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Catalysis challenges in fluid catalytic cracking: a 49 year personal account of past and more recent contributions and some possible new and future directions for even further improvement

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Abstract

Generally speaking, catalytic cracking is an old process. However, it is impressive to observe how many improvements have been made over the years, and continue to be made. Advances in the catalyst and the process have been numerous, and every prediction pointing to the demise of the process has proven to be wrong. This paper will relate some personal involvement and contributions to the improvement of the catalyst and process, both as they relate to gas oils and metal laden reduced crude and residuum. Among others these include the incorporation of kaolin into synthetic silica-alumina microspheres so as to reduce cost, and more importantly create a 'house of cards' pore structure for large pore formation; 40 years later kaolin is still the predominant additive (25–75% by weight). A later contribution included the widely used XZ-36 Davison catalyst of the late 60s. In the late 70s, through the 80s, and continuing into the 90s for reduced crude, there has been the introduction and incorporation of the acidic matrix, vanadia immobilizers, vanadia traps, sacrificial sieves, nickel sinks, highly ground sieves, further enhanced large pores for the catalyst and vanadia valence control and hydrogen recycle for the process. More recent developments include the Magnacat^{TM} process for selectively retaining higher activity catalyst and process additive chemicals for enhancing catalyst performance. Future process developments include the 'Magnetic Hook' concept and still more recently, the patented 'triangular process' and use of 'Magnetic Hooks' to retain high cost specialty additives. Speculation is also offered as to the future use of CO_2 for catalyst regeneration and the use of manganese for cracking catalyst activity.

Keywords: Catalytic cracking; Magnetic Hook; Magnacat triangular process; Manganese activation

1. Introduction

It is a pleasure for me to be invited to participate in this symposium honoring Dr. John Sinfelt and his inspirational and pioneering work in bimetallic reforming.

This afternoon at Dr. Burtron Davis' suggestion, I plan to address the subject of catalytic cracking and including recent developments in which I have been involved, and some newer and future projections, in which some of my newer patents are also involved.

In doing so, I thought it would be appropriate to review where I've come from in catalytic cracking in order to give some meaning to projections into the future.

Former addresses where much of the work reported was carried out include: Sinclair Labs, Harvey, IL; Nalco Catalyst Division Labs, Chicago, IL; Davison Catalyst Co. Labs, Clarksville, MD; Ashland Research Labs, Catlettsburg, KY; Florida Atlantic University, Boca Raton, FL; and last, but by all means not least, in my wife's kitchen and on our back porch, Russell, KY.

I first became involved in petroleum refining catalysis research, including reforming, residual hydrotreating, and catalytic cracking in 1950 when I joined the

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old Sinclair Laboratories at Harvey, Illinois, where I later became Director of the Refining and Catalysis Research Division.

In 1957, I joined Nalco Chemical Company Laboratories as Director of Catalyst Research. Almost at the moment I arrived, I learned among other things that Nalco was being confronted with a very serious new cracking catalyst challenge. The Filtrol Corporation, a major cracking catalyst manufacturer, had come up with a new acid treated halloysite clay microsphere which was showing great promise and threatening to wipe out the three synthetic catalyst manufacturers; American Cyanamid, Nalco and Davison. The synthetic silica-alumina catalysts, which were popular at that time, were selling for US$ 325–350/ton, which would be an unbelievably low price today, but the clay based catalyst was selling for US$ 225/ton, and since it was a good catalyst, it threatened to eliminate all competitors. Though I and Dr. David G. Braithwaite [2], then Vice-President for the Catalyst Division of Nalco, and later to become President and CEO of Nalco, looked into the possibility of duplicating the halloysite catalyst, we found that there were no adequate competitive deposits of halloysite of reasonable size available. In desperation, I reviewed some other possibilities and familiarized myself with other clays and including kaolin clay. Kaolin clay was and is a very cheap material used in filling and coating paper, is uniquely platelet in structure, and has very low metal impurities.

Because of these properties, and especially the low price, I suggested that we might try to dilute or extend the synthetic silica-alumina gel with kaolin. My thought was that perhaps this way Nalco could come up with a material that could compete price-wise. Of course, everyone expressed the thought that this was a poor suggestion. It was pointed out that the attrition resistance of such a microspherical catalyst, filled with kaolin would be poor, and furthermore, it was known that kaolin had little or no cracking activity.

But, I was allowed to give it a try, and after much trial and error, came up with a way of blending kaolin into synthetic silica-alumina gel and still keep it attrition resistant. At that time, a second thought occurred based on a great deal of familiarity and personal involvement with the structure of RD150, the Sinclair–Baker, highly successful commercial platinum reforming catalyst [1]. For that catalyst, one of our researchers (M.F.L. Johnson) discovered that large crystallite alumina trihydrate, when combined with monohydrate alumina gel in the right proportions (about 70/30), produced a dual pore structure catalyst of most unusual activity and aging properties. Therefore, I speculated that it might be possible to combine the kaolin with a silica-alumina gel in a similar way so as to also form a dual pore structure which I describe as a ‘house of cards’ (Fig. 1). All synthetic catalysts at that point had only very small pores. With this new structure, there would possibly come a new catalytic material with an entirely new pore structure, and because of accessibility might possess new cracking and regeneration properties. After much experimentation a new, cheap, attractive, attrition resistant ‘house of cards’ dual pore catalyst was produced containing about 45% kaolin [2]. Fig. 2 shows the resulting pore structure compared with that of a synthetic silica-alumina gel, being manufactured at that time, and compared with our new kaolin extended catalyst. The change in pore diameter distribution and the increase in larger pores was dramatic.

Of course, the activity of the catalyst when tested in the laboratory, because of the inactive kaolin, was only half of the synthetic-acidic silica-alumina gel activity. Nevertheless, I speculated that in commercial use, this catalyst because of these unusual properties, would perform better than demonstrated in a small catalytic test unit. With perseverance and lots of luck, approval was obtained for a trial run on a commercial scale at a small refinery, Aurora Gasoline, in Detroit, Michigan in 1957 [3]. As luck would have it, it turned out to be surprisingly successful and highly competitive, and also more resistant to metals, and later on because of its low price, was picked up by Chevron Oil Corporation, who also began using it in large quantities. This became known as the Nalco ‘Semi-Synthetic’ cracking catalyst, and so an era of new catalyst technology began.

It was not long before American Cyanamid and Davison also learned how to make it, and Fig. 3 shows a comparison of the pore structures of these three catalysts, all showing similar pore distributions.

Today some 40 years later, almost to the day it was introduced, that same and/or similar cracking catalyst structures, all dependent on incorporating kaolin, is still utilized in many or most commercial cracking catalysts. Over the past 40 years, this unique structure

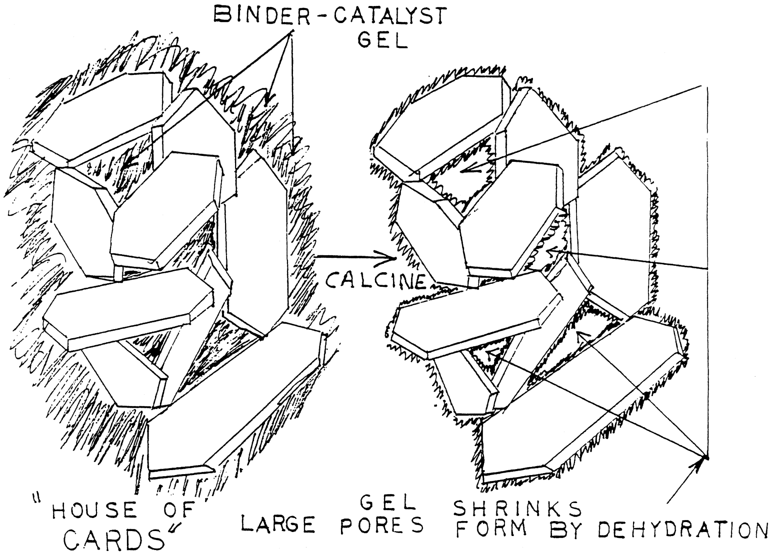

Fig. 1. Schematic representation of a 'House of Cards' structure of clay.

