The Founders and Innovators of Catalysis Science

Sir Hugh Taylor and Irving Langmuir (1932 Nobel Prize) were the first “deans” of catalysis in the U.S. A slightly younger Paul Emmett was to join them in this lofty arena. From 1927-1937, his work laid a the foundation that transformed catalysis from an art to a science.

Emmett was born in Portland, Oregon, the son of a railroad man. He was introduced to chemistry by his high school teacher. He and a high school classmate, Linus Pauling (who became one of the most influential scientists in American history) graduated from Oregon State University and pursued their doctorate degrees at the California Institute of Technology. At that time, Cal Tech was just beginning a graduate program and had awarded only four Ph.Ds. in chemistry until Emmett and Pauling's class of four graduated.

His work with Stephen Brunauer at the Fixed Nitrogen Lab (FNL) laid the foundation for the characterization of heterogeneous catalysts. The BET method (named for Brunauer, Emmett, and Edward Teller) is the standard for measuring the surface area for heterogeneous solids. Seventy five years after publication, it is still one of the 10 most cited papers in chemistry. In addition, Emmett and Brunauer developed the chemisorption method to measure the surface area and dispersion of metals on a supported catalyst, which is still the classic method for performing this task. They developed the basic kinetics for ammonia synthesis in this new and emerging field.

CAER Expands Briquetting and Binder Development

The University of Kentucky Center for Applied Energy Research/American Coal Ash Association co-organized the international conference, which boasted around 600 attendees from 16 countries besides the U.S.

WOCA 2013

The biennial World of Coal Ash Conference was welcomed back to the south this spring. Once again held in Lexington, Kentucky, The University of Kentucky Center for Applied Energy Research/American Coal Ash Association co-organized the international conference, which boasted around 600 attendees from 16 countries besides the U.S.
This year’s plenary speakers were: Bruce H. Watzman, National Mining Association, Senior Vice President for Regulatory Affairs “Future of Coal Utilization”; and to add an international flair, Craig Heidrich, Chief Executive Officer Ash Development Association of Australia Inc. “Coal Combustion Products: A Global Perspective”.

The papers presented are now available for viewing at the Ash Library. Remember the peer-reviewed journal: Coal Combustion and Gasification Products, as it is an excellent refereed journal for the coal combustion product industry, in which authors may publish valuable journal articles. If you think your WOCA paper might be rewritten into a refereed journal article, contact editor-in-chief, Dr. Jim Hower.

An offsite reception was held at the Headley-Whitney museum in Lexington. Under a large white tent, attendees were treated to live music and southern food delicacies.

As always UKCAER and ACAA wish to sincerely thank the exhibitors and sponsors of this event. Without their participation, this conference would not exist.
Emmett and Brunauer also defined the chemisorption and dissociation of nitrogen as the rate limiting step of the reaction. Gerhard Ertl, winner of the 2007 Nobel Prize, credits Emmett’s work and discussions with him as being the initial basis for his work in this area.

In 1937, Emmett left the FNL to develop a chemical engineering department at The Johns Hopkins University. During WWII he joined the Manhattan Project and headed a group working on the barrier for uranium isotope separation. He then joined the Mellon Institution where he became a pioneer in the use of radio-tracers in catalysis research.

His work led to the acceptance of the oxygenate mechanism for Fischer-Tropsch synthesis. Emmett returned to Johns Hopkins in 1956 and remained there as the W.R. Grace Professor until he retired in 1970.

Emmett and his first wife, Leila, were extremely devoted to each other. Leila was fluent in French and helped Emmett with translations as well as developing the index for each of the seven volumes of the influential Catalysis series that Emmett edited. Leila could have been a role model for youth rehabilitation. She was convicted in her early 20s of embezzlement and spent a year in prison. Emmett met his second wife on a visit to Australia. She had been married to the Australian Ambassador to India and was one of Nehru’s favorites but this marriage ended in divorce (after the five year waiting period required then) before her marriage to Emmett. His second marriage lasted only about a year. He then married Pauline Emmett, a sister of Linus Pauling, who was a devoted companion during his final years.

Edward Teller
(1908 – 2003)

A native of Hungary, Edward Teller was from an upper middle-income Jewish family. He attended school with other talented students and five of them eventually migrated to the U.S. where they became known as the “Five Martians” to signify their amazing brilliance. The five were Leo Szilard, who envisioned the atomic bomb; Eugene Wigner, Nobel Prize winner; Theodore von Kármán, whose work in aeronautics led to supersonic flight; Johny van Neuman, leading mathematician who pioneered computers; and Edward Teller. In addition to their exceptional intellectual abilities, all were fiercely opinionated, politically active, and strongly opposed all forms of totalitarianism. It is amazing that a country with a population of only about ten million could produce five such superior intellects in such a short period.

