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Process Innovation in Petroleum Refining

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The advent of the internal combustion engine and the rapid growth in its use, beginning in the early years of this century, created huge demands for petroleum products and gave refiners the opportunity and incentive to innovate. Refiners responded and introduced new processes which completely revolutionized refining technology. This is a study of those innovations - who made them, when and why.Specifically, it is directed to these questions:

Was the innovation a departure from contemporary practice or did it evolve from existing processes?

Was it invented in the laboratories of a refining company or elsewhere?

Was it invented to satisfy an economic need or to apply a technical advance?

What company made the innovation?

The study began, however, as a investigation of refining innovations introduced since World War II. Quite a lot happened in this period; railroads became dieselized; jet aircraft became commercial; home heating with oil became widespread; high performance automobiles became popular. And it was the age of research*. Yet contrary to expectations these changes did not make great demands on refining technology and only one important new process was introduced - catalytic reforming in 1949. It was necessary to review periods of greater change to find significant innovation.

Refining is the production of special-purpose products from crude oil, and extremely variable raw material. The refiner's problem is to produce satisfactory products at minimum costs and since the cost of crude is about three quarters of total refining costs, refiners have sought to maximize the yield of the most valuable products - kerosene prior to about 1910 and gasoline thereafter - and to refine cheap crudes. In

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* The number of research scientists and engineers in the petroleum refining industry increased from 1,800 in 1950 to 3800 in 1964 (3,600 in 1966) - Employment of Scientists and Engineers in the United States 1950-1966, National Science Foundation, NSF 68-30

addition refiners have sought to develop continuously operating processes and scale them up to large size so as to minimize operating and capital costs and maintain uniform quality.

In addition improvements in engines and competitive forces created demands for better quality products which have tended to work against the goal of minimum costs. Improved engines for example require better fuels which lead to improved engines. As will be seen improving quality usually means reducing yields, running expensive crudes, or as a last resort, developing new processes.

In this century, the refining Industry has done little to create new markets or new products. Of course, traditional fuel markets consume such large quantities of petroleum that other outlets are tiny by comparison.

PETROLEUM PROCESSES

Three processes - distillation, cracking and reforming are the core of the modern refinery. Distillation separates crude oil into fractions boiling at different temperature ranges. Cracking converts high boiling to lower boiling material, especially gasoline. Reforming increases the octane number of gasoline stocks. (Octane number is an important index of gasoline quality; it measures the tendency of gasoline to knock in the engine.)

There are several less important processes used in a typical refinery. Polymerization, alkylation and isomerization were introduced to convert waste gases into gasoline. With the advent of catalytic cracking and catalytic reforming the original need has become less important but the products are very good gasoline stocks, so the processes are still used. Solvent extraction which was introduced to improve kerosene from aromatic crudes is now used primarily to improve lubricating stocks and to isolate aromatics for chemicals and high-test gasoline. Hydrogenation which was introduced as an alternative to cracking is used to remove sulfur from various stocks and to only a slight (but growing) extent for its original purpose.

The initial development of these processes is discussed in Part II.

Core Processes

Crude Distillation

The first continuously operating still was invented by M.J. Trumble and was first used in a refinery erected by the Santa Fe Railroad in 1911. A railroad company's introducing a major petroleum innovation may seem incongruous but it really isn't. They used heavy fuel oil for their locomotives and they did not care to produce lighter products. All they

needed was a simple low-cost distillation process which was just what the first Trumble still was. As invented, the pipe still was less valuable to the full-line refinery. Subsequently, as it was more fully developed, especially by Shell, which acquired the rights to it in 1914, it became a key refinery element and was used as the basis of other continuous processes.

The traditional shell still was simply a pot over a fire and attached to a condensor. As the oil was gradually heated the more volatile material tended to distill first followed by heavier materials as the oil got hotter. Separation was poor and cleaning the still after every batch was troublesome because of the coke which precipitated. Also the shell still could not be made very large.

Trumble's approach was to separate heating from fractionation. The oil was pumped through a run of pipes in a furnace and into a flash tower.

The Trumble process was:

- A substantial departure from contemporary practice
- Invented by an independent inventor
- Innovated by a company on the fringes of the oil industry

Cracking*

Batch Thermal Cracking

Prolonged heating of petroleum as for example in slow distillation cracks (decomposes) heavy stocks and produces lower boiling materials. The phenomenon was used in the early kerosene refineries but the first process specifically designed for cracking was invented by Burton and Humphrey at Standard of Indiana and installed in their Whiting refinery

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*The history of petroleum cracking has been described by John L. Enos in his book, "Petroleum Progress and Profits" (M.I.T. Press, 1962) on which this discussion is based.

in 1913. It was little more than a shell still operated at elevated pressure. It was obsolescent when it was introduced because the pipe still was already in existence and using a large direct fired pressure vessel is poor engineering.