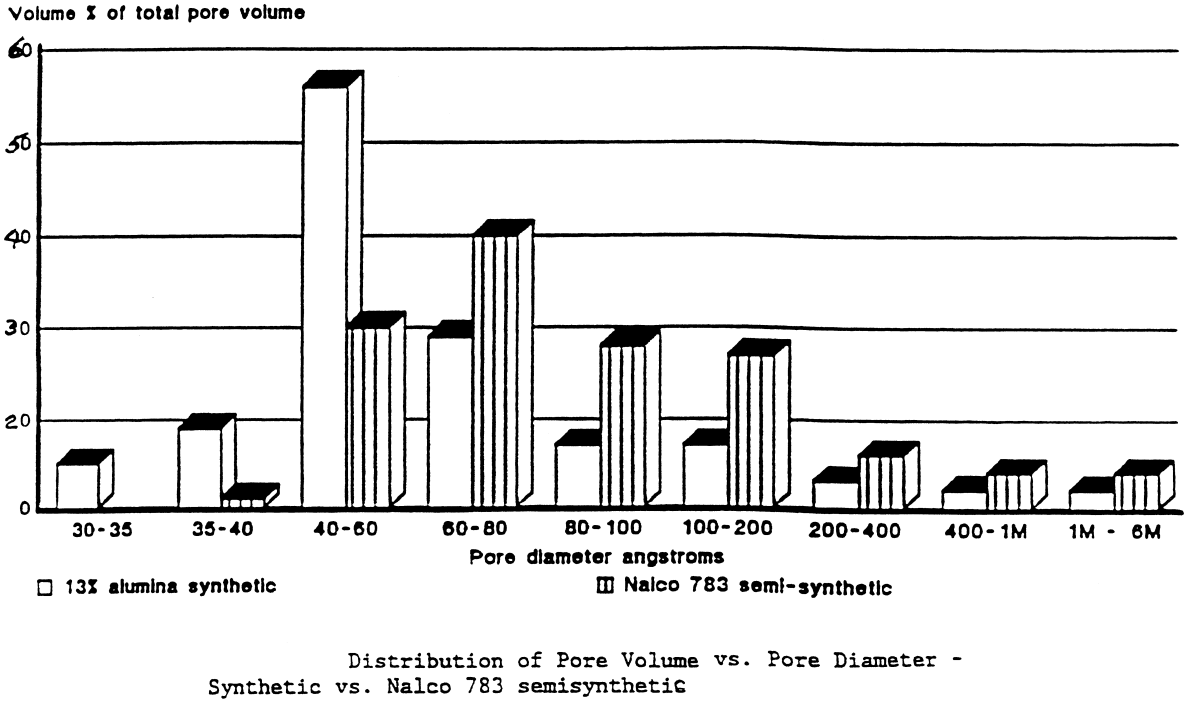

Fig. 2. Distribution of pore volume vs. pore diameter for synthetic vs. Nalco 783 semisynthetic catalysts.

has probably saved the petroleum industry billions of dollars, both because of the reduction in raw material costs and by enhancing profitability due to the enhanced selectivity, ease of regeneration, and increased operating activity. Four or 5 years later, when the next big breakthrough in catalyst performance occurred, namely the introduction of rare earth exchanged zeolite, this new structure now provided a means of

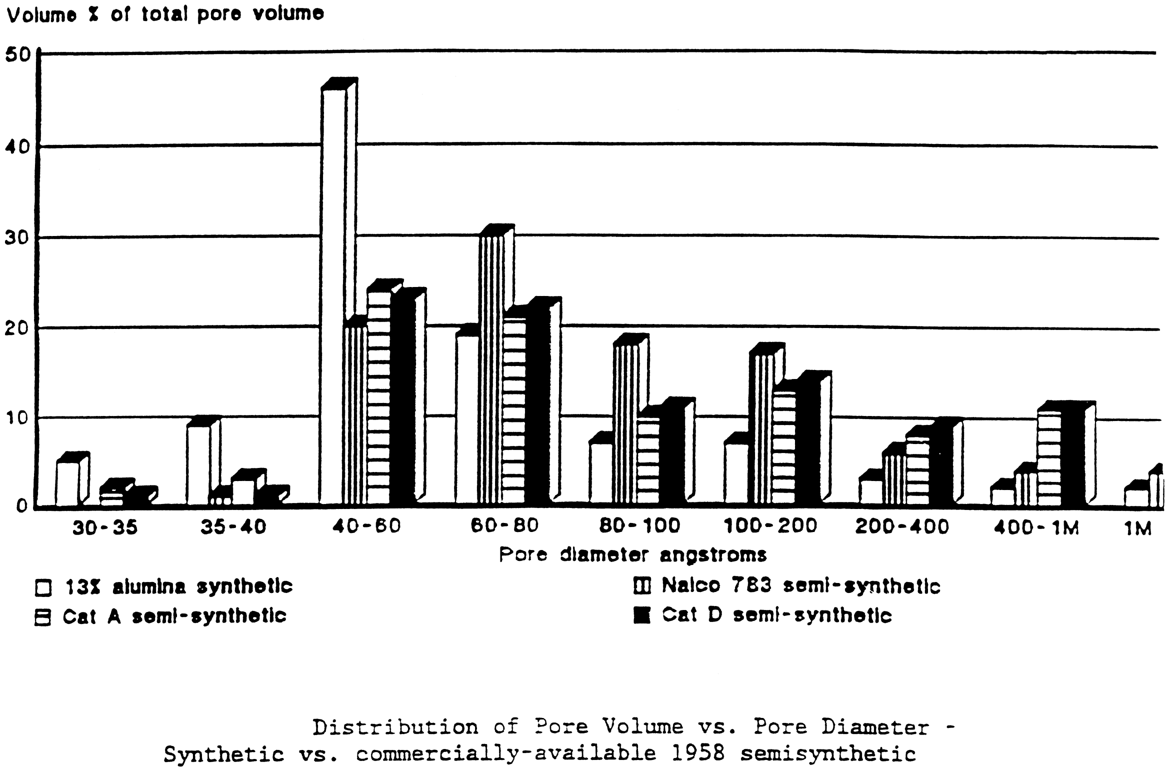

Fig. 3. Distribution of pore volume vs. pore diameter of the synthetic vs. commercially available 1958 semisynthetic.

achieving easy access of hydrocarbons to the zeolite crystals, and so its use was continued and even accelerated.

In the intervening years (1959–1965), I continued to be active in catalyst research for a while, then went into other research activities and management responsibilities. I did not get back into cracking catalyst research until 1965 at Davison Chemical Co. as the Director of Research and later Vice-President. Here a great deal of attention was given to exploitation of the zeolite promoted catalysts, which zeolites were introduced by the brilliant work of Charlie Plank and Ed Rosinski in the early 60s [4]. As a culmination of research experience and application our research produced XZ-36, a prototype of a new family of zeolite containing cracking catalysts, also containing clay and possessing large pores, which our Davison research team introduced commercially in 1967 [5] (Fig. 4), and sold in large volume for some period of time.

AN IMPRESSIVE
RECORD FOR
XZ-36

XZ-36 has been tested in almost 40 units during its first nine months of service with highly successful results. Typical data from those units with sufficiently high XZ-36 content to show meaningful results are summarized in Table 3.

These data are from operations in all parts of the U.S., on all types and sizes of units and against all kinds of zeolitic catalysts — competitive as well as our own. We believe you will agree the results are impressive.

Fig. 4. Typical commercial for XZ-36 — prototype of a new family of zeolite containing cracking catalysts.

As we all know, research breakthroughs show a growth curve when a new technology is introduced. Developments and improvements rise quickly and then, even considering a considerable amount of further effort to improve, improvements come very slowly. And so in research a productive research team looks for ways of finding these breakthroughs, or in other words, a new ‘S’ shaped growth curve.

As mentioned previously, the next big breakthrough, that therefore appeared in terms of technology beyond that of the kaolin based ‘semi-synthetics’ came with the introduction of rare earth promoted zeolite containing catalysts by Plank and Rosinski in 1964. This development was so striking, that it lead to their being elected to The Inventor’s Hall of Fame with such as Edison and Bell in Washington, D.C., and resulted in a new and striking jump in commercial catalyst performance, both activity, and selectivity wise, and resistant to deactivation and metal poisoning. This development continued into the late 1970s when further increases in catalyst performance again slowed down. There were some improvements in the zeolites, such as the development of Ultra Stable Y Zeolite, and ZSM-5, (which by the way, was a great achievement by Mobil) and some variations in rare earth technology, but they were really new advancements on this growth curve. This was generally the situation throughout the 70s.