Teller left Hungary in 1926 because of the government’s persecution of Jews. He studied in Germany, obtaining a Ph.D. under Werner Heisenberg, Nobel Prize winner for his development of the uncertainty principle. Under a Rockefeller fellowship, he studied in Sweden with Niels Bohr, developer of quantum mechanics and Nobel Prize winner. He met George Gamow (theoretical physicist and early developer of the big bang theory) who offered him an opportunity to join him in the Physics Department at the George Washington University in D.C. The two soon published theoretical papers that attracted much attention. They organized meetings featuring theoretical physics and it was at one of these that Niels Bohr announced the splitting of the atom: the atomic bomb soon followed.

While still in Hungary, Teller was riding the streetcar one day, deep in thought, and failed to exit until it started moving. Jumping off, he lost his footing and slid under the wheels of the car, losing his right foot. He used a large cane to walk the rest of his life. Even so, he was an outstanding table tennis player and in Germany lost only to his thesis advisor, Heisenberg; friends debated whether the losses were due to Heisenberg’s ability or Teller’s political acumen.

Teller was responsible for many scientific advances. The Jahn-Teller effect has become a standard for chemists and is so common that today it is not referenced. He and Gamow made major advances in our understanding of the reactions of the sun. Teller developed the theoretical basis for the BET (Brunauer, Emmett, and Teller) method for measuring the surface area of solids. He wrote theoretical manuscripts that helped lay the foundation for what has become the density functional theory and the Monte Carlo method, both commonly used standard approaches today.

Teller’s work at Columbia University eventually became the Manhattan Project. He then moved on to the University of Chicago and then Los Alamos to work on theoretical approaches for the development of the atomic bomb.

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Economic Development in Eastern Kentucky Requires Integration of Energy Resources

Roger Ford, CEO of Patriot Bioenergy Corporation

“A typical vice of American politics is the avoidance of saying anything real on real issues.” President Theodore Roosevelt’s words have no more truer meaning today than they did when spoken over 100 years ago. So it is with energy and economic development policy that old strategies must be replaced with a new energy-economic development paradigm. We must address the age-old dilemma—the bust in the boom-bust cycle of coal production—that is now coupled with overregulation by the government and new market conditions that place us at a competitive disadvantage. To avoid potentially irreversible economic damage in less than a generation, our response must be swift in pivoting to a bold strategy that breaks the long-standing, vicious boom-bust economic cycle.

Government and political leaders need to recognize that they must reconstruct a consensus development framework, but should entrust entrepreneurs and businesses to lead on breaking through traditional strategies and barriers to create market-based sustainability and innovation, focusing on current strengths in the energy sector, while incorporating new energy-economic development by tapping the potential of alternative energy.

In Eastern Kentucky, poverty rates continue to rise. The latest statistics show in 31 Southeastern Kentucky counties, nearly 200,000 people, or nearly 30% of the population, live in poverty. Coal employment is at its lowest point since 1950. Likewise, coal severance tax revenue, a key source for the region, continues to decline. Some suggest replacing coal jobs with tourism jobs. That is, replace high income jobs with minimum wage jobs. This is not a reasonable solution. While tourism is important, it is not a replacement for coal wages.

As a native of Pike County, I see the emergence of an economic dichotomy in our Commonwealth. One—the “Golden Triangle (Louisville, Lexington, northern Kentucky)—is diversifying economically and the other—rural Eastern Kentucky—is struggling in a post-coal mining era. Our region is plagued with generational unemployment and underemployment, educational brain-drain, and drug addiction. Efforts to address this have been made in piecemeal fashion, but a vision that incorporates options that promote the whole energy potential of Eastern Kentucky, while also putting in place an incentive framework to encourage and promote entrepreneur risk-taking for new job creation, is required.

Therefore, to say something real on issues, it is time to create a new energy-economic paradigm in Eastern Kentucky. The nexus lies not only in responsible and continued use of fossil fuels, but in the need to look beyond the monolithic coal economy to the undeveloped potential of alternative and renewable energy, thereby developing an integrated strategy for a new rural economy. Adopting a true ‘all-of-the-above’ energy strategy, based on sound market-based principles, is a good first step.