Burton recognized the need for a process to crack gasoline in 1909 when Indiana was part of the Standard Oil Trust but was unable to get support for development. After dissolution of the Trust in 1911 Indiana became an independent company and Burton's work was supported. Indiana as an independent had considerable incentive to develop cracking because they had a large gasoline market and operated on purchased crude. Burton, who became president of Indiana in 1918 was reluctant to support development of continuous process.

The Burton process was:

- An extension of contemporary practice
- Invented by employees of a large refining company
- Invented to satisfy a specific need
- Innovated by the inventing company, a large refiner

Continuous Thermal Cracking

The Burton-Humphrey process being a batch process could not be scaled up and it did not work well with heavy crudes. But despite considerable awareness of these shortcomings at Standard of Indiana that company did not develop a continuous process. Their last designs were close however.

Continuous cracking systems based on the pipe still were developed by Standard Oil of New Jersey and Universal Oil Products.

Tube and Tank Process

Jersey began in 1918 to develop a continuous process which would crack heavy (low cost) crudes and which would be royalty free. They were successful by 1920, but their operating managers were reluctant to Innovate. The Jersey process called Tube and Tank was installed in independent refineries before it was used by Jersey. This process was anticipated by Carelton Ellis, an independent inventor.

Dubbs Process

Universal Oil Products which began as an asphalt producer developed a continuous thermal cracking process based on the patent applications of Jesse Dubbs. The process was first successfully operated in 1922 by Shell who also contributed to its development. Shell had not been able to acquire a license to the Burton-Humphrey process and was at a competitive disadvantage.

Jersey's Tube and Tank process and the Dubbs process were technically very similar being essentially a pipe still operated under pressure with provision for recycle of partially cracked material. They were:

- Extensions of contemporary practice
- Invented or anticipated by independent inventors
- Invented to satisfy a specific need
- Developed by a large refiner (Jersey) and by a development company (UOP) together with an aggressive refiner
- Innovated by Shell and (reluctantly) by Jersey.

Fixed-Bed Catalytic Cracking

Thermal cracking was made obsolete by the development of catalytic cracking. The first process was invented In 1929 by Eugene Houdry, an independent inventor, who wanted to produce a superior gasoline. When

Houdry ran out of money, his work was supported by Vacuum Oil and when they lost interest by Sun Oil. Sun was interested because the Houdry process produced a high quality gasoline and Sun's marketing strategy was to sell a single high-grade lead-free grade of gasoline. Eventually Sun needed more money too and Vacuum (then Socony-Vacuum) contributed to the final development. The first units were installed by Socony in 1936 and Sun in 1937.

The Houdry Process was:

- A substantial departure from contemporary practice
- Invented by an independent inventor
- Invented to satisfy a specific need
- Innovated by Socony-Vacuum then a large refiner and Sun

Moving Bed Catalytic Cracking

The first Houdry process produced higher yields of gasoline than thermal cracking as well as better quality but it was a semi-continuous process and difficult to operate. It used two beds of catalyst, one on stream while the other was being regenerated. Socony Vacuum immediately set to work to develop a continuous process based on a clay treating process they had developed. Their approach was to move the bed of catalyst pellets through the cracker then through a regenerator. The first unit went on stream in 1943.

The moving bed process was:

- An extension of contemporary practice
- Invented and developed in the laboratories of a large refiner
- Invented to satisfy a specific need
- Innovated by a large refiner

Fluid Bed Catalytic Cracking

An alternative approach developed by a group of companies was to use a fluidized bed and circulate powdered catalyst from reactor to regenerator in a stream of gas. Much of the development work was done by Standard of New Jersey who introduced the process in 1942.

The incentive to develop fluid cracking varied. M. W. Kellogg and UOP designed and (in Kellogg's case) built thermal crackers. They would lose much of their business if they could not offer a catalytic process. Jersey and presumably other refiners needed a catalytic process to remain competitive but wanted to avoid high royalties.

The development of fluid cracking is unusual in that it utilized a basic engineering principle that was discovered during the development period namely, a bed of solid particles through which a stream of gas flows behaves like a fluid. This important principle which is now widely used was discovered at MIT and its use in cracking was patented by W.K. Lewis who consulted for Jersey.

Fluid cracking was:

- A departure from current practice
- The key invention was invented by an independent inventor
- Invented to satisfy a specific need
- Largely developed in the laboratories of a major refiner-Standard Oil of New Jersey
- Innovated by the developer

Catalytic Reforming

Catalytic reforming like catalytic cracking has its roots in thermal processing. it happens that cracked gasoline has higher octane rating than straight run (untreated) gasolines. By 1930 quality requirements had increased to the point where refiners could not

make a satisfactory product using all of their straight run gasoline and it became customary to reform i.e. thermally crack them. While this improved quality the yields were poor; like all thermal conversions it produced a lot of gases and heavy tars. There were several attempts to develop a catalytic process. The most nearly successful was hydroforming, developed by M.W. Kellogg and innovated by Standard of Indiana in 1941. It used a hydrogenation catalyst developed by Standard of New Jersey.