2. New catalytic breakthroughs — experimental

In 1977 I joined Ashland Oil as Vice President for Petroleum Research and learned that because of the crude shortage that had suddenly developed at Ashland Oil, (now Ashland Inc.) due to the Iranian crisis, that George Myers, Oliver Zandona, and Lloyd Busch, of Ashland had come up with the idea of developing a new cracking process which could increase yield of gasoline from a barrel of oil by both cracking the heavy gas oil fraction of the barrel being cracked at that time (about 25% of the crude oil barrel) as well as cracking the 1050°F plus fraction at the bottom of the barrel, which represented another 20–25% of the total barrel. They called it reduced crude cracking. (RCCt$^{\mathrm{TM}}$). By development and if successful, exploitation of this technology, Ashland hoped to cut down appreciably on its crude requirements, while at the same time, reduce the production of low profit asphalt coming from the 25% bottoms.

After reviewing this challenge, upon joining the company in 1977, it became apparent to me that Ashland had come up with some very unique ideas on cracking processing, including the two stage regenerator and the vented riser [6–8]. It had however, from necessity, been unable to devote any attention to the severe catalysts requirements, which would, and should be expected.

3. Matrix acidity

At the time, catalysts produced by the three major catalyst manufacturers, Davison, Engelhard, and Filtrol, had been moving in a certain direction in their catalyst development program, which was developing resistance to metal poisoning, namely nickel, vanadium, iron and sodium, as found in gas oil. But these metal poisons were at relatively low concentration, unlike the heavy levels encountered in reduced crude. As a result it appeared that their theoretical and commercial approach to an improved catalyst was to load the catalyst with sieve and lots of rare earth and try to reduce the surface area of the binding silica gel–kaolin matrix as low as possible. The concept was that by reducing the matrix surface area, one would encourage the migration of nickel and vanadia to clusters, and to form low surface area clumps of inactive metal poison. With no further place for these metals to diffuse to, it left only a small portion of the nickel, vanadium and iron oxide to be exposed as surfaces to be active for dehydrogenation (H_2 production) and the associated coking reaction, and matrix acidity, after the introductions of the extremely active zeolites, had become a forgotten technology.

This was a good theory for gas oil. However, as we began checking the yield and activity performance of these catalysts and studied what was happening to the reduced crude portion during cracking, analysis (Robert Wombles [38] of our staff) of the heavy poly nuclear hydrocarbons bottoms that were emanating from the reactor showed that there was still a lot of paraffin hydrocarbon remaining attached to the many polynuclear heavy aromatics remaining. We concluded that the reason that they were not being removed was that the molecules appeared to be too big to enter any zeolite cages for cracking, and perhaps even being too large to diffuse into the catalyst matrix. These catalysts did have good zeolite acidity, but the small [13] pores of the zeolite were apparently unable to provide access to their acidic sites for cracking of these large molecules. We concluded that what was

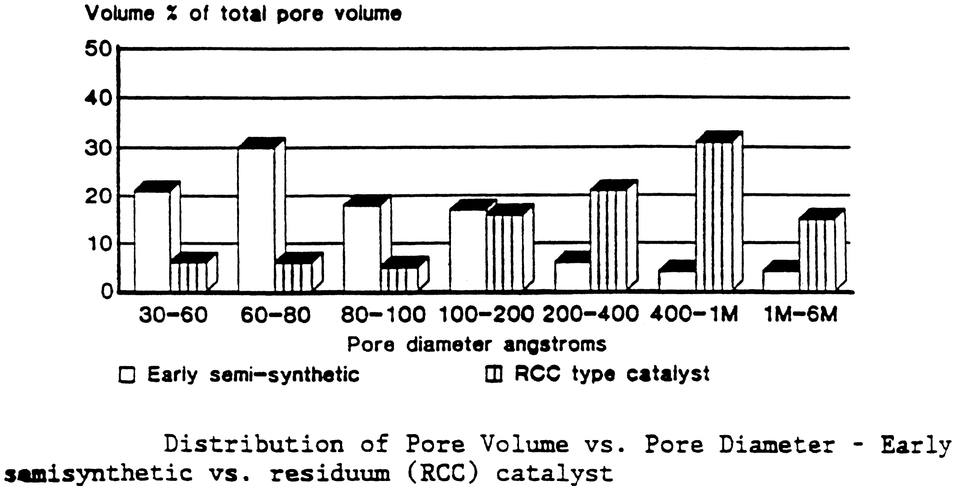

Fig. 5. Distribution of pore volume vs. pore diameter for early semisynthetic vs. residuum (RCC) catalyst.

needed was: (1) to build an even greater proportion of pores in the very large pore region, which we did (see Fig. 5) (Note how much larger these pores were compared to the early 1958 semi-synthetic pores), (2) to seek to return to an external zeolite binding acidic matrix, which might enable the catalyst to strip valuable paraffinic fragments from heavy poly-nuclear aromatics, thus increasing both gasoline and light cycle oil yield, and reducing slurry oil yield.

As a result our research focused on this problem of increasing the cracking activity of the matrix. At that time (1980–1984), our efforts to achieve this desirable catalyst was helped by collaboration with Davison Chemical Company. Out of that cooperative work, there resulted a matrix which did have significant cracking activity, and sure enough, with this new matrix, an increase in the yield of valuable products at constant conversion resulted.

The success of this particular objective set off a new technology jump [9,10] which then lead to an entirely new era of investigation, and the name ‘matrix acidity’ became a household word, by which to focus on such a property. It was found that for a preferred catalyst, it was desirable to have about a 50–50 balance between matrix acidity and zeolite acidity, and we so claimed this in a number of patents [11,12].

As we looked into all the other problems facing us in achieving a catalyst capable of processing residual material, having a high Conradson Content, large asphaltene molecules and high molecular weight hydrocarbons, all of which contain much sulfur, nitrogen, oxygen, sodium, nickel, vanadium and iron, we also recognized that an acceptable catalyst would have to be acceptable price-wise. And so we began to focus on each of these many problems and challenges individually and collectively.

4. Vanadia immobilization

One that was early focused on was vanadium. Our work had shown that if we treated a standard catalyst with varying amounts of vanadia, and exposed these catalysts to an oxidizing and or high temperature steam atmosphere, the surface area, activity and the crystalline zeolite content of the catalyst would fall off very rapidly (Fig. 6) and certainly showed that vanadia was much more destructive than sodium, iron or nickel. But the question remained how and why did this happen.

In fact, that was one of the early discoveries which I still recall making. I remember the event quite vividly. We had shown for example, that loss of catalyst activity after severe high temperature steam plus oxygen treatment was related to vanadia content in the catalysts and our work had also shown that loss in activity by vanadia treatment also related to loss in crystalline zeolite content. One day we were driving through New Jersey while on vacation, Alice was driving and I was relaxed and reviewing test results which

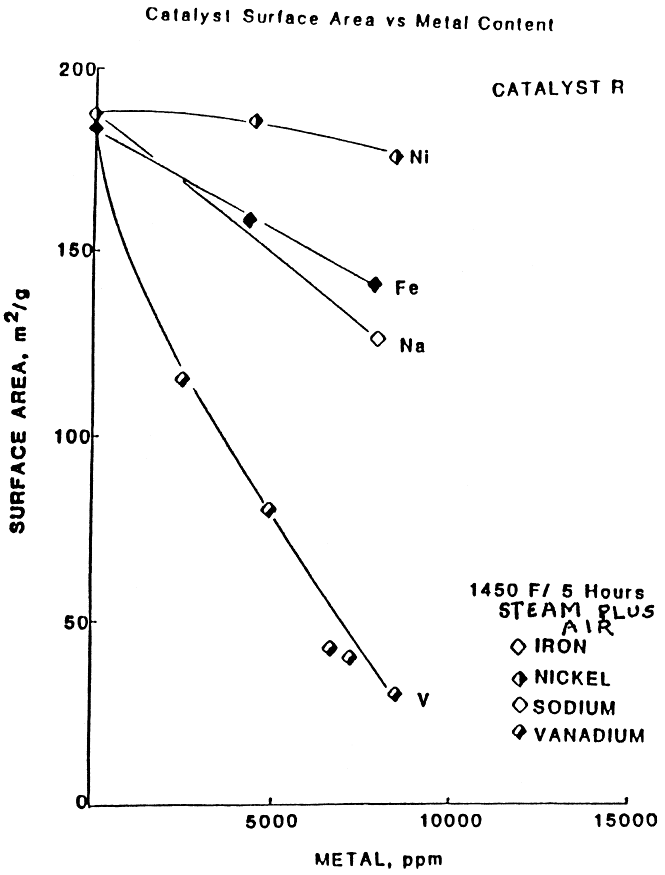

Fig. 6. Illustration of role of metals in determining catalyst surface area vs. metal content.

