CIRCULATING FLUIDIZED BED TECHNOLOGY

Edited by **Prabir Basu**

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Edited by
Prabir Basu

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PREFACE

The process of Circulating Fluidized Bed is generating increasing interest among practicing engineers, researchers and academicians. Unlike many other gas solid contacting processes, it was primarily developed by some industries for roasting and combustion purposes and, later, the rapid commercial success of this technology drew attention of other researchers. Since the commercialization of this process outpaced fundamental research, a number of important gaps in the understanding of this process remained. The lack of information in those areas inhibits an optimum exploitation of this technology. Thus, in-depth research work started in some industrial laboratories and universities around the world. A need for exchange of views and information on this research was felt. How such a lack of information exchange inhibits the growth of a technology is best described by Prof. Arthur Squires who remarked,".......it took 18 years for Winkler's discovery to cross the ocean ....."

In the present age of information explosion such delays were inconceivable; the technology was thought to be sufficiently developed to deserve an exclusive discussion forum. However, inspite of the efficient information channels, no one was aware how many centres around the world were engaged in research in Circulating Fluidized Bed. Consequently, an International conference on this technology was planned for a small number of papers and a modest attendance.

This conference was proposed by the Technical University of Nova Scotia and sponsored by the Canadian Society for Chemical Engineering and the Canadian Society for Mechanical Engineering. Strong encouragement and financial support came from a number of industries and government institutions. The Pergamon Press, Institute of Energy, U.K and the Japan Society of Energy & Resources helped publicise the conference. The Continuing Education Division of the Technical University of Nova Scotia provided the administrative and technical support. The Premier of the province of Nova Scotia, the Hon John Buchanan, delivered the welcome address and an illuminating banquet speech. The Federal Minister for Supply and Services the, Hon. Stuart McInnes delivered a thought provoking keynote address. A rapporteur format of discussion was adopted at the conference to permit more opportunity to assimilate information through discussion. The Chairpersons and Rapporteurs were instrumental in achieving this objective.

The conference was successful both in terms of number of delegates and of papers presented. Two hundred and fifty delegates from 17 countries attended the conference. More than half the delegates were from industries. Thus the conference sessions saw a lively exchange of views between the practising engineers and academicians.

A number of prominent experts in Circulating Fluidized Beds were invited to prepare overviews in subjects of their speciality. Discussion papers were selected on the basis of extended abstracts. Full version of the selected papers were refereed by two experts in respective fields. The authors modified their papers following the reviewer's comments. The modified papers have been included in this volume. Discussions of all sessions were taped. Some delegates failed to use the microphone; as a result some good discussions could not be recorded. However, all taped discussions were transcribed and included at the end of the papers on which the discussions were held. An index based on the key words supplied by the authors is added at the end of the proceedings.

Dr. Feridun Hamdullahpar arranged review and subsequent modification of the papers with his characteristic devotion. This proceedings is the result of hard work of the authors and the reviewers who used valuable time to improve the quality of the papers printed here.

The advice of Dr. G.D.M. Mackay and Dr. A.M. Al Taweel was invaluable to the organisation of this conference. Dr. P.K. Nag Mr. P. K. Halder, Miss Catherene Patterson and Miss Mary Meidel provided commendable service.

Delegates at the conference demonstrated interest in continuation of this conference for exchange of views on Circulating Fluidized Bed. An international committee was formed to advise future International conferences on Circulating Fluidized Beds. A permanent Secretariat for the conference has been formed at the Technical University of Nova Scotia. This office will be responsible for publications of the proceedings and assisting in the organisation of future conferences. The next conference is scheduled to be held at the University of Compeigne , France in 1988.

It is hoped that this proceedings, a collection of papers of lasting value, will serve as useful reference to engineers and scientists.