The current reforming process which uses platinum catalysts was invented by Vladimir Haensel of UOP and was innovated by Old Dutch Refining in 1949.

It is not surprising that a small company innovated catalytic reforming because in a way it was the small refiner's process when it was introduced. The small refiner needed a new process to produce high-octane blending stocks while large refiners had other alternatives, especially catalytic cracking with its large capacity (and large capital investment).

Incidentally, UOP had close ties with small refiners and for many of them, acted as their engineering department.

Catalytic Reforming was:

- A departure from contemporary practice
- Invented and developed in the laboratories of a research and development company
- Invented to satisfy a specific need
- Innovated by a small refiner

Secondary Processes

The first solvent extraction process using liquid sulfur dioxide was invented by Lazar Edeleanu in 1907 to upgrade Roumanian kerosene. Extraction removed components which could not be separated by distillation. The process was developed and innovated in Europe by Royal Dutch Shell in 1916. They tried to introduce it in California in 1915 but were unable to get satisfactory equipment in this country. Several companies used it to upgrade California kerosene in the mid twenties but it was a minor process until used to refine lubricating oils. Tidewater and Shell innovated this application in 1927. Subsequently other solvent systems were developed and the process was applied to other separations, but the major use remains in refining lubricants.

Solvent extraction gives the refiner a way to produce high quality lubricating oils from a variety of crude oils and become less dependent on certain costly crudes e.g. Pennsylvanian.

Solvent extraction was:

- A substantial departure from contemporary practice
- Invented by an independent inventor
- Invented to satisfv a specific need
- Innovated and developed by a major refiner

Polymerization, Alkylation and Isomerization

Thermal cracking and reforming produced large quantities of gases which had value only as refinery fuel. Polymerization, alkylation and isomeration processes were developed in the thirties to convert these gases to gasoline. They are relatively expensive processes but, as it happens the gasolines have a high octane rating and refiners could market them in aviation fuels and now in motor fuels.

[illegible]

The first solvent [illegible]
was invented by [illegible]
Extraction [illegible] by distillation.
The process was [illegible]
in 1916. They [illegible]
unable to get [illegible]
used [illegible]
a minor process [illegible]
Shell [illegible]
systems were [illegible]
but the major [illegible]

Solvent [illegible]
lubricating oil [illegible]
on certain [illegible]

[illegible]

In 1935 Phillips Petroleum and Pure Oil introduced thermal polymerization processes. They were immediately made obsolete by catalytic polymerization which was invented by UOP and innovated by Shell also in 1935. Shell had been developing a polymerization process of its own based on sulfuric acid; they expected to make components for aviation gasoline. In 1939, Anglo Iranian Petroleum described an alkylation process. It was installed that year by Shell, Texas and Jersey.

In 1941 Shell introduced a process which they invented to isomerize butanes for alkylation feed stocks. This is still the principal use but isomerization has been used to a slight extent to increase the octane rating of straight run naphthas.

Catalytic Polymerization was:

- A substantial departure from contemporary practice
- Invented and developed in the laboratories of a research and development company
- Invented to satisfy a specific need
- Innovated by a major refiner

Alkylation was:

- An extension of contemporary practice
- Invented and developed in the laboratories of a large refiner
- Invented to satisfy a specific need
- Innovated by three large refiners

Isomerization was:

- A substantial departure from contemporary practice
- Invented and developed in the laboratories of a major refiner
- Invented to satisfy a particular need
- Innovated by the developer

Olefin Hydration

Another approach to using waste gases is to convert them to chemicals. The first petroleum company to do so was Standard of New Jersey which in 1920 innovated the olefin hydration process invented by Carleton Ellis. Shell followed in 1931 when they began to produce ammonia by the Mont Cenis process. Union Carbide, however, did far more to create a petrochemical industry than any petroleum company.

Olefin Hydration was:

- A substantial departure from contemporary practice
- Invented and partly developed by an independent inventor
- Invented to satisfy a specific need
- Innovated by a major refiner

Hydrogenation

Hydrogenation which Jersey introduced in 1929 is a peculiar case of process innovation. They hoped to convert very heavy oils to lighter products and adapted methods developed by Friedrich Bergius in Germany to hydrogenate coal tar during the first World War. This has not proved to be particularly attractive although there are a few installations in operation. It has received considerable attention since about 1960 but so far catalytic cracking has proved to be the more economical approach. Jersey anticipated other uses for hydrogenation e.g. removing sulfur, which are more widely applied. On paper, hydro-treating looks like the ideal petroleum conversion process but costs are high because really good catalysts are not available.

