

COMBUSTION FIRES CAREER OF 1997 GUNNAR NICHOLSON GOLD MEDALIST PHILIP E. SHICK

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SULFITE PULPING AND RECOVERY PROCESSES ADVANCED THROUGH RESEARCH.

A SINGLE DROPLET SHOOTS THROUGH SUPER-HEATED gases. The rising eddies toss it out of a gently descending arc and fling it only so high as the forces of gravity will permit. Then down it falls, burning brightly into nothingness.

More droplets follow the first, some bigger, some smaller. Temperatures grow hotter or cooler, velocities change, arcs expand and condense. Some droplets spatter against the far wall, others fall partially consumed to the floor below.

On the computer screen, the droplets are mere pixels, or groups of pixels that travel across the screen. The program that drives them was written a number of years ago by Philip E. Shick, the 1997 TAPPI Gunnar Nicholson Gold Medalist. Writing in BASIC on a Texas Instrument desk-top computer—the kind with two 5-1/4-in. disk drives—Shick devised a way to model the flight pattern of black liquor drops in recovery boilers.

Shick used the information “to determine the most critical factors determining the amount of smelt carry-over into the convection sections of the boiler, a major

cause of boiler plugging,” said Thomas M. Grace, a former research professor with the Institute of Paper Chemistry who now heads his own company in Appleton, WI. “This work was the forerunner of the much more sophisticated recovery boiler models now used by boiler manufacturers and paper companies in improving recovery boiler performance.”

Grace, a TAPPI Fellow, worked with Shick in preparing a comprehensive report on smelt-water explosion studies and tying those together with studies of similar explosions in other fields. He noted that Shick “developed innovative approaches to inter-

preting the reasons for the effects of sensitizer chemicals in the smelt and in the water” and that he “helped clarify the role of viscosity in inhibiting explosions.”

Shick published many other studies during his career, including a comprehensive literature survey of sodium-base sulfite recovery processes with T. T. Collins Jr. and others on non-sulfur pulping.

Shick is probably best known for his work with sulfite recovery systems and for contributing to the development of the caustic-carbonate process “which has



Phil Shick

become the predominant process for producing semi-chemical pulp for the production of corrugating medium in the United States," according to William O. Kroeschell, a former TAPPI President, a TAPPI Fellow, and 1987 Distinguished Service Award winner.

A number of corrugating-medium mills that are dependent on hardwood pulp can thank Shick for their continued operation, Kroeschell indicated. "The non-sulfur caustic carbonate process has allowed those mills to continue, with a significant improvement in the environment," he said.

The Gunnar Nicholson Gold Medal is awarded to those individuals "who have made preeminent scientific and engineering achievements of proven commercial benefit to the world's pulp, paper, board, and forest products industries," notes Philip E. Nethercut, former TAPPI Executive Director and a TAPPI Fellow. In advocating the caustic-carbonate semi-chemical process, Shick fully met those qualifications, Nethercut believes.

Shick's work led to several U.S. and Canadian patents ranging from fabricatable stiff-when-wet corrugated paperboard, to methods for treating spent sulfite pulping liquors, to a recovery system for sodium-base sulfite pulping liquor, and several more.

For many years Shick served on the Recovery Boiler Research and the Black Liquor Recovery Boiler Advisory Committees of the American Paper Institute (now the American Forest & Paper Association). He also participated in TAPPI recovery boiler and recovery process seminars and served as technical program chairman of the 1972 International Sulfite Pulping and Recovery Conference. He was named a TAPPI Fellow in 1983.

Shick fondly remembers the early support he got at TAPPI meetings. He especially remembers answering questions after his first presentation. One person who started to badger the neophyte presenter with a series of questions was hissed by the audience. "It was my first paper and I was getting heckled, and they stood up for me," he said. "The technical people, especially, have just been real nice."

IN THE BEGINNING...