I happened to have brought along with me. I decided to plot vanadia content versus loss in catalyst activity and also versus loss in zeolite crystallinity, both showing a considerable drop as the amount of vanadia on catalyst was increased. To my somewhat pleasant surprise, I found a direct correlation between loss of activity and loss of crystallinity, both related to vanadia, and when cross plotted showed a direct relationship going to zero activity at essentially zero zeolite content (Fig. 7). So it seemed quite obvious that vanadia was destroying activity by destroying zeolite, and not by just neutralizing acid sites. That had been surmised in the past, but not proven. It had also been known that sodium was also a poison for zeolite activity, but here our studies showed that there was little loss in crystallinity (Fig. 7). But the direct experimental evidence for a one to one relationship with vanadium, but not sodium, told us that vanadium was doubly destructive, and as we know, also very mobile, and therefore we intensified our work in seeking to develop vanadium resistance.

We were also able to reduce the poisoning effect of nickel activity slightly by incorporating fresh alumina, titania, or zirconia gel [13] into the catalyst formulation to form for example, such as nickel aluminate, but we did not have quite as much success with this approach and furthermore, the introduction of antimony as an inhibitor for nickel by the Philips Company had already been shown to be rather successful, and therefore not an area for productive new research.

So our focus was on vanadia, how to reduce its dehydrogenation and coke forming tendency, but more importantly how to keep it from literally ‘running’ all over the catalyst surface and destroying the zeolite. At that time, we noted that V_2O_5 which melts at about

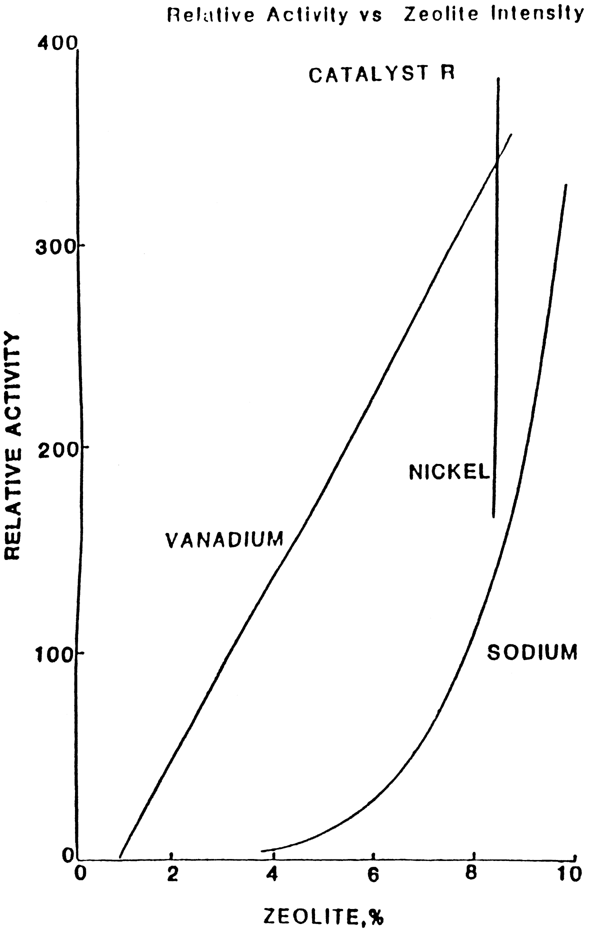

Fig. 7. Relative activity vs. zeolite intensity for various metal poisons.

1250°F, a typical regenerator temperature, had undoubtedly reached its melting point and was therefore easily migrating throughout the catalysts, destroying zeolite as it went.

So what we sought to do then was to explore various approaches to stop or inhibit vanadia movement.

One way was to see if we could slow down the movement of vanadia throughout the catalyst, and we determined that if we could keep vanadia at a lower valence (high oxide melting point — VO_2, V_2O_3, 3578°F) it should not be nearly as susceptible to migration. So one of the approaches was a process scheme in which a small amount of carbon was maintained on the surface of the catalyst after regeneration to help keep vanadia in a reduced state [14]. This proved to be helpful, and utilized to some extent in commercial operations. Fig. 8 shows how coke on catalysts, or a hydrogen reducing atmosphere protects catalyst from deactivation at 1450°F.

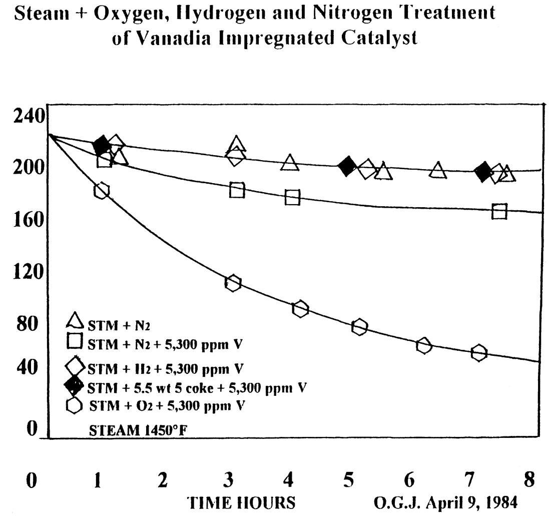

Fig. 8. Steam plus oxygen, hydrogen and nitrogen treatment of vanadia impregnated catalyst (from Oil & Gas J., April 9, 1984).

We also concluded that there should be other ways to stop vanadia, one being to immobilize it by causing it to react with some other atom or oxide. We came up with the word ‘vanadia immobilization’ and ‘vanadia immobilizers’ and began to use words like this to help search for and help describe what we were trying to do. Specifically we began to search for various compounds that would interact with vanadia to prevent migration, by forming high melting temperature solids with vanadia, and thereby prevent migration (Table 1) [15]. This was also successful, and a number of patents too numerous to mention, covering this approach were obtained.

5. Sacrificial sieves

Another approach we tried, since the vanadia was obviously destroying sieve, was to include other cheap, naturally occurring sieves for vanadia to ‘chew on’ [16]. This also proved helpful and we called them ‘sacrificial sieves.’ To a certain extent, that technique was also practiced.

Table 1
Vanadia immobilizers

Group	M.P. (°F)[a]
IIA — Mg, Ca, Sr, Ba	1740
IIIB — Sc, Y, La	1800–2100
IVB — Ti, Zr, Hf	1700–2000
VB — Ng, Ta	1800–2000
VIIB — Mn, Tc, Rc	Less than 1750
VIII — Ni, Ru, Rh, Pd, Os, Ir, Pt	Less than 1600
IIIA — In, Tl	Less than 1600
VA — Bi, As, S6	Less than 1600
Lanthanum Series — All	Less than 1800
Actinide Series — All	Less than 1800

[a] This table shows the melting points of oxides of the various groups of the periodic table in the elements most stable valence, when mixed intimately with vanadium pentoxide, which normally melts at 1250°F.

Table 2
Resid cracking (new terms)

1	‘Acidic matrix’
2	‘Valence control’
3	‘Vanadia traps’
4	‘Sacrificial sieves’
5	‘Vanadia immobilizers’

6. Small pore trapping

Another idea was to trap the mobile vanadia in very small pores, so as to reduce vanadia migration pressure, and so the use of chabazite, naturally occurring zeolites and clays with small pores, and others such as, for example, zeolite 5 A, mordenite, and ironite were also investigated and proved helpful. We called these ‘vanadia traps’ [17].

Table 2 lists some of our internal ‘code words’ so to speak, to describe and focus on specific constituents or properties or problems to be dealt with to be incorporated into the targeted RCCt catalyst.

7. Normal paraffin cracking

Another realization was that since we had a lot of normal paraffins resulting from this process, and since normal paraffins are more difficult to crack , we should incorporate ZSM-5, and this was also included in several formulations and patents [18], so as to increase octane number.

Table 3
Other concerns for resid catalysts

1	Resistance to high temperature and steam.
2	Hydrogen recycle activation to reduce coking mechanism.
3	Resistance to heavy basic nitrogen molecules.
4	Resistance to heavy asphaltene fouling, plugging and coking.
5	Ability to crack resistant heavy molecular weight normal paraffins.
6	Acceptable burning rates for heavy coked microspheres.
7	Cost-low or at least reasonable.
8	Enhanced ability to deal with sulfur.
9	Ability to strip paraffinic fragments off of polynuclear aromatics.

With these contributions and combinations incorporated, a new residual catalyst [DZ-40] was developed that was reported on earlier [9,10].