Hydrogenation was:

- A substantial departure from contemporary practice
- Invented by an independent inventor

- Invented to satisfy a particular need and adapted to satisfy an analogous need in refining
- Innovated and developed by a major refiner

Product Innovations

Two major product innovations, tetraethyl lead and lubricating oil additives were brought to the petroleum industry by General Motors. Refiners, especially Standard of New Jersey, did much of the development work.

Summary and Analysis

Of the thirteen process innovations considered, nine were departures from contemporary practice. The basic criterion for placing an innovation in this group was whether most investigators were following another approach (or ignoring the problem). Thus the Trumble still was a substantial departure because others were trying to develop ways to operate the shell still continuously. This is, I think, a significant difference.

Independent inventors were surprisingly important; they invented five processes - pipe still, solvent extraction, hydrogenation, fixed bed catalytic cracking and olefin hydration. In addition they anticipated major aspects of continuous thermal cracking and fluid bed cracking. Universal Oil Products invented catalytic polymerization and catalytic reforming. Refiners invented only four processes, the Burton Process, moving bed cracking, alkylation and isomerization. Interestingly, independents invented five of the nine revolutionary innovations and contributed significantly to another. Universal Oil Products invented two more of the revolutionary innovations. Refiners can claim full

credit for inventing only one revolutionary innovation and that is a minor one - Isomerization.

All of the innovations were invented to satisfy clearly identified economic needs.

Two companies, Shell and Jersey introduced eight of the thirteen innovations. Jersey introduced hydrogenation, fluid cracking and olefin hydration. Shell introduced solvent extraction, catalytic polymerization and isomerization. They introduced continuous thermal cracking and alkylation (along with Texas) almost simultaneously. The two leaders did not innovate the pipe still, batch thermal cracking, fixed bed catalytic cracking, moving bed catalytic cracking and catalytic reforming. Four of these - moving bed cracking being the exception - make a special category. They are the first embodiment of basic methods which became the core of modern refining. They were especially novel and it looks like the leaders were unwilling to be too radical. And the revolutionary core processes were introduced by smaller companies like Sun Oil. On the other hand large refiners like the two leaders did innovate the major improvements like continuous thermal cracking and fluid catalytic cracking which required a lot of engineering talent and large financial resources.

In general the results of this study parallel and reinforce the conclusions reached by Myers and Marquis in their study of industrial innovations. Their investigation was much broader than the present study and they were able to discuss incremental innovations which they showed were important in overall technological progress.

The present study does not bear on this point except inferentially, Only fairly large advances are discussed but it must be recognized each has been considerably improved since its first introduction.

Also Myers and Marquis collected and analysed data on ideation and information sources. The present study did not consider this area, nevertheless, it supports one of their conclusions. They found that major information inputs were general in nature and widely accessible. In the case of petroleum processes only fluid cracking depends on a principle which was discovered during the course of development. The Houdry process depended on finding a particular catalyst formulation but the fact of catalytic cracking e.g. with aluminum chloride was known and, in fact, had been considered by Burton and Humphrey.

Myers and Marquis showed the effectiveness of demand pull vs. technology push; i.e. recognition of demand or need is a more frequent factor in innovation than recognition of technical potential. Each of the innovations described in this study was purposely developed in response to a widely recognized economic need.

Myers and Marquis also found that adopted innovations, that is, innovations developed by another firm, were a significant portion (23%) of the innovations they studied studied. Two of the thirteen important petroleum innovations - catalytic reforming and catalytic polymerization - were developed by UOP and innovated by refiners. Hydrogenation was adapted from a process developed to treat coal and strictly speaking the Tube and Tank process was an adaption since it was developed by Jersey and first installed by an independent refiner but this is a rather special case. In addition the Dubbs process, sulfuric acid alkylation and olefin hydration were at least partly developed outside of the innovating firm.

Finally in what may be their most important conclusion, Myers and Marquis say that innovation is more than R&D. A conclusion which is abundantly substantiated by the present study.

The two leading innovators, Shell and Jersey were bitter rivals during this period for world leadership in all aspects of the petroleum industry. And in Jersey's case the record shows that the company did use R&D as part of overall competitive strategy. When Walter Teagle became president in 1917 he saw that Jersey was a technically backward company and stimulated by the large royalties his company was paying Indiana for the Burton process undertook to remedy the situation. In 1918 Jersey hired E.M. Clark from Indiana - it appears to have gutted Indiana's research effort - and gave him the dual responsibility of developing a continuous cracking process and improving the company's level of technical competence. The two chores were incompatible and the company organized a well planned and extremely effective function, the Development Department, to develop major advances.

Shell on theother hand had maintained a high level of technical competence and did not organize a separate research department until 1929.

Standard of Indiana provides a contrary example. Until about 1920 it was the most innovative of the Standard Oil Companies. But after the huge success of the Burton process, the company did not innovate a successful process. Apparently Burton who became president in 1918 did not see the need for further technical innovation and discouraged it. This is probably what drove Clark to Jersey.* Also the company devoted its attention to acquiring reserves of crude oil during the twenties and early thirties.