Shick was born Jan. 7, 1918, in Kendallville, IN, up in the northeast corner of the state. His family moved to Van Wert, OH, southeast of Fort Wayne, IN, when he was seven or eight years old. Both of his parents were teachers—his father taught high school math, his mother taught third grade.

"It's possible that they instilled certain study habits. My dad offered me \$5 if I brought home all 'A's on my first report card. And I did. So I'm the kind of guy who always tried to do the best."

Those characteristics served Shick well. "When I was a senior in high school, I was shy. I'd never gone anywhere on my own, never had a car. One of my teachers persuaded me to take one of the state tests for college." He took the test and ranked first in the county. "And that kind of put me on the map."

His mother then noticed that Harvard was offering national scholarships. It was an effort at the time to diversify the student body and attract students from around the country. The school wanted to bring in people who didn't otherwise have the financial resources to attend. So Shick applied for the scholarship and had to go to Fort Wayne to take a qualifying exam.

Shick's father was in charge of the local sewage treatment plant at the time. He had gone from teaching school to working for the Kendallville electric railway and was then transferred to Van Wert, OH, to supervise the office there. When the parent company ran into financial problems, the electric railway closed. Shick's father tried to get a local franchise to continue the service, but didn't get it.

"I was very bitter. Here my dad was trying to earn a living and they wouldn't let him," Shick recalled.

So Shick's father took a job reading meters. Then he became the city's representative when it put in a sewage collection system and treatment plant. When that was done, he got the job of running it.

"It was at this point that he took me in the truck over to Fort Wayne to take my exams for college. It was a cool day and I was up against these guys who had gone to prep school and so forth. But I didn't do too badly. As we were leaving, we had to walk into a cold wind and my dad stopped and had to hold back for a while because of chest pains," Shick said.

"And I thought, 'well you fat old man,'" he recalls now with regret. "I later learned that he'd had angina for years." He died of it 11 years later, while Shick was at Westvaco. "So you never know about making judgments."

Shick did well enough on the test to get an offer from Harvard. "I didn't bargain about it." The money was enough to cover tuition, and he also worked in the dining hall. Shick got by on less money than the minimum and only got home for Christmas the first year.

"It was not the greatest, most pleasant experience in life," Shick admits. "There was tremendous competition. There were guys right and left who had placed first in their high school class." But everyone was willing to help, including his father's former employer back in Kendallville, where his grandfather on his mother's side had been superintendent. That grandfather had emigrated from Sweden and worked in the woods for a while. He was skilled in furniture and cabinet making and died at age 92, which gives Shick expectations of liv-

ing at least as long.

Shick was graduated *cum laude* from Harvard in 1939. He went on to earn a master's degree from the Institute of Paper Science in 1941 and a PhD there in 1943. He had an occupational deferment during World War II; he was considered essential to the jobs he worked on during that period and was never called to serve. His older brother, who had served in World War II, died a few years ago.

"I faced a little bit of a dilemma at one point and resolved it by writing a letter to Prof. Grinnell Jones, who taught industrial chemistry at Harvard. I asked him what I should do, should I volunteer or what. He said it takes only 40 days to make a lieutenant, but it takes four years to make a chemist."

Shick took the advice and continued with his profession. His first full-time job was as a research chemist with Masonite Corp. in 1943.

"I left Masonite because I couldn't get along with the boss. He was a 'bull of the woods' type," Shick explained. As an example, the boss would call a meeting to outline something to be done. Shick suggested an alternative and the boss got so upset that he broke up the meeting. "The next time we got together it was his idea, same thing."

Shick later became more tolerant of that sort of behavior but decided he didn't want to work for a man with such an attitude and temper. He wrote a Christmas card to Dan Adams and said he was going to leave. He got a telegram saying "come see us" and ended up going to West Virginia Pulp and Paper Co. (Westvaco) in 1945.

Originally, they were going to have Shick run a pilot plant based on precipitated calcium carbonate, but the pilot plant wasn't ready when he started. So he started off being assigned to a group project to "make a silk purse out of a sow's ear." The project was to make the hardwood kraft fiber as good as their long (Virginia pine) fiber.

