atoms and complexes, Yen applied ESR and NMR techniques, and the focus was very much on the vanadium complexes.^[33-40] Obviously, Yen believed the vanadium complexes were responsible for the asphaltene disk stacking he observed in the X-ray diffraction measurements. Yen interpreted the stacking as the representation of aggregation, and he believed, the aggregation is initiated by the charge transfer of the vanadium complexes and the porphyrin structure. To this date, the possible forces involving in the asphaltene stacking/aggregation processes remain an active research topic.^[41-43]

Yen's colloidal view and structural model drew intense research since the 1980's and well into the 90's when more sophisticated statistical mechanical theories, such as the analytical solutions of Ornstein-Zernike equation, became available for analyzing microscopic measurements. These measurements include small angle X-ray and neutron scattering that had been applied to measuring complex fluids.^[44-49] These relative new microscopic techniques and their corresponding statistical mechanical analysis methods more or less supported the colloidal system. However, asphaltene's physical phenomenon at different thermodynamic states largely remained unchecked. In the meantime, the field engineers continue to monitor asphaltene and treat it by using the known-to-be-effective thermodynamic approach^[50] that is based on a much large length scale, compared to those uprising new measurements and the statistical mechanical theories.

From a practical point of view, asphaltene can be well controlled in the field with known techniques and most field engineers are aware of the know-how. However, there has been always scientific curiosity about what really asphaltene is. Polymer, colloidal, simple solution, and fractal system views help explain a range of asphaltene experiments in 1990's, leaving a wealth of research for this somewhat obscure species. Yet, there are no clean-cut theories that can unambiguously explain the wide variety of asphaltene behaviors that exhibit on both thermodynamic and statistical mechanical axes. In addition to the colloidal model, treating asphaltene as a fractal system with a proposal of its fractal dimension first appeared in 1989. This suggests that asphaltene could be more than just a colloidal system ^[51-61], despite the fact that a colloidal system may exhibit a fractal geometry within a diffusion limited process.^[62] However, asphaltene aggregation process is more than just a simple diffusion limited process.^[63] As a result, the same question continues to be asked: is asphaltene solution a simple colloidal system, if not, what is it?



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Since 1950 -1960's, there were many attempts in identifying asphaltene molecular weights and structures and Yen was at the center of it. Yen's indirect approach by comparing the X-ray spectra of asphaltene with known chemicals is not really an accurate method, even though it is scientifically legitimate,.^[15] Nevertheless, his work proposed a baseline about the involvement of polynuclear aromatics in the asphaltene structures. On the neat structure, Yen's X-ray work was phenomenal and the data he collected from many sources remains one of the most trustable databases. On asphaltene-containing solutions, Yen did not explore their properties, mainly because the then existing microscopic techniques were not mature enough to directly characterize a colloidal structure to the extent required by theories. As for the phase study, Yen briefly explore the liquid crystalline phase using microscopy in 1990's.^[63] The finding was exploratory, innovative and intriguing, but this work did not provide a full description of asphaltene liquid crystalline phases as did the recent work by Bagheria et al.^[64]

As one can see, Yen's approach was always on the track toward defining the asphaltene system following the classical scientific route as discussed earlier in this article. Despite his multi-decade's work, it is far from complete. However, Yen's model set a starting point and remains as the basic structural standard, from where other views start to emerge, develop, and proceed beyond the simple structural elucidation of his model. To date, over half of a century after Yen proposed the model, we are still in the juncture of how to scientifically define the asphaltene system. In the foreseeable future, there will be more research and controversy injecting into this community; however, it is certain that Yen's model will remain a center of discussion for a long time to come.