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*There is a curious parallel to Burton's reluctance to develop continuous thermal cracking. Eugene Houdry was similarly disinclined to develop a continuous catalytic cracking process and it was not until after moving bed and fluid cracking were installed that the Houdriflow process was develope

The low rate of innovation in petroleum processing - since the war - despite growth in R&D - could be explained by assuming that there was no need for innovation. This explanation can be defended strongly since the refining industry was able to respond to significant changes in market demand without having costs rise excessively or, which is pretty much the same thing, without suffering poor yields.

What is implied here is that there is some tacitly recognized standard of adequate performance and not that opportunities for significant improvement of refining technology have been exhausted.

As a matter of fact there is one area where the industry is seeking for a significant advance in processing technology. One of the refiner's continuing goals has been to maximize yields of high value products e.g. gasolines and distillates. Progress in this direction since 1910 is shown below.

Average Yield of Gasoline and Distillates from American Refineries

	Gasoline	Distillates % by volume	Sum
1909	11	64	75
1920	26	62	88
1930	42	14	56
1940	43	20	63
1950	43	25	68
1960	45	27	72
1967	44	33	77

Data from U.S. Bureau of Mines

Other products produced in a refinery especially heavy fuel oil, coke, and waste gases are less valuable than the crude from which they are made. The 1967 average refinery yields of these products were:

Residual Fuel Oil	7.77
Coke	2.5
Still Gas	3.9
	14.1%

Typically 14% of the crude goes to products having lower value than crude. Actually these yield figures are somewhat misleading since they are volumetric yields. If they were given on weight basis or, more appropriately, on energy content, yields of residual oil and coke but not gas would be higher. What these figures reflect is the difficulty of converting heavy oils to lighter products efficiently. The coke for example comes from pyrolytic decomposition of heavy oil and to a somewhat larger extent from deep cracking where it is deposited on the cracking catalysts. Both methods produce large quantities of gas. Refiners are aware of this problem and there is considerable interest in perfecting hydrocracking which can convert heavy oils but is not economical.

The main thrust seems to be improving hydrocracking rather than seeking alternatives. The situation is reminiscent of the development of continuous distillation, polymerization and reforming. In these cases the bulk of the development effort was expended on improving contemporary methods which were made obsolete by a clever innovation. If history repeats itself hydrotreating of black oils will be made obsolete in the same way. The successful process will probably be invented by an independent, by a firm on the fringes of the oil industry or by a small

refiner which operates on purchased crude. Probably there are other opportunities for innovation but which are not recognized as needs.

A need which is common to many firms within an industry probably is not perceived as a need but as a fact of life. The firm which does perceive a need and which responds by innovating is likely to be one which has a competitive disadvantage and feels the need with particular intensity. Consider catalytic cracking for example. Houdry's first supporter was Vacuum which at that time had inadequate crude reserves marketing outlets and refining capacity. When Vacuum merged with Socony these difficiencies were alleviated and the company lost enthusiasm for the development. Then it was taken up by Sun which had a special need for the process because of their strategy of marketing a single grade of gasoline.

Perhaps the Houdry success would have aroused greater interest if it had promised increased yield as well as quality improvement (as it happened, the process did give increased yields but they weren't apparent early on). A refiner will feel the need for improved quality when his competitors produce better quality than he does and his customers recognize it. When his products are competitive, quality improvement is not perceived as a need and in fact it is not a need.

This is only slightly less true of yields and costs. As long as a refiners' costs and yields are about the same as his competitors improving them is perceived as nice to do but not as a pressing need. A refiner operating on purchased crude is likely to be very conscious of yields and be interested in introducing processes which promise to conserve crude. He would probably try to acquire crude reserves rather than to innovate new processes however.

Rivalry provides impetus to perceive even to seek out needs. The rivalry between Jersey and Shell unquestionably contributed to their being especially innovative companies. It led them to innovate continuous thermal cracking, for example.

This suggests ways to reduce process innovation. One is to make the industry more homogeneous. As the several companies come to resemble each other the likelihood is reduced that any one company will feel a peculiar need strongly enough to innovate. A second way is to increase technical cooperation between companies and reduce rivalry. This could be accomplished by relatively open exchange of technical information and making advances available to all comers at modest royalties.

The refining industry has been trending in precisely these directions since the twenties. Petroleum companies have integrated into all aspects of the business - crude production, transportation, refining, bulk distribution and retail marketing. Also they have tended to operate over larger geographic areas. As they become integrated differences between them disappear.

Furthermore they have become more cooperative after the ferocious legal battles which accompanied development of thermal cracking. Jersey made hydrogenation available to any refiner that wished to participate in developing it. Fluid catalytic cracking was a joint development of several refiners as well as Kellogg and UOP. The result has been to reduce both the incentives for innovation and the penalties for non-innovation.