Shick's assignment was mechanical refining, of hardwood pulp especially, to determine how to get the most from the fiber. His team tried a number of inventive methods. One had a tritter that stirred fibers in with a pot full of marbles, which did a tremendous job of defibration. The team also conducted a variety of mill trials.

"I had a clear picture that if you could make better pulp you could make better paper. That's just common sense, but a lot of people say it's just not so; that what you do in the lab doesn't mean anything," Shick said. "Our paper machine trial proved otherwise."

Shick's efforts to produce the "silk purse" at Westvaco were short-lived. "In evaluating refining, I had never asked permission from the local mill manager, who was on the board of directors, to take samples at his mill," he recalled. "I reported on what I had found in a technical

report that went to all of management. I understood that made him mad... And I'm still like that where, even though I may not have gotten permission, I'll do things to get it done."

So during the downturn of 1948, the board of directors decided they needed to cut some costs. "They decided they would let the youngest and the unmarried guys go—and there were two of us," Shick said.

Shick sent off applications to a number of places, made some contacts at the TAPPI meetings, and then went to Florida for the first bit of vacation he'd had in quite some time.

He then moved back home to Van Wert, OH, for the interim and found a message waiting to get in touch with Russ Savage, VP of research at Mead Corp. They were looking for someone to fill a vacancy for a top researcher on staff. He came on in 1948 and worked in pulping, refining, papermaking research.

"Again, there's a carryover," Shick said. "I'd done a lot of fiber research. They were purchasing high-priced northern sulfite for their long fiber for most of their white paper grades in Chillicothe, OH."

Shick did lab tests and printing evaluations of the paper made at Mead and discovered a way around the earlier question. He wasn't going to make a silk purse out of a sow's ear; he was going to compensate for it. "I backed off on the refining of the short fiber and beat the heck out of the long fiber. It did a nice job, had adequate strength, held pigment well, and was just about the same if not quite as good as sulfite."

Mead switched over, "and I calculated that was worth US\$ 250,000 or US\$ 300,000 a year to that operation, back when that was a lot of money," Shick said.

THE MEAD RECOVERY PROCESS

While working for Mead Corp., Shick was fortunate to be assigned to do a literature survey and to evaluate methods of recovery for neutral sulfite pulp, "because they had a mill at Lynchburg, VA, that manufactured sulfite." They were interested in finding a recovery process to reduce the amount of by-products dumped into the local river. Through the literature search, Shick discovered a couple of options, including a pyrolysis process.

Shick synthesized the various ideas and proposed what later became known as the Mead Recovery Process. He tested some of the key steps for the carbonation process on a small scale in Chillicothe, OH. "The next year we designed and built a pilot plant that was installed in Sylva, NC," he said. The process was tested for about two years.

"This is where I really got a taste of operating a recovery furnace, except instead of a conventional, full-size furnace we had [a small-scale pilot furnace] designed by



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Babcock & Wilcox,” Shick explained. “It was a box inside of a box, with the space between filled with water. So you had very cold walls, and it wasn’t pressurized, so it wasn’t a steam vessel...it was just a water-cooled box. You can imagine burning wet liquor inside of a water-cooled box and get some idea of the problems we faced, at least initially.”

Admittedly, a lot of things in the first design didn’t work out as anticipated and a number of modifications were made after the first month of testing. The firing nozzle was moved high up in the furnace, for example, so that it fired directly onto the bed from five or six feet up. “A configuration like that could easily put the fire out, but with the right balance and particle size it worked,” Shick said. A chrome ore lining was also installed. “That gave a little bit of heat retention,” he continued, “normally it’s done to protect the tubes, but here it was done to keep the thing warm.”

So the first year it ran, but it was very tough. “The second year, we added about four feet to the height—making it about 11 feet—which vastly improved it. It gave the liquor a better chance to dry before it hit the bed.”

Eventually, that process was redesigned for commercial operation, with the first installation at Lynchburg, VA, and another at Watervliet, MI. None are active any more, as far as Shick knows.