Other considerations and concerns were also addressed, some successfully and some not so successfully, but all helped to further performance. One processing step, the recycle of hydrogen to the riser was perceived as a possible way to reduce coke, as well as keep vanadia in a lower valence stage. Our preliminary work showed it had promise, which became an important addition to the process, was placed into practice, and did reduce coke formation (Table 3, see item 2).

8. Vanadia on stream additive immobilizer

Another approach that came from this work was related to the idea of chemically immobilizing vanadia by means of continuous on-stream addition of immobilizer. This approach was explored and found successful and was patented [19] and led to the introduction of the additive called ‘MVP$^{\text{TM}}$’ (maximum vanadium protection), which is being marketed by Nalco/Exxon. Its success has also been reported at the NPRA meeting in San Antonio, TX, March, 1997 [20]. Again, one of our research approaches to vanadia treatment went commercial 2 years ago.

Details of that paper can readily be obtained, as space does not permit presentation of all of the results here. However (Fig. 9) does show the drop in catalyst addition rate to maintain activity and selectivity as a function of run days on a high metal containing feedstock after starting addition of the additives. By

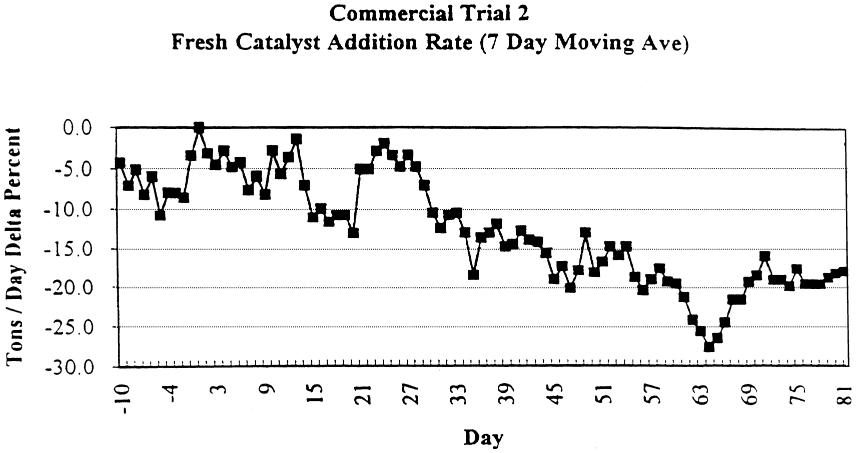

Fig. 9. Fresh catalyst addition rate (7-day moving average during commercial trial 2).

day 75, catalyst addition rate had dropped 20–25%, in spite of a significant rise in vanadium and sodium at about day 50 (see original paper).

Stonecipher et al have reported that ‘MVP^{TM}’ passivation technology has now been applied in 12 different FCC units as of last March. Daily payout ratios to the customer have reportedly ranged from 2/1 to 10/1. Benefits have been achieved ranging from yield improvements to catalyst savings, to use of more and heavier ‘feeds.’

9. Electro magnetic separation — a still newer approach

With these directions for catalyst improvement for the attack pinpointed, which have just been described, we also explored still other means of dealing with all of these contaminants. One of the possibilities that arose related to the amount of iron and nickel, depositing on the catalyst, and my personal familiarity with the pioneering work of Professor P. Selwood at Northwestern University in Magnetochemistry. Here among much other work, Professor Selwood had reported on the magnetic properties of nickel deposited on some of his catalysts. Considering the amount of iron and nickel on our spent catalyst, we speculated as to whether this amount of iron and nickel, depositing on resid catalysts would have magnetic properties, and whether this would facilitate separation of old catalyst from new. With this in mind, studies were made to determine if these catalysts did have magnetic properties, how to measure the catalyst’s magnetic properties and explore just how we could actually separate old catalysts from new by magnetic separation. This we were able to do and a patent was obtained [21]. Scientists at Nippon Oil in Japan had independently and simultaneously come up with the same idea, and for a while we exchanged information on our common approach. There were however, severe problems with early electromagnetic separation processes which were that first, the means of separation involved use of powerful but expensive electromagnets which also consumed a lot of energy, and secondly, also involved a complex means of separating out the more magnetic particles.

10. Magnacat^{TM} process

More recently, about 1987–1988, I learned that a new highly magnetic permanent magnet material, containing rare earth, (neodymium–boron–iron alloy) had been developed, and that a new magnetic roller separation device was also being developed which might be used to exploit this magnetic material. I, therefore, set about to explore, and if successful, exploit the technology to help see if it were able to reduce the cost of reduced crude processing by a new separation process, similar in some ways to the electromagnetic process, but cheaper to build and operate (Fig. 10). In so doing, I determined in fact that we could get good separation

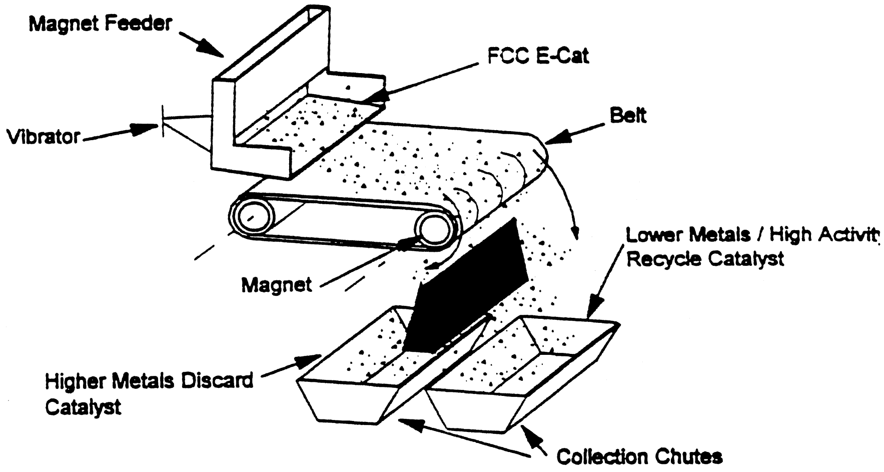

Fig. 10. Schematic for magnetic separation of spent catalyst by Magnacat process.

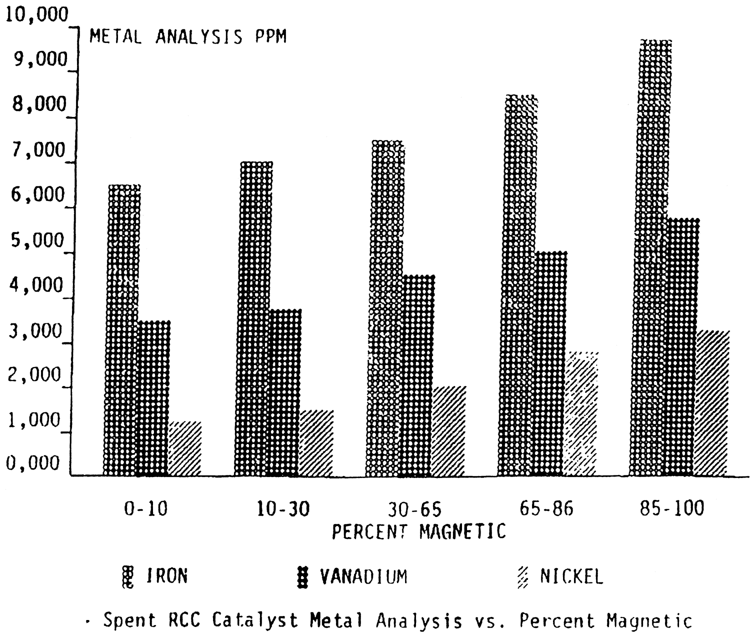

Fig. 11. Spent RCC catalyst metal analysis vs. percent magnetic for catalysts loaded with V, Fe or Ni.

between higher and lower metal containing particles, and more importantly, more active and less active catalysts [22] (Figs. 11 and 12). And so the 'Magnacat$^{\mathrm{TM}}$' concept was born [23] (Fig. 13), and was introduced and placed into commercial practice by Moore and Goolsby at our Canton, Ohio refinery about 3 years ago. It has proven very successful, showing savings of 10–20 cents/barrel of reduced crude. The results were reported at the NPRA meeting in San Antonio, TX, last March, 1997 [24]. M.W. Kellogg has licensed the process and recently announced plans to install a unit in a second refinery.