The question remains - what did refiners get for their investment in R&D since 1950? In the first part of this period they had a lot to learn about catalytic cracking and catalytic reforming. Catalytic mechanisms were investigated and improved catalysts were developed. The

processes were improved and extended to heavier and less tractable stocks. Knowledge of these processes has advanced to the point where it is becoming feasible to develop computer controls for them.

These are valuable contributions yet some petroleum companies are disatisfied with their research departments. In the early sixties for example one major refiner reduced its product and process research staff by over 50%. Many others introduced planning functions with elaborate analytical schemes for project evaluation.

Presumably management dissatisfaction stems from lack of tangible results i.e. innovations from research. I heard one oil company executive challenge research to show a single instance where a research advance in petroleum led to improved company performance. This is difficult to do (although thermal cracking clearly helped Indiana) in fact the financial performance of Shell and Jersey the two leading innovators is not noticeably different from Gulf and Texas which are definitely non-innovators.

The petroleum industry has developed a system which hides and delays the need for process innovation. Fiddling with organization of research departments and elaborating evaluation methods are unlikely to improve matters. The petroleum industry - like many mature industries - is reluctant to innovate unless forced to do so by outside pressures The need to reduce air pollution is such a pressure and is likely to lead to a burst of innovation.

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Part II Case Histories

Distillation of Crude Oil - The Trumble Process

Crude petroleum is a mixture of many compounds some of which are gases well below room temperature and some still liquid above 1000°F. The petroleum refiner separates this mixture into fractions which boil within a narrow temperature range. Originally three fractions were produced - kerosene, lighter materials which were discarded, and residuum which was sold for fuel oil or worked up into lubricants. Separation was by distillation in direct fired shell stills - a cylindrical vessel lying on a fire box and connected to a coil of pipe in a box of cold water. The still was partially filled with crude oil and gently heated. A large proportion of light materials would distill over. As this happened the fire was built up to heat the oil to a higher temperature and distill over the heavier compounds. It is impossible to get sharp separation between fractions in simple distillation and the products from shell stills had to be redistilled. This was not serious in the first kerosene refineries but as more products were produced e.g. gasoline and gas oil and as product specificatons become more rigorous, the refiner had to install more and more redistillation capacity. (5)

The shell still has serious limitations. It is a batch process. Capacity is limited because as still size increases the ratio of heat transfer surface to volume of oil decreases and eventually further increase in size become uneconomical. Long contact of oil with a hot surface decomposes the oil leaving a layer of coke which reduces efficiency of heat transfer. It is dangerous to have large volumes, say 20,000 gallons, of oil over a fire. It is wasteful of heat to condense and then redistill the vapors.

Prior to 1910 some of these difficulties were partly overcome. Distillation was continuous in bench stills which was a series of stills lying side by side. Crude oil was heated gently in the first still and the vapors separated. The warm bottoms automatically flowed to the next still where they were more strongly heated and so on through several steps. Often the bottoms from the last still were cooled by crude oil in a heat exchanger. Agitation by steam or mechanical means reduced coking. Heat could be conserved and redistillation limited by using fractionation columns instead of simple condensor

Limited still size is inherent however.

With the advantage of hindsight one can see how to eliminate the shell still. What is needed is a vessel with high surface to volume ratio, preferabl one which is heated from all sides. This gives rapid heating but it also implies small volume so the oil would have to flow through rapidly. Rapid flow increases heat transfer and minimizes coking. But efficient pumping requires little boiling in the still thus a separate chamber corresponding to the head space in a shell still is needed where the vapors separated from the liquid. Finally the vapors are to be condensed but unlike shell stills all the volatile materials are vaporized at the same time so one can use a column to condense the vapors. This system was invented by Milo J. Trumble in 1910. Ideally the vapors should be run into a true fractionating column but that wasn't done until about 1920. (4)

In the Trumble process crude oil was pumped through a run of pipe in a furnace - the pipe still - and to the top of a tower - the evaporator - where it cascaded over a series of umbrella shaped baffles. The vapors separating from the oil were collected in a central pipe. The hot residuum was passed through a heat exchanger where it heated fresh cold crude. In the original installation vapors were simply condensed. Later three or more fractions were collected. The vapors were partially condensed and redistilled in "dephlegmators" using the heat in the vapors from the evaporator. (2, 7)

Trumble's first patent was (U.S. 996 736) issued in July of 1911. Subsequent patents were issued in September of 1911 (U.S. 1,002,474) and August 1913 (U.S. 1,070,361). The first installation was in 1911 for producing fuel oil for the Santa Fe Railroad at Fellows, California. Another Trumble unit was built for the General Petroleum Company at Vernan, California in 1912. General Petroleum also acquired the Santa Fe plant. (2,7)

In 1913 Captain John Barneson, an ex-pipe line operator, who formed General Petroleum (8) joined with Trumble in the Trumble Refining Company

to exploit the Trumble patents. In 1914 this company was sold to Shell Oil Company for $1,000,000. Shell in turn formed the Simplex Refining Company to license Trumble patents and build Trumble units. (1)

Shell's first U. S. Trumble unit was built in 1915-16 at Martinez, California and significantly an experimental unit was also built at this refinery.(1) By the end of 1916 Shell had installed 11 Trumble units world wide. (4)

The advantages of the Trumble system were reduced operating cost, dramatic improvements in thermal efficiency, and somewhat reduced capital costs compared to conventional refineries. (16,7) A pipe still system can be scaled up to very large size although this advantage is not specifically mentioned in the literature of the time.