Just as the pilot operation had run into problems converting commercial processes to small-scale, the commercial-scale recovery operations experienced problems adapting pilot-scale methods to full-scale operations.

The pilot originally used Raschig rings in the tower for packing. Babcock & Wilcox decided to use drip-grid

packing because that has a lower pressure drop than when using Raschig rings. “And there’s some merit to that because it’s hard to get deposits out of Raschig rings,” Shick said. But there are some complicated absorption-desorption mechanisms involved that lead to problems.

In this case, H_2S can be absorbed rather quickly because it reacts immediately with the hydroxyl radical to form a sulfide radical, Shick explained. “ H_2S ionizes $H + HS$, so it’s ionizable and it reacts in an ionic manner with a hydroxyl ion; you’ve got an ionic reaction that goes very rapidly. That’s not true with carbon dioxide. Carbon dioxide is fairly insoluble, and, after it’s dissolved, it’s not fixed. It’s got to react now as an unionized material, with a hydroxyl ion most likely, but it’s a slow reaction and the resulting product is a bicarbonate ion.

“So, the drip-grid packing, not holding liquor, didn’t have the volume to complete the reaction of the CO_2 to absorption,” Shick said, “and the towers didn’t work as well as the pilot plant work from which they were extrapolated.” There were also problems in precisely controlling the levels of CO_2 and with corrosion.

It was at this point in development, before problems showed up with the system, that Shick got an offer to become the research director for National Container, which was in the process of merging with Owens-Illinois.

NEW JOB, NEW CHALLENGES

An unhappy first marriage in Chillicothe, OH, contributed to Shick’s decision to take the research job in Jacksonville, FL. He left Mead in 1956 at about the time the Lynchburg operation was starting.

“One of the reasons I suspect I was hired into National Container was that my good friend and classmate Fred Shellhorn knew of my work at Mead. And they were having terrible trouble with their recovery at Big Island, VA, in particular. He didn’t tell me that when I was hired but that was about my first assignment, to go down to Big Island and see what I could do.”

One of the first problems Shick found was in how calibrations and analyses were being conducted. From his work on the carbonation process and in controlling the pilot plant, Shick had developed analytical techniques that permitted him to analyze mixed liquors and to calculate balances in the system, so he could see that different methods were needed.

“They had a bigger problem, too, which became more important as time went on,” Shick said. The small furnaces used at the mill were just barely adequate for the operations there.

Those furnaces were designed, like so many other things in life, based on a false principle, he said. “Instead

of using a direct-contact evaporator to control the liquor, they had a venturi scrubber that they put black liquor through and it did some quenching, but to keep from burning up the back end of the furnace—or smelting it up—they introduced large quantities of tertiary air to chill the gases.”

The first efforts to control that problem were to use bigger fans and to put in more tertiary air. But that increased the entrainment and promoted combustion of the entrained particles. Part of the liquor would be pyrolyzed and then re-entrained in the black liquor in the venturi. “So it went round and round and complicated various operations in the recovery and they lost steam.”

Shick suggested spraying water into the upper furnace gases to knock down the temperature, but the idea was rejected by the manufacturer. Quite independently, Joe Theiler, then mill manager at Big Island, came up with the idea of spraying water into the furnace.

“So then I had a compatriot,” Shick said. The system they came up used a fuel-oil gun to atomize water into the furnace. “Boy, that worked like a charm.”

SMELT-WATER EXPLOSIONS

Another problem Shick dealt with extensively was smelt-water explosions. Together with Tom Grace, Shick did literature studies and developed some ideas on the mechanisms that lead to smelt-water explosions.

“Smelt-water explosion has been compared to liquid-liquid explosion” Shick said. “You have one very hot liquid and give it a chance to mix with a volatile liquid at a lower temperature and you can get an explosion.”