Prabir Basu

Halifax

Conference Chairman

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THE STORY OF FLUID CATALYTIC CRACKING: THE FIRST "CIRCULATING FLUID BED"

Arthur M. Squires

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ABSTRACT

From December 1938 onward, a student of Warren K. Lewis and Edwin R. Gilliland at Massachusetts Institute of Technology (M.I.T.) blew fluid catalytic cracking (FCC) powder upward through a one-inch pipe at air velocities to about 3 m/sec. In mid-1940, a consortium led by Standard Oil Company of New Jersey and the M.W. Kellogg Company used the M.I.T. data to design a fluid-bed substitute for a 100 barrel per day pilot cracking reactor of another type, whose performance had been disappointing. Fluidized standpipes elevated the pressure of FCC powder in the new system. D.L. Campbell, H.Z. Martin, and C.W. Tyson of Jersey Standard had invented this essential feature in April 1940, less than 4 months before gas oil was charged to the new system, on August 4, 1940.

KEYWORDS

History of technology; catalytic cracking; standpipe; slidevalve; cyclone; star feeder; powder; blowout velocity; Fuller-Kinyon pump; management of research and development.

INTRODUCTION

I tell here the story of the development and implementation of the fluid catalytic cracking (FCC) process. This first application of a fluid bed of a Geldart Group A powder for catalysis remains, after more than 40 years, the petroleum refiner's premier tool for converting heavy feedstocks into gasoline. The combination of standpipe and slidevalve for recirculating a fine powder emerged from the FCC development. The first three commercial fluid crackers, although they operated in the bubbling regime, were "circulating fluid beds" (CFBs). Their developers appreciated, however, that a CFB might be devised to operate at much higher velocity — even beyond "blowout" — and indeed, FCC designs have evolved with high-velocity reaction zones for both cracking and catalyst regeneration (Squires, Kwauk, and Avidan, 1985).

I am able to give many particulars of the FCC story through a recent acquisition of a large number of M.W. Kellogg Company internal documents from the 1930s and 1940s. In telling my story, I will follow these as well as my other sources in using English units. The documents permit me to correct errors in my earlier account earlier histories (Gohr, 1956; Jahnig, Campbell, and Martin, 1980; Gornowski, 1980; Jahnig, Martin, and Campbell, 1984) have emphasized the contributions of Standard Oil Company of New Jersey and its subsidiary, Standard Oil Development Company (here jointly called "Jersey Standard"). For several crucial ideas and experiments I will supply dates that have heretofore been omitted or given incorrectly (Enos, 1962). The Kellogg documents raise questions that I hope to pursue in further investigations, and my FCC story still lacks something on the contributions of five other companies (see below) that participated in the FCC development.

CATALYTIC RESEARCH ASSOCIATES

By late 1928, Eugene Houdry had discovered a porous clay that catalyzed the cracking of gas oil at atmospheric pressure to yield a gasoline of higher octane number than thermal cracking could provide. He had learned how to regenerate his clay catalyst, extending its life, by burning off the coke byproduct of cracking. In the early 1930s, Houdry acquired backing, first, from Vacuum Oil Company (later Socony-Vacuum after a merger with Standard Oil Company of New York, and now Mobil), and later from Sun Oil Company. In June 1936, Socony-Vacuum commissioned a Houdry unit for 2,000 barrels per day (bbl/d); and Sun operated a 15,000 bbl/d unit in March 1937. By November 1938, ten units were under construction, and in late 1941, fourteen Houdry units operated in the U.S.

Houdry had given Jersey Standard a number of opportunities, both before and after 1930, to buy into his development, but Jersey consistently left their meetings convinced that its work with I.G. Farben on hydrocracking was a better opportunity. In 1935, knowing that Houdry was about to commercialize his process, Jersey began a small program on catalytic cracking at atmospheric pressure. In 1937, Jersey asked Houdry's terms for a license. Houdry wanted $50 million. Jersey thought this far too much and made a counter-offer that Jersey calculated would eventually cost it $15 million. Houdry refused the offer, and Jersey elected to develop its own catalytic cracking process, independent of Houdry's patents. Houdry's entire development had cost him and his associates $11 million at the time it was commercialized. The FCC development would cost $15 million; in hindsight, Houdry's $50 million was outrageous.