The Trumble system was unnecessarily complicated and could have been much simplified if the dephlegmators (Shell's second Martinez unit had six of them) had been replaced by bubble towers. Strangely Shell which had considerable knowledge of fractionating columns didn't make this advance. The construction company Badger and Sons did about 1920. Shell first replaced the dephlegmators with Heckman columns (a kind of bubble tower) about 1925, (4) but this was being treated as a general practice in the literature of the time. (3)

Little has been written about Trumble but he was described as an "unlettered practical man". (4) I don't know what his background was, nor what were his original connections with the oil industry, apparently he was not connected with an oil company however.

There were some special conditions which may have contributed to the invention and early development of the Trumble system in California. It was first used on heavy crudes which contained large amounts of water and couldn't be handled in shell stills. Initial units were in fuel oil refineries where distillates were of secondary importance. California refineries did not have access to low cost coal as did Eastern refineries. (1,4,5) None of the first installations was in an existing refinery and both General

Petroleum and Shell were entering the California refining industry.

1. Beaton, Kendall *Enterprise in Oil* Appleton-Century-Crofts New York 1957 Pp. 84-93

2. Bell, A.F.L Important Topping Plants of California, Trans. Am. Inst. Min. Eng. *52* 185-216 (1915)

3. Camp, H.W. Developments in Topping Plant Design, Oil and Gas J. *23* No. 41 116-17 (1925)

4. Forbes R. J. and O'Beirne, D.R. *Technical Development of the Royal Dutch/Shell*, E. J. Brill, Leiden 1957 Pp. 306-312

5. Miller, Walter and Osborn, H. G. History and Development of Some Important Phases of Petroleum Refining in the United States in Dunstan, A.E., Nash, A.W.; Brooks, B.T. and Tizard, Henry Eds *Science of Petroleum*, Oxford 1938 Vol. 11 Pp. 1466-69

6. Thompson, N. W. The Trumble Refining Process, J. Am. Soc. Tech. Eng. *39* 831-4 (1917)

7. Wadsworth, J. M. *Removal of the Lighter Hydrocarbons from Petroleum by Continuous Distillation*, U.S. Bureau of Mines Bulletin 162 GPO 191

8. White, T. T. *Formative Years in the Far West*, Appleton-Century-Crofts New York 1962 Pp. 261, 387

Solvent Extraction - Edeleanu Process

Aromatic hydrocarbons can be extracted from petroleum fractions by a solvent which dissolves aromatics but is immiscible with the more saturated hydrocarbons that make up the bulk of the petroleum. Tars, colored, bad smelling and unstable compounds usually accompany the aromatics leaving a purified oil. Alternatively one could extract the saturates and leave aromatics, tars, etc., behind. Currently several solvent extraction processes employing a variety of solvents are used to extract aromatics for chemical manufacture and to refine petroleum fractions especially lube oil stocks.

The first process to be developed used liquid sulfur dioxide was invented in 1907 by Lazar Edeleanu to refine Roumanian kerosene. Unless it is purified Roumanian kerosene is an inferior lamp oil because the aromatics in it discolor on standing, leave a crust on the wick and burn with a smoky flame. Distillation although a cheaper process will not separate materials which boil close together. (1,5)

Royal Dutch Shell began experimenting with the Edeleanu process in 1912 and first used it commercially in Europe in 1916. (5) The American company attempted to install it in the Martinez, California refinery in 1915 (Californian like Roumanian crudes are heavy and aromatic and produce a poor lamp oil.) but U.S. manufacturers could not produce satisfactory equipment. Shell did not have a unit on stream in California until 1927. (2) Apparently Standard of California, Associated Oil and Union Oil had units in operation to refine kerosene in 1926 (3.4) Shell and Tidewater began using Edeleanu extraction to refine lube oil stocks in 1928 (6) to remove aromatics and tars which lower the quality of lubricants.

Rights to the Edeleanu Process were owned by Allgemeine Gesellschaft fur Chemische Industrie. Edeleanu was director of the company.