Government planning failed in the past to integrate energy development. An example is found in the failure to build hydropower generation into flood control dams. One can easily see this failure when one looks at the number of dams nationwide. According to the U.S. Army Corps of Engineers, there are approximately 79,000 dams in the United States. Of those, the Federal Energy Regulatory Commission regulates approximately 2,300 hydroelectric dams, with approximately 240 additional dams that produce hydroelectricity for an approximate total of 2,540 hydroelectric dams. That is little more than 3% of the total number of dams producing hydroelectricity. Absurdly, this demonstrates a failure to strategically plan on the part of government planners.

In Eastern Kentucky, a similar example of systemic failure to strategically plan for a post-mining era reveals itself. While a limited scope has sought to strategically think about post-mine land use, one could contend that the lack of proper economic planning delays this effort. As China, Japan, and India, continue forward with de-politicized energy development, we continue to promote an ‘either-or’ proposition.

Competing interest groups must reconcile for common purpose toward greater efficacy. We must consider how resources can be integrated to add market value, to create high wage jobs in Eastern Kentucky.

Post-mine land redevelopment, which integrates alternatives and renewable energy resources with fossil fuels, charts a path toward energy innovation in Eastern Kentucky. Localization and decentralization enhances both rural job creation and energy security.

As a path forward, I propose a new energy paradigm that moves us beyond the ‘either-or’ political posturing. As we break through, we will create sustainably sound
The Founders and Innovators of Catalysis Science...continued

He became the driving force behind the development of the hydrogen bomb and eventually became known as the 'father of the H-bomb,' a term he did not like.

Teller was a co-founder of the Lawrence Livermore National Lab and served as its director for many years. He also was a driver of a defense system that came to be called 'star wars' during the Reagan administration.

Because of his testimony during the Robert Oppenheimer hearings, he lost many friends. It is likely that due to the discord generated by the Oppenheimer hearings, neither Oppenheimer nor Teller were awarded the Nobel Prize though the accomplishments they made in physics merited one.

Economic Development in Eastern Kentucky Requires Integration of Energy Resources...continued

communities that are economically diversified and growth-oriented. Within Eastern Kentucky exists opportunities for this new paradigm. It requires all government to recognize that action is required now and that structural reform is needed to bring about this transformation. Political activists must be flexible in the best interests of the region, because a changing global market, along with responding to increasing local energy and economic demands, require us to properly exploit these opportunities. We must unite and set in place a plan that diversifies our region in an environmentally responsible framework, using all energy resources, developing new educational skill sets, and breaking the detrimental impacts of the 'boom-bust' economic cycle, permanently.

Geoffrey Wilkinson
(1921 – 1996)

Geoffrey Wilkinson was born in a poor neighborhood of Springside, England that was demolished soon after his birth because of the low quality of the housing. From this humble beginning, his excellent academic record won him a Royal Scholarship at Imperial College in 1939, graduating in 1941. He continued at Imperial for about a year and then went to Canada to work in nuclear research. After leaving Canada in 1946, he began working with Prof. Glen Seaborg, a future Nobel Prize winner, and taught at Berkeley for four years. At the end of his stay in Berkeley the prospects in England were not good for an inorganic chemist so he went to MIT where he worked on olefin complexes.

In 1951 he became an assistant professor at Harvard University and remained there until 1955. While at Harvard his attention was drawn to a compound that has become known as ferrocene \([\text{Fe}(\text{C}_5\text{H}_5)_2]\). In a publication with R. B. Woodward and others, he proposed the unique structure that accounted for the stability of the compound. This work led to an explosion in research with these types of compounds and developed into a sub-special interest area of organometallic chemistry.

Next he returned to England as chair of inorganic chemistry at Imperial College, remaining there until his retirement at 65. He relied more on the quality of his ideas than on the quantity of his work to establish his position in chemistry. He teamed with Prof. F. Albert Cotton of the U.S. to write Advanced Inorganic Chemistry which has undergone many editions and has become a standard text through the world.

Arriving at the university on the day that he was to attend his last graduation ceremony before retirement, his opening remark was, “Why in the hell did I agree to this?” Nevertheless, he spent the next half-hour presenting a synopsis of his career all the while drawing precise chemical structures on the blackboard.

In 1973, he received a Nobel Prize for his work primarily based on his definition of the ferrocene structure and for the inorganic catalyst \([\text{RhCl(PPh}_3)_3]\) which had been aptly named the Wilkinson Catalyst.