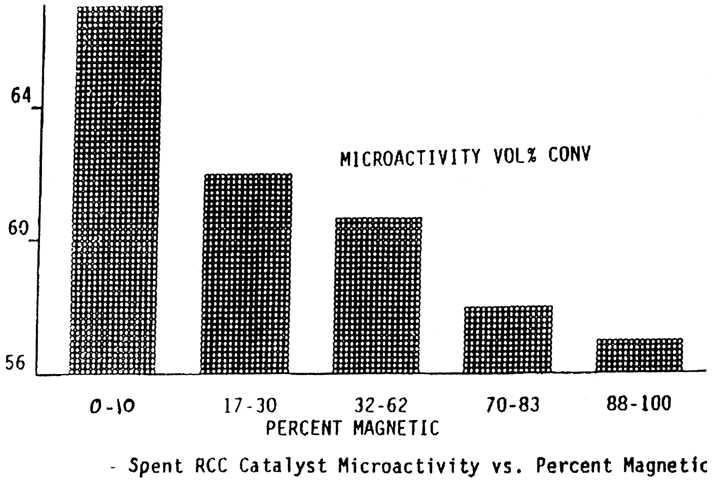

Fig. 12. Spent RCC catalyst microactivity vs. percent magnetic.

Fig. 13. Illustration of announcement for magnetic separation of old catalysts.

11. Superparamagnetism

Incidentally, in the course of focusing on the magnetic properties of these catalysts, I noted and so reported on the effect of temperature on the small crystallite form of magnetic material which had been formed. A property similar to this had been described in other studies on ferro magnetism and described as 'superparamagnetism. This property is not fully understood yet, but it obviously behaves as a very small ferro magnetic particle, probably below 50–100 Å Angstroms. At this crystal size it has very interesting magnetic properties at low temperature in the presence of a magnetic field, but at higher temperatures because of its small crystal size, is not magnetic, and in the absence of a magnetic field, does not manifest itself. This property still needs to be studied further and understood. This represents an opportunity to create these superparamagnetic particles and use them even more efficiently for separation as well. A patent covering this technology has also been obtained [25].

12. The triangular magnetic processing concept

Subsequently, I began to study more thoroughly the properties of a highly contaminated cracking catalyst from our reduced crude converter (RCC$^{\mathrm{TM}}$) and began to discover considerable differences in the metal content, and, therefore, the magnetic properties of larger particles when compared with smaller particles (Fig. 14), and the location of this contamination of iron, nickel, and vanadium (Fig. 15). Among other things I have discovered that there is an inverse relationship between particle size and metal content and magnetic properties. If the outer peripheral surface area (portal area) per unit of mass of a catalyst is determined as a function of particle size, it seems apparent that magnetic properties and metal (except for mobile vanadium) pick up, is depositing on this outer surface at a constant rate per unit of outer surface (as we earlier reported on). For a particle 20 μ in diameter, there are 216 particles for every particle 120 μ in diameter, and therefore for the 216, 20 μ particle there is six times as much exposed outer surface area. In other words, for a given mass of material there is six times as much outer exposed surface area for the 20 μ particles as the

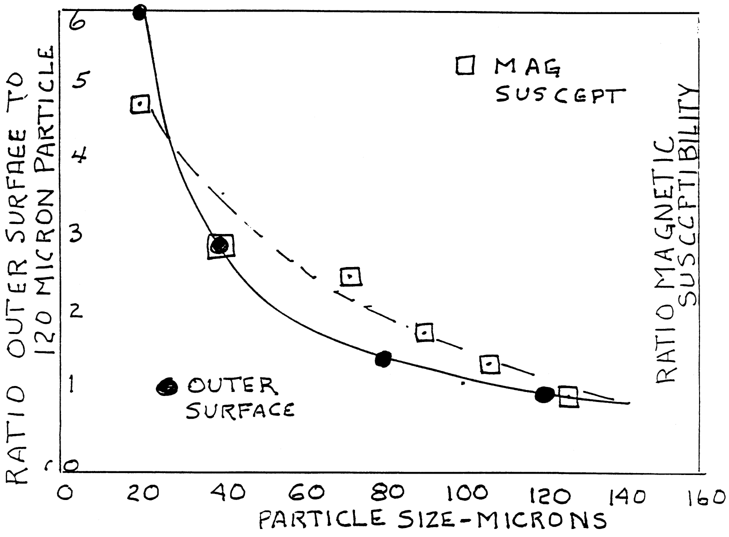

Fig. 14. Ratio of outer surface area and ratio of magnetic separation vs. particle size.

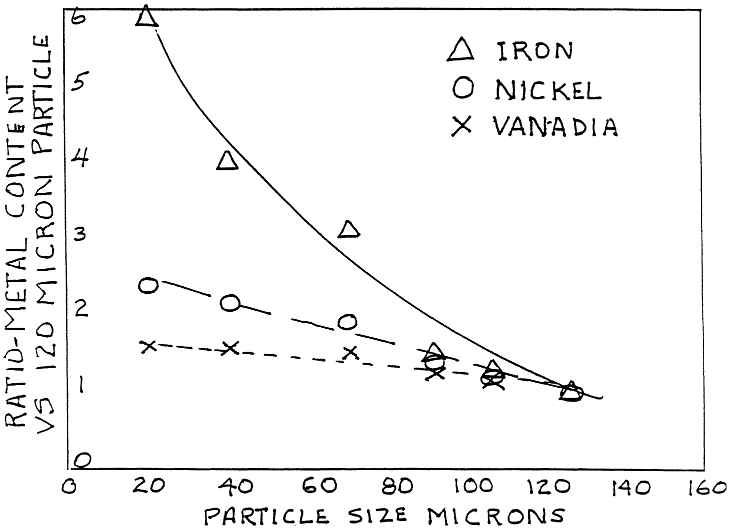

Fig. 15. Ratio of metal content vs. 120 μ particles as a function of particle size.

120 μ particle, and therefore, six times as much metal to be expected, and therefore, also magnetic susceptibility. For the incoming oil, the amount of outer surface available on which to deposit metal is all that seems to count. And no distinction seems to be made as to where that surface is, whether on a large or small particle. In some ways this might be expected, but it is certainly gratifying to find it to work out so close to theory.

As a result of this more recent work, a new concept and process seemed reasonable, namely classification, magnetic separation and attrition processes, and which our patent counsel, Mr. Richard C. Willson, Jr. and I called the 'Magnacat' triangular process' (Fig. 16). In this process, more magnetic particles are separated from less magnetic particles and larger particles are separated from the finer particles by either magnetic separation or elutriation and the larger par-

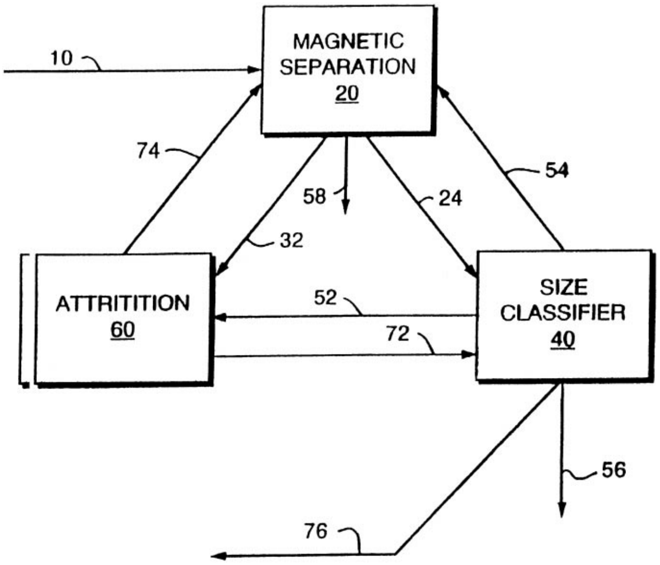

Fig. 16. Triangular process utilizing attrition, magnetic separation, and size classifying.

ticles subjected to attrition, so as to remove a considerable amount of the outer surface, probably 10–50 Å thick, which contains much of the nickel, iron, and to some extent the vanadium. Studies undertaken by Dr. Brian Sales of Oak Ridge Laboratories for me and so reported in this patent showed this to be the case [26]. This leaves an attrited, lower metal containing a more active particle, and also smaller in size for better fluidization properties. This patented process is still a gleam in my eye and how long it will take to reach commercialization remains to be seen. Certainly, it is still another way to deal with the metal contaminants and also a way, coincidentally, to improve fluidization [27]. This in itself has many potential economic benefits. This new process is suggested as a means of fine tuning equilibrium catalysts for maximum efficiency.