In 1934, Reginald K. Stratford of Imperial Oil Limited in Sarnia, Ontario, a Jersey Standard subsidiary, believed he saw a catalytic effect upon adding relatively small amounts of fine clay, a discard from the clay-treating of lube oils, to oil undergoing thermal cracking in a coil at high pressure (Stratford, 1940). In time, Imperial Oil would implement Stratford's "Suspensoid Cracking" by revamping four tube-and-tank thermal crackers, increasing the octane rating of product from 73.5 to 81.7 (Ford, 1941). But in 1936, Jersey Standard's Process Division was not impressed by results from its work emulating Stratford's procedure, and the Research Division was enjoying better success in experiments cracking oil vapor over powdered clay catalyst at essentially atmospheric pressure. By March of 1938, soon after Jersey's decision to get by without Houdry, the Research Division had developed (at Bayway, New Jersey) a continuous 1/2 bbl/d pilot unit in which oil vapor conveyed powdered catalyst through a coil immersed in a bath of molten lead. Jersey had also worked with pelleted catalyst using Houdry's approach: fixed beds operating cyclically. Experiments in a fixed-bed pilot plant for 100 bbl/d at a refinery in Baton Rouge, Louisiana, showed that best yields were obtained in early moments of a period of oil cracking. This result reinforced Jersey's view that major improvements could result from making the process continuous and providing for flow of catalyst back and forth between a cracking zone and a regeneration zone. Should the catalyst be circulated in form of powder or pellets? Before February 28, 1938 (Enos, 1962), D.L. Campbell proposed the Fuller-Kinyon pump, widely used to introduce cement into pneumatic-conveying systems operating at about three times atmospheric pressure, as a means for feeding catalyst into a pipe together with oil vapor or air in a a means for feeding catalyst into a pipe together with oil vapor or air in a continuous cracking process.

In 1937, Anglo-Iranian Oil Co., Ltd. (now British Petroleum) approached the M.W. Kellogg Co. to solicit help in developing a catalytic cracking process. After initial studies in fixed beds, Kellogg conceived a process using granular catalyst in moving beds (Degnen, Nelly, and Keith, 1942), and built a moving-bed cracking unit for 1,500 bbl/d at Anglo-Iranian's Llandarcy, Wales, refinery (Squires, 1982). William J. Degnen (1982) recalls that he and his colleagues at Kellogg's Jersey City laboratory noticed early in the work for Anglo-Iranian that granular catalyst used in moving beds had a distressing tendency to break apart and yield a fine powder. In mid-April 1938, Degnen (1942) filed a patent application disclosing use of a Fuller-Kinyon pump to overcome pressure losses in a powder-catalyst process in which the cracking or regeneration zone could be either a horizontal pipe run (with several reversals of flow at return bends, i.e., resembling a trombone cooler) or a zone "of relatively large cross sectional area" with upward passage of powder and oil vapor or air. In the latter mechanical configuration, Degnen conceived that a "cloud-like accumulation of the catalyst particles" would appear in the region of expanded cross section. He conceived that only a portion of the particles entering the region would be conveyed upward out of the region, and he provided for withdrawal of the remainder of the catalyst from the lower portion of the region. As Degnen (1982) has observed, patent attorneys later opined that his April 1938 application disclosed equipment capable of being operated with the formation of a fluid bed with bottom withdrawal of catalyst powder. It does not appear that Kellogg pursued Degnen's idea, nor that it had much influence upon the FCC development, beyond, perhaps, helping to prepare decision-makers at Kellogg to abandon their moving-bed approach when Jersey Standard revealed its progress with powdered catalyst.

In mid-1938, Kellogg approached I.G. Farben to solicit its cooperation in commercializing Kellogg's moving-bed cracker. When Farben told Kellogg that Jersey Standard owned all of Farben's petroleum patents outside of Germany, Kellogg invited Jersey's cooperation. On October 12, 1938, four companies — Jersey, Kellogg, I.G. Farben, and Indiana Standard — formed a consortium to develop a catalytic cracking process that would not infringe the Houdry patents. Indiana Standard had worked with pelleted cracking catalyst. Within a week, Anglo-Iranian joined the group. Both the Texas Company (now Texaco, Inc.) and Universal Oil Products (UOP) had worked on fixed-bed catalytic processes, and joined, together with Royal Dutch Shell. Three of the companies (Texaco, Shell, and Indiana Standard) had cooperated earlier with Jersey and I.G. Farben on hydrocracking.