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The Founders and Innovators of Catalysis Science...continued

Gabor Somorjai was born in Hungary to Jewish parents. He was studying chemical engineering at the Budapest University of Technology and Economics when the Soviets invaded Hungary in 1956. He participated in the Hungarian Revolution, afterwards leaving his homeland to immigrate to the U.S. Somorjai thus was part of a second generation of super-scientists to leave Hungary at the benefit of the U.S. Many felt that Somorjai should have joined Gerhard Ertl in 2007's Nobel Prize in Chemistry but, like Ipatieff, he was left to say, "From Nobel I get praise but no award."

Somorjai joined IBM after receiving his Ph.D. in 1960 and remained there until 1964 when he joined Berkley as an Assistant Professor. As a chemist, Dr. Somorjai felt the need to understand and visually describe surface interactions at the molecular level. Unable to find what he needed, he developed necessary techniques and instrumentation. His unique, chemical approaches to the study of surfaces elevated it to surface science with him as the "developer of modern surface chemistry."

Prof. Somorjai is the recipient of many awards; including the Wolf Prize in Chemistry in 1998; the Linus Pauling Award in 2000; the National Medal of Science in 2002; and the Priestly Metal in 2008.

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The Founders and Innovators of Catalysis Science...continued

Gehard Ertl (1936 - )

Gehard Ertl was 71 years old when he was awarded the Nobel Prize in chemistry in 2007. Born in Germany, he spent his career at German universities and research institutes. Following stints at three universities, he joined the Fritz Haber Institut der Max Plank-Gesellschaft in Berlin as a director. It is appropriate that he became associated with the name Fritz Haber since Haber received a Nobel Prize for discovering the method to synthesize ammonia and Ertl’s Nobel Prize was heavily influenced by his studies of the catalytic mechanism for ammonia synthesis.

Ertl began his research career just as surface science instruments were becoming available commercially. However, to make effective use of these instruments the scientist had to become a machinist. The results produced by Ertl make it apparent that he excelled in this as he did in his scientific studies.

Ertl’s entry into his ammonia synthesis studies followed his hearing famed scientist Paul Emmett lecture on the subject. Ertl’s entry followed by about 40 years Emmett’s pioneering work on the mechanism of ammonia synthesis. Emmett’s work occurred near the end of the wet chemistry studies, while Ertl’s work ushered in the new era of sophisticated instrumentation for catalytic studies.

Ertl’s research showed outstanding organization and steady progression to more difficult studies. His initial work involved studies of the arrangement of surface atoms and how hydrogen chemisorbed and arranged themselves on the surface of metals, such as palladium, platinum and nickel. In the 1970s he shifted his attention to ammonia synthesis. His work demonstrated conclusively that Emmett’s conclusion that the rate limiting step was the dissociation of nitrogen. Ertl also used surface instruments to show where the atoms were located on the surface and how potassium promoted the reaction. Most importantly, Ertl outlined the step by step mechanism for ammonia formation and provided the activation energy needed for each step of the reaction.

Ertl next moved on to the study of carbon monoxide oxidation, a reaction that was much more complex than ammonia synthesis. This continued Ertl’s fundamental studies of reactions that have a major impact on human welfare. Carbon monoxide oxidation is a key reaction in the automobile exhaust converter. Ertl’s work uncovered and explained a surprising observation. He demonstrated that the rate of the reaction underwent oscillations and that these were due to a similar oscillation of the surface coverage of the reactants. Again Ertl provided a solid, detailed description of the mechanism of a complex reaction that has very great importance for industry.

Gehard Ertl

CAER Expands Briquetting and Binder Development...continued

Major equipment within the briquetting and binder development laboratory includes:

- Komarek Model B-220 briquetter
- Komarek Model B-100 briquetter
- 40-cm (16-inch) diameter pan pelletizer
- 91-cm (36-inch) diameter pan pelletizer (Mars Mineral)
- 2-stage, 122-cm (48-inch) diameter roller drum
- 9-ft ribbon/paddle mixer
- 80 L dough style blender
- Gravimetric feeders (~20-300 kg/hr)
- Volumetric feeder
- 65-kW pellet/briquette dryer
- Delivery and collection conveyors
- Knife mill dedicated to biomass preparation (~100 kg/hr)

The facility also contains briquette-testing equipment (compressive strength meters and test stand, attrition mills, drop shatter apparatus, etc.), controlled environment chambers for curing, and a vibrating screener for fines removal. A wide range of equipment for chemical and physical testing and for sample preparation is also available at the CAER web site (http://www.caer.uky.edu/services/analyticalaboratory.shtml).