From the studies, they learned that the composition of the smelt is an important factor. Shick proposed a concept that essentially says you don’t have smelt water as such at the interface. “What you’ve got is a concentrated solution of smelt on a hot smelt surface, in contact with a dilute solution or water. You can picture gradients of flash point or boiling point vs. concentration,” he explained.

“Salt in water changes its critical temperature and pressure relations. Salt seems to have a very strong relationship with water. So salt in smelt is one of the sensitizing combinations. There you have the possibility of salt in smelt at the interface and of caustic at the interface.”

FAMILY LIFE

Once the merger was complete, Shick moved to the Toledo, OH, offices of Owens-Illinois. It’s there he met his second wife, Margaret. She worked in the laboratory there. They knew each other for a long time, “but it was against my rules to date anyone from work, especially anyone from my department,” he said. “But I broke my own rule. I’d just gotten a new car, a red convertible. It

was some sort of special occasion and I asked her if she’d like to go for a ride in my convertible. We ended up going to supper and I started dating her.”

That was in the early 1960s. They soon married and had two children, Alan and Anthony. Allen, 33, was fascinated with airplanes at an early age. He also liked the idea of being a biology teacher, but ultimately went to work for Piedmont Airlines, which was later acquired by USAir. The job allows Alan the time and free travel to pursue his second love—roller coasters. In his off hours, Shick’s elder son meets with other American Coaster Enthusiasts (ACE) to ride roller coasters all over the country. Alan has ridden about 300 roller coasters, including those in England and Wales, and follows all developments in the theme park industry.

Tony, 29, took somewhat the same path as his father. He was valedictorian of his high school class of about 900, then got a scholarship to Toledo University.

“We had our kids late in life,” Shick said. “I started to set aside money for their education and put it in stocks and bonds. It was their money to spend as they wished. They both worked their way through college, living at home to cut costs, and kept their investments.”

Tony finished in chemical engineering at the top of his class, then he and his wife-to-be started looking for another college. Tony ended up at the University of Houston in a highly theoretical, mathematical program. After a few years there, he decided it wasn’t what he really wanted. He’d wanted to be a college professor, but it looked to him as if all they did was work to get grants. He lost interest, in spite of excellent grades, and decided to get a master’s degree instead of a PhD. He found work in the area with a petrochemical plant as a first-line supervisor—which I don’t think disappointed him because he likes people,” Shick said. Tony is now head of the department. His wife, in turn, finished with a PhD in biochemistry and is doing process engineering for biochemical products to treat cancer and immune system diseases.

Shick retired in October of 1982, just before turning 65 years of age. Owens-Illinois was offering buy-out packages at the time, and Shick was “really looking forward to retirement,” so he took the offer and immediately went into consulting. He had a two-year contract with Owens-Illinois. He was “the” expert on non-sulfur pulping, in which the company had a proprietary interest.

WHO INFLUENCED YOUR CAREER?

Among the most influential people in Shick’s life were teachers, from his parents to high-school teachers and professors at Harvard and the Institute of Paper Chemistry.

There were several people at the Institute whom Shick admired, including George R. Sears, one of his

instructors. "I don't know that I ever told him, but he was a good solid man and an excellent lecturer."

And there was Johannes A. Van Den Akker, the 1968 Gold Medal awardee, who served as one of Shick's thesis advisors.

"I did a thesis on lacquers for coating food containers. It wasn't really practical but it was something for the war effort. I ran viscosities with homemade equipment, namely a falling ball viscometer, and I calibrated it against glycerine at given solids and temperature," Shick recalled. "In my arguments for it I said that if the tubes were nonuniform, in as much as the balls must follow the same path each time, that each increment would respond to the rules of viscosity (at least in that the acceleration effects were very small) and that the integral would therefore correspond to the viscosity. So that it would not matter if the tubes weren't completely uniform. He remarked that he liked the reasoning, and I was very proud of that."

"In grade school I had an English teacher who thought I should be a doctor. That wasn't my interest, but it was nice to have somebody who had confidence in me," he continued.