> "This was a formidable grouping and, with four hundred men at Jersey and six hundred in the other companies, represented probably the largest single concentration of scientific manpower in the world. It was also probably the greatest scientific effort directed at a single project, and would be surpassed only by the development of the atomic bomb" (Enos, 1962).

The eight companies controlled the better part of the research facilities of the petroleum industry. The group adopted the name Catalytic Research Associates (CRA) and would drop I.G. Farben in late April 1940, Jersey Standard holding itself liable for any claims that I.G. Farben might make against CRA (Howard, 1947).

CRA held its first technical meeting on November 30, 1938 (Schwarzenbek, 1982). Chief spokesmen for Jersey and Kellogg were, respectively, Eger V. Murphree and Percival Cleveland ("Dobie") Keith, Jr. CRA chose Jersey's powdered catalyst approach, Murphree stating that Jersey could generate design data by February 1939 for converting its 100 bbl/d fixed-bed cracker at Baton Rouge to powder operation. It would be renamed "PECLa" — Powdered Experimental Catalyst Louisiana. E.J. Gohr's group at Jersey Standard was responsible for design of PECLa, providing "snake" reactors, in which oil vapor or air conveyed catalyst upward and downward through vertical runs of pipe. Figures 1 and 2 illustrate features of the design. Initially, the cracking zone comprised 240 feet of 4-inch pipe, affording 8 seconds of vapor contact at a vapor velocity of 30 ft/sec. Figure 1 shows a revision of early March 1940 for longer contact times. Gohr's group would also design PECLa's revision to a fluid bed in mid-1940 as well as Jersey Standard's commercial fluid catalytic cracking installations. Kellogg and UOP would design and build cracking installations for other members of CRA.

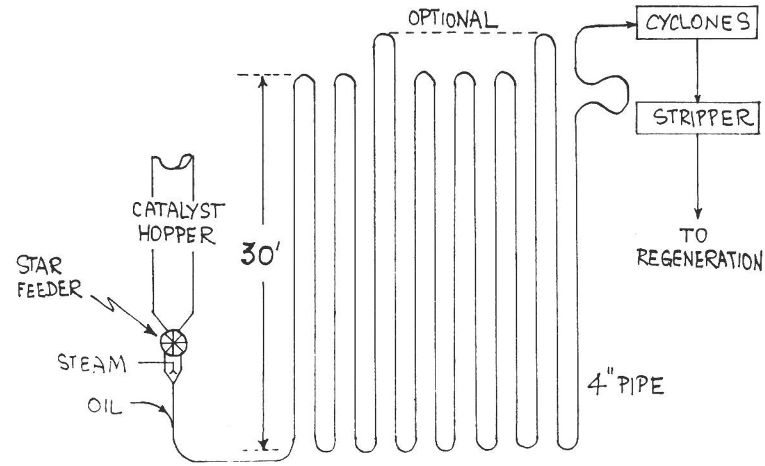

Fig. 1. The "snake" reactor at PECLa after March 1940.