Reference

- 1. Boussingault, J. B. Ann. Chim. Phys. 1837, 64, 141
- 2. Yen, T.F.; Erdman J.G.; and Pollack S.S., Analytical Chemistry, 1961, Vol. 23, pp. 1587-1594.
- 3. Yen, T.F.; Erdman J.G.; and Pollack S.S., American Chemical Society Division of Petroleum Chemistry, Preprints, 1961, Vol. 6, No. 1, pp. 21-36.
- 4. Yen T.F.; Erdman J.G.; and Saraceno A.J., American Chemical Society Division of Petroleum Chemistry, Preprints, 1961, Vol. 7, No. 3, pp. B53-B66.
- Nellensteyn F.J., "Bereiding en constitutie'van asphalt (Manufacture and constitution of asphaltic bitumen," Dissertatie Technische Hoogeschool, Delft, 1923
- 6. Pfeiffer J.Ph. and Saal, R.N.J., "Asphaltic Bitumen As Colloid System," presented at the sixteenth colloid symposium, held at Stanford University, California, July 6-8, 1939
- 7. Yen, T.F. et al., ACS Div. Petro. Chem., Preprints, 1961, Vol. 7, No. 3, pp. B53 B66.
- 8. Yen, T.F. et al., Anal. Chem., 1962, Vol. 34, 694 700.
- 9. Yen, T.F. et al., ACS Div. Petro. Chem., Preprints, 1962, Vol. 7, No. 1, pp. 5 18.
- 10. Yen, T.F. et al., ACS Div. Petro. Chem., Preprints, 1962, Vol. 7, No. 3, pp. 99 111.
- 11. Dickie, J.P. and Yen, T.F., 1968 J. Mass Spec., Vol .1, 501
- 12. Yen, T.F. et al., ACS Div. Petro. Chem., Preprints, 1968, Vol. 13, No. 1, pp. 59 75.
- 13. Yen, T.F. et al., Inst. Petro., 1969, Vol. 55, pp. 87 99.
- 14. Sill, G.A. and Yen, T.F., Fuel, 1969, Vol. 43, pp. 61 74.
- 15. Pollack S.S. and Yen T.F., Anal. Chem., 1970, Vol. 42, No. 6, pp. 623 629.
- 16. Dickie, J.P. and Yen, T.F., Analytical chemistry, 1967, Vol. 39, No.14, pp. 1847-1852
- 17. Boduszynski, M.M., Energy & Fuels 1987, Vol. 1, pp. 2-1.
- 18. Sheu E.Y., J Phys Condense Matter 1996, Vol. 8, p. A125. 1
- 19. Miller J.T.; Fisher R.B.; Thiyagarajan P.; Winans R.E.; and Hunt J.E., Energy & Fuels 1998, Vol. 12, p. 1290.
- 20. Groenzin H. and Mullins, O.C., Energy & Fuels, 2000, Vol. 14, p. 677.
- 21. Qian K.; Rodgers R.P.; Hendrickson C.L.; Emmett M.R.; and Marshall A.G., Energy & Fuels, 2001, Vol. 15, p. 492.
- 22. Hughey C.A.; Rodgers R.P.; and Marshall A.G., Anal Chem. 2002, Vol. 74, p. 4145.
- 23. Cunico R.I.; Sheu E.Y.; and Mullins O.C., Petroleum Sci. Technol. 2004, Vol. 22, pp. 7-8.
- 24. Schuler, B.; et al. *Energy & Fuels* 2017, Vol. 31, 6856-6861.
- 25. Zhang, Y., chapter 3. In *Chemistry Solutions to Challenges in the Petroleum Industry*, Rahimi, P.; Ovalles, C.; Zhang, Y.; Adams, J., Eds. American Chemical Society: 2019.
- 26. Zhang, Y.; Siskin, M.; Gray, M. R.; Walters, C. C.; Rodgers, J. R., Energy & Fuels 2020, Vol. 34, 9094–9107.
- 27. Yen T.F.; Baker E.W.; Dickie J.P.; Rhodes R.E.; and Clark L.F., American Chemical Society Division of Petroleum Chemistry, Preprints, 1976, Vol. 12(2), A59-A71.
- 28. Baker E.W.; Yen T.F.; Dickie J.P.; Rhodes R.E.; and Clark L.F., Journal of American Chemical Society, 1967, 89, 3631-3639.
- 29. Yen T.F.; Boucher L.J.; Dickie J.P.; Tynan E.C.; and Vaughan G.B., American Chemical Society, Division of Petroleum Chemistry, Preprints, 1968, 13(1), 59-75.
- 30. Yen T.F.; Boucher L.J.; Dickie J.P.; Tynan E.C.; and Vaughan G.B., Journal of Institute of Petroleum (London), 1969, Vol. 55, 87-99.
- 31. G. B. Vaughan G.B.; Tynan E.C.; and Yen T.F., Chemicals Geolology, 1970, Vol. 6(3), 203-219.
- 32. Yen T.F., Naturwissenschaften (Berlin), 58, 267-268 (1971).
- 33. Tynan, E.C. and Yen, T.F., American Chemical Society Division of Petroleum Chemistry, Preprints, 12(2), A89-A101 (1967).
- 34. Boucher, L.J.; Tynan, E.C., and Yen, T.F., *Inorganic Chemistry*, 7, 731-736 (1968).
- 35. Yen, T.F., Boucher, L.J., J. P. Dickie, Tynan, E.C.and G. B. Vaughan, American Chemical Society, Division of Petroleum Chemistry, Preprints, 13(1), 59-75 (1968).
- 36. Boucher, L.J., and Yen, T.F., Inorganic Chemistry, 7, 2665-2667 (1968).
- 37. Boucher, L.J.and Yen, T.F., Inorganic Chemistry, 8, 689-692 (1969).
- 38. Boucher, L.J., D. E. Bruins, Yen, T.F., and Weaver, D.L., *Journal of Chemical Society, D,Chemical Communication (London)*; 7, 363-364 (1969).