The services of the briquetting and binder development facility are available for industrial, academic, or government projects ranging from small scale research initiatives to larger-scale production runs.

To learn more, contact:
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Keith Hall
(1918 - 2001)

W. Keith Hall was born in McComb, Ohio, a small town of about 1,000 inhabitants. He died at his farm in Mill Run, PA where he did not just live on his farm – he actually produced the crops.

Hall completed his B.S. at Emory University in 1940 and spent the summer at Georgia Tech studying high explosives. Following his father’s advice to ‘make as much money as possible before the war starts,’ he began working at the U.S. Bureau of Mines where George Kistiakowski and Louis Hammett were exploring high explosives for the military. Shortly after joining the Bureau, WWII started; Hall considered enlisting but was told that he would be assigned to do the same job he had, but at the lower Army pay. He did not join the Army. His Bureau work was to investigate explosives for the trigger of the atomic bomb with Kistiakowski directing the last portion of this work at Los Alamos.

Following the war, Hall remained at the Bureau working for Robert Anderson and H. H. Storch researching Fischer-Tropsch synthesis. According to Hall, Storch was a wonderful person although he could be “pretty positive about many things!”

In 1951, Hall joined Paul Emmett at the Mellon Institute, while working on his Ph.D. at the University of Pittsburgh. Hall’s lab partner was famed scientist, Dick Kokes, who was an exceptionally hard working scientist with outstanding creative skills in designing experiments. Hall found he could make rapid progress by telling Dick that a problem could not be solved, and find that Dick would return the next morning with the answer.

When Emmett left Mellon in 1954, Hall was named to replace him. This was an ideal position with six post-docs and ample travel funds. Hall remained at Mellon until 1970 when he joined Gulf Oil. Hall did not fit within the Gulf organization and, when George Keulks offered him a Distinguished Professorship at the University of Wisconsin at Milwaukee, he left. He remained there until 1985, when he retired and returned to become Professor at the University of Pittsburgh.

Robert Grubbs
(1942 - )

Robert H. Grubbs was born between Possum Trot and Calvert City in Kentucky’s Marshall County. He attended Paducah High School and then went to the University of Florida where he obtained his B.S. and M.S. degrees, working with Prof. Merle Battista, an excellent student mentor in addition to his research in inorganic chemistry. He then went to Columbia University where he worked with Prof. Ronald Breslow, again working with an excellent mentor, in 1958. After a year’s post doctorate at Stanford University working with Prof. James Coleman, he became a faculty member at Michigan State and remained there for about ten years. In 1978, he joined the California Institute of Technology and has remained there. He is currently the Victor and Elizabeth Atkins Professor of Chemistry.

Prof. Grubbs’ research has been in the general area of inorganic chemistry. One of the areas of his research involved the use of coordination complexes as catalysts for the conversion of alkenes. One of these complexes proved to be exceptionally active and selective for olefin metathesis. This catalytic reaction can be used to convert less desirable alkene or alkene mixtures to more desirable products. The catalyst that he developed is known today as a “Grubbs’ catalyst”. This type of catalyst was quickly taken up by researchers for scientific study as well as becoming an important catalyst for industrial use.

Grubbs received the 2005 Nobel Prize in Chemistry for his work in olefin metathesis. Kentucky seems to be unique for the production of inorganic chemists who advance to the Nobel Prize. William Lipscomb, University of Kentucky graduate, received a Nobel Prize in 1976 for his pioneering work in boron chemistry.

To be continued in next issue.

Burt Davis has been with the Center for Applied Energy Research since its inception and has published over 700 refereed articles.

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CAER Spring Filled with Student Tours

Elementary, middle school, and high school students from around the area monitored building efficiency, saw how fresh flowers can freeze quickly via liquid nitrogen (below), and discovered that algae is not just pond scum, during tours of CAER this spring (right).

The students hailed from Russell Cave Elementary, which celebrates its decade long partnership with CAER this year; Clark County Middle School through its partnership with Bluegrass PRIDE; and a group of female high school students from Fayette County’s “Green Team.” (bottom left/right)

There were around 150 students in total. While the tours were more detailed to suit the groups’ grade levels, all seemed fascinated by the science. The students were impressed when told that the newest building on CAER’s research campus uses only around 60 percent of the energy as a regular building its size. They were equally as enthralled with the idea that algae could be used to capture carbon dioxide emissions from power plants.

In addition to the demonstrations, researchers discussed their backgrounds, education, careers, and the need for future energy experts.

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