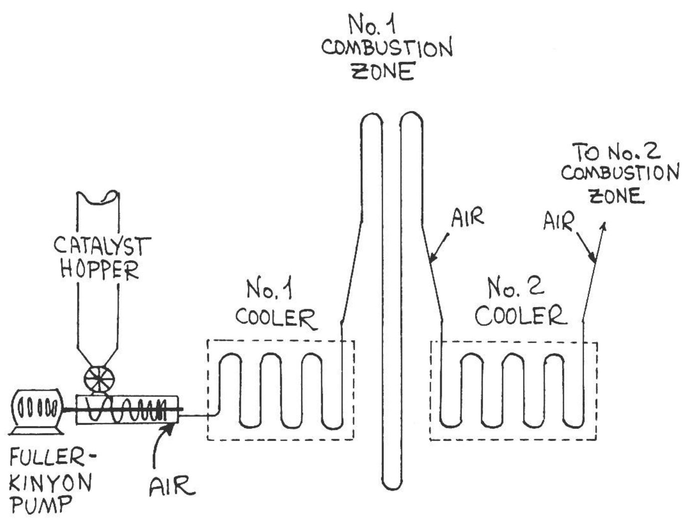

Fig. 2. "Snake" reactor for catalyst regeneration. There were four combustion zones, each following a catalyst cooler.

Warren K. Lewis of Massachusetts Institute of Technology (M.I.T.) had consulted for Jersey Standard since 1920 and, in January 1938, proposed that powdered catalyst could be stripped of oil vapors by allowing the catalyst to flow downward over alternately pitched baffles against a rising flow of steam (Enos, 1962). Lewis' younger colleague, Edwin R. Gilliland, also consulted for Jersey's catalytic cracking effort, and Gilliland (1970) has described the circumstances surrounding his invention, together with Lewis, of the CFB for fine powders:

> "Dr. Lewis and I had been working with Standard Oil Development Company on their catalytic cracking work and in the fall of 1938 we attended a several day meeting at Bayway with E.V. Murphree's group reviewing their work on catalyst activity, product quality and the flow of the solid with the gas oil in horizontal tubes. They ... were having difficulties with plugging particularly when the flow was interrupted and restarted. ...
>
> "After the last day of the meeting, Dr. Lewis and I took the Merchants Limited train back to Boston [a New Haven Railroad express running from New York City to Boston] and we discussed the SOD work. We decided that vertical flow would be less susceptible to plugging and would give some advantage due to the slippage of the solid relative to the vapor. On the train, I calculated the expected slippage on the basis of Stokes' Law and the predicted bed concentration as a function of solid and gas feed rates and solid particle size. These calculations suggested that the vapor velocity would need to be low to obtain a significant increase in solid concentration due to gravity relative to the concentration ratios of the feed when using the powdered catalysts. We concluded that this method of operation might be attractive but the low velocities ($\sim$0.1 ft/sec) for the vapor would require very large diameter reactors. ...
>
> "We called Murphree the following day and told him of our discussion and suggested that we thought it would be worthwhile for SOD to try vertical flow. Murphree said that the SOD group was so committed to the program on horizontal flow that they would not be able to try the idea for some time, but he ... would provide us with funds to hire some graduate students to study the flow of fine powders with air in vertical tubes if Doc and I thought the idea was promising. Within a few days we hired a masters student, John Chambers [1939], and he did a good program involving considerable ingenuity. The data soon showed that there were conditions where the slip between solid and gas could be several hundred fold greater than predicted by Stokes' Law and this made it possible to use much higher velocities than predicted. We also noticed the "bubble" type flow and used colored particles as tracers to observe the solid mixing and concluded that there was rapid mixing in the bed. Scott Walker [1940], another graduate student, joined the program somewhat later.
>
> "Dr Lewis and I had a number of meetings with the SOD group to review our results and we sent them a number of reports on the work. It took us some time to convince them of the advantages of vertical operation. The SOD group were concerned about the back mixing, but we pointed out that while it was detrimental for the chemical kinetics that it would give good internal heat transfer and that the solid could be flowed like a liquid."

Enos (1962) gives December 13, 1938, as the date of a letter from Murphree to Lewis authorizing him to spend money on fluidization experiments. Chambers (1986) recalls that Lewis phoned during M.I.T.'s Christmas break, which ran that year from December 23 to January 2, to ask Chambers to return early and assume an urgent task. Chambers worked until mid-April, very much on his own, not seeing Lewis except after hours — he lived in Lewis' home, tending the furnace. Walker (1940) inherited Chambers' rig, modifying it in the summer of 1939 to permit work with hydrogen and carbon dioxide as well as air.