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- 39. Tynan, E.C., and Yen, T.F., Fuel (London), 43, 191-208 (1969).
- 40. Yen, T.F.; Boucher, L.J., Dickie, J.P.; Tynan, E.C.; and Vaughan, G.B., Journal of Institute of Petroleum (London), 55, 87-99 (1969).
- 41. Ghosh A.K., Fuel, 2005, Vol. 84, 153–157.
- 42. Spiecker, P.M.; Gawrys, K.L.; and Kilpatrick, P.K., Journal of Colloid and Interface Science, 2003, Vol. 267, 178–193
- 43. Mostowfi, F.; Indo, K.; Mullins, O.C.; and McFarlane, R.; Energy & Fuels, 2009, Vol. 23, 1194–1200
- 44. Herzog, P.; Tchoubar D., and Espinat, D., Fuel, 1988, Vol. 67(2), pp. 245-250
- 45. Ravey, J.C.; Ducouret, G., and Espinat, D., Fuel, 1988, Vol. 67(11), pp.1560-1567
- 46. Overfield, E.; Sheu, E.Y.; Sinha, S.K.; and Liang, K.S., Fuel Sci. Technol. Int. 7 (5–6) (1989), p. 611.
- 47. Sheu, E.Y.; Detar, M.M., and Storm, D.A., Journal of Macromolecular Science-Chemistry, 1991, Vol. A28 Pp. 159-175, Supplement: Suppl. 2.
- 48. Storm, D.A.; Sheu, E.Y.; and Detar M.M., Fuel, 1993, Vol.72(7), pp. 977-981
- 49. Sheu E.Y., et al., Journal of Colloid And Interface Science, 1992, Vol. 153(2), pp. 399-410
- 50. de Boer, R. B.; Leerlooyer, K.; Eigner, M. R. P.; Van Bergen, A. R. D. Screening of Crude Oils for Asphalt Precipitation: Theory, Practice, and the Selection of Inhibitors. SPE Journal 1995, 10 (01), 55-61.
- 51. Crickmore, P.J. and Hruska C., Fuel, 1989, Vol. 68 (11), pp. 1488-1489
- 52. Raghunathan P., Chemical Physics Letters, 1991, Vol.182(3-4), pp. 331-335
- 53. Lin, J.R.; Lian H.J.; Sadeghi K.M., and Yen, T.F., Fuel, 1991, Vol. 70(12), pp. 1439-1444
- 54. Mukhametzyanov I.Z. and Kuzeev I.R., Colloid Journal of The USSR, 1991, Vol. 53(4), pp. 644-
- 55. Monsoori JA et al., Journal of Petroleum Science and Engineering, 1993, Vol. 9, pp.17–27.
- 56. Toulhoat H et al., "Characterization by atomic force microscopy of adsorbed asphaltenes," *Colloids Surf., A: Physicochem. Eng. Aspects*, 1994, Vol. 91, pp. 267–283.
- 57. Liu Y.C.; Sheu E.Y.; Chen S.H., and Storm, D.A., Fuel, 1995, Vol.74(9), pp. 1352-1356
- 58. Anisimov MA et al., Asphaltene Aggregation in Hydrocarbon Solutions Studied by Photon Correlation Spectroscopy," *J. Phys. Chem.* 1995, Vol. 99, pp. 9576–9580
- 59. Rassamdana, H. and Sahimi, M., AICHE Journal, 1996, Vol. 42(12), pp. 3318-3332
- 60. Rahmani NHG, "Fractal structure of asphaltene aggregates," Journal of Colloid and Interface Science, 2005, Vol. 285, pp. 599-608,
- 61. Rahimi, H. and Nazar A.R.S., Energy & Fuels, 2010, Vol. 24, pp. 1088-1093
- 62. T.A. Witten Jr, L.M. Sander, Phys. Rev. Lett. 47 (1981) 1400-1403
- 63. I. K. Yudin et al., Journal of Petroleum Science and Engineering, 1998, Vol. 20(3-4), Pp. 297-301
- 64. Bagheri, S.R., et al., Energy Fuels, 2010, Vol. 24 (8), pp 4327-4332.