13. Magnetic Hook separation process

I more recently devoted attention to the concept of introducing or adding a ‘Magnetic Hook’ continuously to the catalyst. In other words, by continuous addition of a highly magnetic substance in the feedstock to the catalyst during processing, it is possible to achieve an even better time related separation of old, inactive highly magnetic and poisoned particles from new fresh particles. And so the ‘Magnetic Hook’ technology has now been patented and probably will be introduced sometime in the future after Magnacat$^{\mathrm{TM}}$ units begin to be commercialized in larger number, and customers have had a chance to better familiarize themselves in general with the concept of magnetic separation [28–33]. The ‘Magnetic Hook’ additives can consist of one or more of the heavy rare earths, iron, manganese or chromium.

14. ‘Magnetic Hook’ separation and recycle of high priced additives

Finally, and still more recently, it has developed that there are many new high priced additives representing or involving separate microspheres which are being introduced continuously to the FCC unit to further enhance the process. These are: additives for sulfur control, vanadia immobilization, matrix acidity, and high cost oxidation catalyst additives, to name a few. These and others are very expensive and are designed to improve the gasoline product, yield, burning rate, metal resistance, sulfur removable from gasoline and effluent regeneration gases, octane number, or just better operation of the fluid unit. Unfortunately, these high priced additives are lost along with the rest of the catalysts

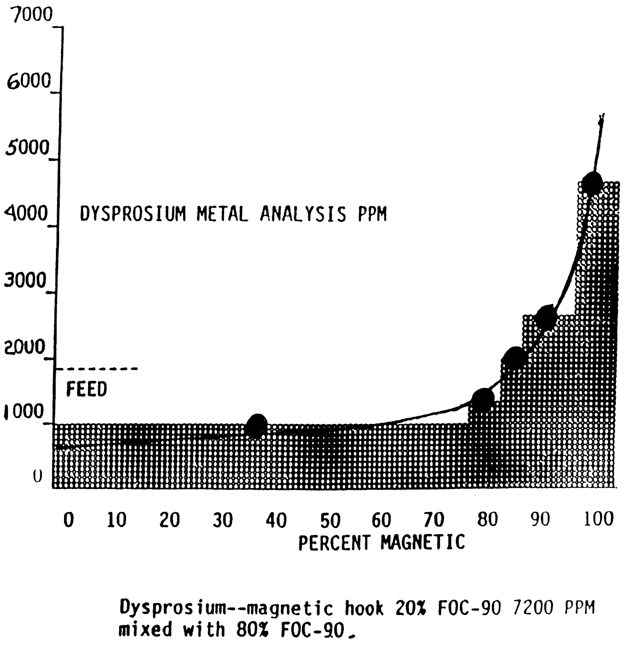

Fig. 17. Dysprosium-Magnetic Hook 20% FOC-90 7200 ppm mixed with 80% FOC-90.

when equilibrium catalysts are dumped to make room for fresh catalysts. So here we have a situation where perhaps a catalyst costing US$ 5000/ton or more, is lost along with equilibrium catalysts when equilibrium catalyst is discharged to make room for fresh catalysts, costing US$ 1500/ton or even less. So, I have introduced the concept, which is now patented [34] ‘magnetic activated additive’ and covers adding magnetic material to a virgin high cost catalyst (additive) thereby allowing one to selectively retain these additives in a Magnacat^{TM} like separator. Fig. 17 shows an example of separation when 20% of an expensive catalyst is impregnated with 7200 ppm of dysprosium, a high paramagnetic element, and mixed with untreated catalyst and then subjected to magnetic separation. Note the rather clean separation with even a small amount of a rare earth ‘Magnetic Hook.’

15. Coke burn off with CO_2 — another direction

One other new possible technical direction for the FCC is one that we explored some years ago [35–36]. As is well known, an FCC unit produces large amounts of CO_2. Whether real or not, in this day, there is certainly concern for the possibility of global warming due to CO_2 production. Recent tentative agreements, as of this writing, to reduce CO_2 production globally are about to be acted upon. This new concept, which would still require much development work, although Dr. Jim Hoffman [33,36] and I have demonstrated its feasibility, also utilizes CO_2 to remove the hydrogen, ‘the H reaction’ (Hettinger and Hoffman) and carbon containing coke formed by catalytic cracking. We have proposed utilizing CO_2 to react with coke to produce CO and H_2O. For example, CO_2 plus coke (contains carbon and hydrogen) produces $CO + H_2O$, and combining this CO with hydrogen from the reactor, would enable formulation of more liquid fuels by the Fischer–Tropsch reaction. In view of its possible favorable image impact for the petroleum industry, it should be explored in more detail, by the Department of Energy, or one or more petroleum companies. It should also be noted that combustion of FCC coke is an exothermic reaction, and is needed to balance the endothermic reaction of hydrocarbon cracking. However, with reduced crude cracking, the regeneration burning reaction is so exothermic that a cooling means is provided to remove the large excess of heat. With CO_2 combustion, a heat balance must be established between the two reactions. We envisioned a system including possibly a two stage regenerator system, where CO_2 would be used in a first stage to remove most of the hydrogen on the coke, and some carbon, and with possibly a second regeneration or regenerator which would release enough heat to carry out cracking. The CO_2 effluent could then be transferred to the first stage. Unreacted CO_2 would be recycled through the system, and would also serve as a heat sink, CO_2 having a much higher heat capacity that N_2.

Even still more recently is my discovery that manganese can effectively and positively replace the rare earths as a promoter for zeolite containing cracking catalysts, especially when processing heavy and metal ladened feedstock. At this point in time it is hard to predict where this will lead, but manganese also has many interesting properties differing from the rare earths, and so it will be interesting to see what happens [39].

16. Conclusions

And so it is exciting and indeed fun for me to see a process in which the objectives of the process and the products sought may be changing, but that somehow the process seems able to break through and come up with new ways of utilizing it. Unfortunately, there does not appear to be a great appreciation at present for the process by the public, in spite of its extremely critical role in the world of transportation. These days when we reflect not only on the future of catalytic cracking, but how to deal with such things as sulfur in the product, sulfur in the effluent gas from combustion, aromatic and olefins gasoline limitations, gasoline boiling point distribution, or possible new petrochemical products to name a few attention-getters, there is no doubt in my mind that additional innovations will continue to come along and continue to keep this catalytic process, a key process, in the hands of the petroleum industry, for many decades to come.

Warren Letzsch, a recognized authority on catalytic cracking, who has been involved in catalytic cracking for some 30 years, and more importantly has been involved in many phases of catalytic cracking, both processing wise and catalyst development wise, recently addressed this same subject when he presented a paper at the NPRA meeting in San Antonio in March, 1997 [37]. Addressing the future of catalytic cracking, he pointed out, rightly so, that even though catalytic cracking is now some 60 years old, it is still being utilized extensively and new processing techniques are still evolving. He also predicted, and I agree, that there would continue to be new leaps (growth curves) in cracking technology leading to further catalyst and catalytic processing improvements, and equally important more units increasingly devoted to residuum cracking.

Acknowledgements

Forty-nine years is a long time to be involved in this exciting field of catalysis, and I hope it is not yet over for me.

I would like to take this opportunity to recognize all of the individuals who have encouraged me over these adventuresome years, without whose encouragement and inspiration I would have not have been able to experience the excitement of these years. To Dr. Curtis Singleterry, Chemistry faculty par excellence, Aurora University. Without his help and encouragement, I would not have been able to even finish college. To Dr. Nathan Kornblum, Purdue University, who took a young, just discharged, bomber pilot (1945), with a wife and no money, and guided my career through 2.5 years of Chemistry, to a B.S. Degree at Purdue, and to Graduate School at Northwestern. To Professor Malcolm Dole, Northwestern University, who as my Ph.D. advisor, made each day a discovery adventure in Science. To John W. Teter, an inspiring catalyst leader at Sinclair Labs, who gave me freedom to try my wings and let me go in any direction my research curiosity lead me. To Carl Keith of the Sinclair Labs who demonstrated the joy of the curious scientific mind, and to my daily scientific inspiration and mentor, Bob Van Nordstrand, who was, and still is the man who keeps me on the straight path of good science.

To Dr. David Braithwaite, of Nalco, who as my boss and creative genius, allowed and encouraged me to go the plant and run experiments on a grand scale of multi-ton batches. He allowed me to treat the plant as my laboratory on a commercial scale, not only for catalytic cracking catalysts, but also for hydrodesulfurization and fluid moly reforming catalysts (but that is another story), and then go to the field and help promote it. How invaluable this experience was to the rest of my career.