"My father took some interest in my work; in fact he was very proud of it, though he didn't talk about it. He might pick up a textbook and ask a few questions about it to see if I knew what I was doing, as a teacher would do. He also helped teach high-school students who were having a trouble with their math. He taught them the basics like what plus and minus mean. If you don't learn that you can't do math."

"That's true of a lot of things in life," said Shick. "You've got to learn the fundamentals."

From Harvard, Shick remembers his calculus professor, S. L. Coolidge, in particular, because of the way he made things interesting. "He would pose a problem such as, 'if a man threw a bucket of slop out of the upper window of a house at such-and-such an elevation and a man was walking by at such-and-such a speed, at what time would the slop approach him the fastest?'"

Another professor, W. H. McAdams, who taught chemical engineering, illustrated the importance of entering a problem at the right place.

PROUD MOMENTS

Of the many things Shick is proud of, the first that comes to mind is "that I kept my sense of values," he said. "I've tried to work in a fair and open manner."

Ultimately, it's how you deal with people that seems most important, Shick said. He recalled one of three lab employees who once worked for him at Mead Corp. "Of the three, he did the absolute least. So I decided to try a Dale Carnegie on him and tried to praise him for any-

thing that was any good."

About that same time, Shick's own boss told him he'd have to fire the employee. Shick said he couldn't do it right away after having just praised the employee. "But I went to him and told him that if he didn't change his ways I'd have to fire him." At that time, there was a union in the laboratory, so the employee bid out from under Shick and worked for another year or two until he finally quit or got fired. "When he left he came by and shook my hand. I think he'd appreciated that I had leveled with him at one point."

Shick is also proud that his sons have also earned the respect of their co-workers. Tony, for example, had made a point of working every shift over the course of a year to become familiar with everyone there. When he moved out of that department, they presented him with a hard hat that they had all signed, and "a great many of them said that he'd been the absolute best supervisor they had ever had." Alan, in turn, is training coordinator for his fellow airport workers.

And of course, there is the recovery furnace computer program. For Shick, the program represents a synthesis of his life's work, combining elements of math, chemistry, and experience working with recovery processes. He's proud of the thought and effort that went into developing it.

AND EINSTEIN SAID....

Albert Einstein is credited with saying, "Everything should be made as simple as possible, but not simpler." Shick has taken something of that approach in his work, though sometimes, he admits, trying to simplify too much.

The industry for years sponsored computer studies on recovery operations, which have gotten to be terribly complex, Shick said. That reflects the complexity of the real system. In his own simulations, however, Shick has tried to simplify where possible and write for the operator rather than the scientist. "With suitable use of spreadsheets, such as Lotus, you can do tremendous things in the way of material balances," he said.

Shick started work on a computer program to illustrate the recovery process as soon as he retired in 1982. He was interested in graphically showing what happens inside of a furnace and other things he was never able to do with a hand-held calculator.

In developing the program, Shick had to develop equations for such things as pyrolysis. That's essentially a heat equation, he explained. "In simple form, the rate of combustion is dependent on oxygen concentration, temperature, and relative velocity," he said.

But, of course, reality is more complicated and Shick had to factor in a number of variables. For example, "If

you blow on something it burns more fiercely, like a pile of straw; but if you blow on an individual match it goes out. So I put in a factor that the temperature of individual particles is also reduced to approach the temperature of the air around it as the velocity increases."

A whole range of variables had to be considered and written into the program.

"I look at it a little like Einstein and the universe," Shick said. "It's like a watch; you can't see it all but you know it's got to work and you know something of the engineering and principles involved," he continued. "I don't consider the interactions of particles. Some later

work modeled flow of furnaces that undoubtedly took into account additional factors, but I doubt you can run those on a microcomputer."

Shick completed the program around 1986. About a year later, he proposed that the American Paper Institute (API) buy the program and give it to all their companies. Shick still tinkers with the program. There are changes he would make to make it still easier to use, but the work that's gone into it is well thought out. There's a solid foundation to it, much like the man who wrote it. **TJ**

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