To my very close friend, professor Haydn H. Murray, former Chairman, Department of Geology and now Professor Emeritus at the University of Indiana, and earlier Chief Executive of Georgia Kaolin, who brought me up to speed, and still keeps me up to date on kaolin technology.

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My special thanks and gratitude to Oliver Zandona, George Myers, and Bob Yancey, Sr., of Ashland, Inc. who gave me the opportunity to join with them in the great adventure of the Reduced Crude Cracking process. They were all inspiring men who brought out the best in all of us.

To Richard C. Willson, Jr., Patent Council extraordinare, who was able to turn our inventive concepts and data into a remarkable patent portfolio of protection for the RCC^{TM} process and catalysts.

To Dr. Burton Davis, Associate Director, University of Kentucky, Center For Applied Energy Research, who convinced me to give this talk, and to write this follow up story. Burt is not only a great catalytic chemist, who has made outstanding contributions in coal research, the dehydrocyclization reforming reaction, and Fischer–Tropsch reaction, but he and I have shared a great historical interest in seeking insight into the remarkable personalities of those famous catalytic chemists and engineers who have made major contributions to this extraordinary field of scientific pursuit. I count Burt Davis as one of the most inspiring. It is also a pleasure to reflect on the fact that he is still only in the middle of what is already an outstanding career.

We walk on the shoulders of our scientific associates, and I for one, wish to acknowledge and express my deep gratitude to the many members of my research staff at Ashland who participated and made many day to day contributions to the development of the reduced crude catalyst, for their help over the years, to Dr. James Maselli and his staff at Davison for their help, and to the many others, unfortunately too numerous to mention, and for which I apologise for not being able to include them.

I would however like to cite, and recognise the names of those Ashland individuals who participated with me, and made significant contributions in the reduced crude catalyst adventure (many of whom are coinventers on the listed referenced patents) namely, W. Beck, R. Benslay, D. Carruthers, E. Cornelius, P. Doolin, T. Goolaby, J. Hoffman, R. Kmecak, S. Kovach, D. Lee, C. Lochow, H. Moore, J. Palmer, D. Watkins, D. Wesley and R. Wombles. If I have missed anyone, please forgive me.

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References

[1] W.P. Hettinger Jr., C.D. Keith, J.L. Gring, J.W. Teter, I & EC 47 (1955) 719.

[2] W.P. Hettinger, Jr., D.G. Braithwaite, E.H. McGrew, J.S. D'Amico, U.S. Patent Nos. 3,034,994 and 3,034,995 (1962).

[3] W.P. Hettinger Jr., T.T. Oleszko, Pet. Refiner. 38 (1959) 169.

[4] C.J. Plank, E.J. Rosinski, U.S. Patent No. 3,140,249, 3,140,251, and 3,140,253 (1964).

[5] Davison Chemical Company, Catalagram, 1968.

[6] G.D. Myers, U.S. Patent No. 4,332,673 (1982).

[7] G.D. Myers, L.E. Busch., U.S. Patent No., 4,299,687 (1981).

[8] G.D. Myers, O.J. Zandona, L.E. Busch, 1979, Catalytic Conversion Of Residual Stocks, 1979 NPRA Annual Meeting, San Antonio, TX, March 22–27, 1979.

[9] W.P. Hettinger, Jr., 1987, Development Of Reduced Crude Cracking Catalysts Preprints, Division of Petroleum Chemistry, A.C.S., Advances in FCC, Co-Chairmen M, Occelli, L. Hilfman, Vol. 32, 3 and 4, August 1987, p. 688.

[10] W.P. Hettinger, Jr., 1988, in: M.L. Occelli (Ed.), Development of a Reduced Crude Cracking Catalyst, ACS Symposium Series 375, Fluid Catalytic Cracking, Chapter 19, p. 308.

[11] H.W. Beck, J.B. Carruthers, E.B. Cornelius, R.A. Kmecak, S.M. Kovach, W.P. Hettinger, Jr., U.S. Patent No. 4,480,047 (1984).

[12] H.W. Beck, J.B. Carruthers, E.B. Cornelius, R.A. Kmecak, S.M. Kovach, W.P. Hettinger, Jr., U.S. Patent No. 4,480,047 (1984) Claim 5.

[13] W.P. Hettinger, Jr., H.W. Beck, U.S. Patent No.4,612,298 (1986).

[14] W.P. Hettinger, Jr., J.D. Carruthers, W.D. Watkins, U.S. Patent No. 4,377,470 (1983).

[15] H.W. Beck, J.D. Carruthers, G.B. Cornelius, W.P. Hettinger, Jr., S.M. Kovach, J.L. Palmer, O.J. Zandona, U.S. Patent No. 4,432,890 (1984).

[16] W.P. Hettinger, Jr., H.W. Beck, J.D. Carruthers, E.B. Cornelius , S.M. Kovach, J.L. Palmer, U.S. Patent No. 4,485,184 (1984).

[17] W.P. Hettinger, Jr., H.W. Beck, U.S. Patent No. 4.612,298 (1986).

[18] H.W. Beck, J.D. Carruthers, E.B. Cornelius, R.A. Kmecak, S.M. Kovach, W.P. Hettinger, Jr., U.S. Patent No. 4,588,702 (1986).

[19] W.P. Hettinger, S.M. Kovach, H.W. Beck, U.S. Patent Nos. 4,496,665 and 4,552,647 (1985).

[20] D.L. Stonecipher, W.F. Minyard, D.C. Kowalczyk, 1997 NPRA paper AM-97-29, San Antonio, TX, Passivate Vanadium on FCC Catalysts For Improved Refinery Profitability.

[21] W.P. Hettinger, Jr., R.M. Benslay, U.S. Patent No., 4,406,773 (1983).

[22] W.P. Hettinger, Jr., In J.N. Armor (Editor) Catalyst Today, Vol. 13, No. 1, 11 March, 1992, Elsevier, Amsterdam. Proceedings of the ACS Symposium on New Industrial Catalytic Processes. Honoring J.F. Roth 28-29, August 1991. P.157, Magnetic and Chemical properties of Magnetically Separated Fractions of Equilibrium Cracking Catalysts Laden with Iron, Nickel, and Vanadium, and the Development of the Magnacat^{TM} Process and Magnetic Hooks^{TM} for Selectively Removing Old Catalysts.

[23] William P. Hettinger, Jr., U.S. Patent No. 5,147,527 (1992).

[24] T.L. Goolsby, H.F. Moore, D.C. Kowalczyk, M.L. Zampieri, B.K. Bussey, 1997, NPRA paper AM-97-32, San Antonio, TX, March 16–18, FCC Unit Optimization Using the Magnacat^{TM} Process.

[25] W.P. Hettinger, Jr., U.S. Patent No. 5,190,635 (1993).

[26] W.P. Hettinger, Jr., U.S. Patent No. 5,393,412 (1995).

[27] W.P. Hettinger, Jr., H.F. Moore, T.L. Goolsby, A.V. Peppard, U.S. Patent No. 5,636,747 (1997).

[28] W.P. Hettinger, Jr., U.S. Patent No. 5,171,424 (1992).

[29] W.P. Hettinger, Jr., U.S. Patent No. 5,198,098 (1993).

[30] W.P. Hettinger, Jr., U.S. Patent No. 5,328,594 (1994).

[31] W.P. Hettinger, Jr R.M. Benslay, U.S. Patent No. RE 35046 (1995).

[32] W.P. Hettinger, Jr R.M. Benslay, U.S. Patent No. 5,230,869 (1993).

[33] W.P. Hettinger R.M. Benslay, U.S. Patent No. 5,364,827 (1994).

[34] W.P. Hettinger, Jr., U.S. Patent No. 5,538,624 (1996).

[35] W.P. Hettinger, Jr., S.M. Kovach, J.F. Hoffman, U.S. Patent No. 4,425,259 (1984).

[36] W.P. Hettinger, Jr., S.M. Kovach, J.F. Hoffman, U.S. Patent No. 4,450,241 (1984).

[37] W.S. Letzsch, D. Dharia, J. Ross, 1997, NPRA paper AM-97-6S, San Antonio, TX, March 16–18, 1997, The Future of Fluid Catalytic Cracking.

[38] R. Wombles, Internal Ashland confidential Research Report.

[39] W.P. Hettinger, Jr., S. Mayo, U.S. Patent No. 5,641,395 (1997) Catalysis Today 53 (1999) in press.