1. Anonymous
Research and Practical Work
Perfected Treating Process
Nat. Pet. N. 18 ( ) 47 (1926)

2. Beaton, Kendall
Enterprise in Oil
Appleton-Century-Crofts NY
1957 P. 95.

3. Brooks, B.T.
Developments in American Petroleum
Refining
J. Inst. Pet. Tech. 12 385-92 (1926)

4. Edeleanu, Lazar
Liquid Sulfur Dioxide
Useful for Many Purposes
Nat. Pet. N. 28(9) 41-3 (1926)

5. Gerretson, F.C.
History of the Royal Dutch Shell
E.J. Brill Leiden 1957, Vol. IV p. 27-30

6. Plank, Rudolf
Edeleanu Sulfur Dioxide Process
Used in Treating Lubricating Oils
Nat. Pet. N. 20 (46) 63-71 (1928)

Petrochemicals

American production of organic chemicals began its rapid growth when World War I stopped imports from Germany then the dominant producer. At that time industrial chemists were converting aromatic hydrocarbons which were superabundantly supplied by distillation of coal. These hydrocarbons being more or less byproducts were quite cheap. Aliphatic chemicals like the lower alcohols were produced by fermentation of starch and sugar and by destructive distillation of wood. These are realatively expensive processes and demand for the products was small.

Chemists recognized the possibility of producing organic chemicals from petroleum but a refiner who wished to supply them would have had problems in defining a business opportunity. He could supply aromatics but competition was strong and prices low. Aliphatics could be produced from petroleum especially off-gases from cracking but the demand was miniscule by petroleum standards. Most refiners ignored chemicals. An exception was Standard of New Jersey. In 1920 they acquired rights to an olefin hydration process invented by Carelton Ellis. Shortly thereafter they were producing isopropyl alcohol and had an organization to market it. (Prohibition was in effect which made a substitute for ethyl alcohol attractive to consumers.) By the end of the decade they were producing other lower alcohols and their derivatives.

Jersey became good industrial chemists. They developed an improved process (invented by C.A. Krause) for making tetraethyl lead and in 1924 joined General Motors in organizing Ethyl Gasoline Corp. They produced lube oil additives (Pour point depressants) in 1928. Just previous to World War II

they began investigating butadiene rubber which they had licensed from I.G. Farben. They were preparing to introduce butadiene/acrylonitrile rubber when the war broke out, and switched to producing butadiene/styrene rubbe instead. They developed and introduced butyl rubber in 1941. They began producing ethylene(for tetraethyl lead) by propane cracking in 1939 and by gas oil cracking (with butadiene as a co-product) in 1941.(1)

Shell was the next refiner to enter chemicals. They formed Shell Chemical Company in 1929 for the purpose of developing uses for hydrocarbon gases. Their first venture was production of ammonia which began in 1931. Their work on light gases contributed to refining and they also developed processes for producing allyl and methallyl chloride. This work led ultimately to synthetic glycerine and expoxide resins.(2)

In 1935 Standard of Indiana arranged to supply Union Carbide and Carbon with olefinic off-gases from their Whiting refinery. Previously Carbide, the most aggressive petrochemical company, had been producing olefins by cracking natural gas.(3)

1. Haynes, Williams — American Chemical Industry D. Van Nostrand New York 1949 Volume VI Pp. 398-403

2. Ibid — Volume VI Pp. 380-385

3. Ibid — Volume V P. 210

Hydrogenation

Hydrogenation was introduced to the petroleum industry of the United States by Standard Oil Company of New Jersey. This innovation resulted from joint research by Standard and I.G. Farbenindustrie owner of the rights to the Bergius process which had been developed to hydrogenate coal in Germany during thewar. Adopting the process to petroleum was supposed to have been one of the most expensive development projects undertaken up to that time (1,5,6). The innovation was before its time because of the need to manufacture hydrogen and because the process needed higher pressures than could be handled conveniently in large equipment at that time. When byproduct hydrogen from catalytic reforming became available in the fifties hydrogenation became widely used especially for desulfurizing petroleum products.

In 1925 I.G. Farben approached Standard to undertake joint work on hydrogenating petroleum. An agreement was signed in 1927 and by 1928 a pilot plant was operating at the Baton Rouge refinery of Standard of Louisiana. Three commercial units were under construction or in operation by the end of 1929. (1,4)

This development anticipated all the major application of hydrogenation to refining but initial emphasis was on the conversion of heavy fuel oil, which is only now becoming commercially significant. At that time the heavy demand for gasoline resulted in overproduction and very low prices for heavy fuel oil. Hydrogenation was expected to reduce the yield of fuel oil and to conserve crude. (1,2,8)

Standard and I.G. Farben formed a joint compnay to license the process and invited other refiners to become stockholders. By 1932, refiners who operated over half the domestic refining capacity had become stockholders. It was considered to be a model of rational commercial development. (3,7)

1.	Anonymous	New Process to Yield 100 Per Cent Gasoline From A Barrell of Oil Oil and Gas J. 28 (6) 44,56 (1929)
2.	Anonymous	Refinery Revolution Oil and Gas J. 28 (6) 46 (1929)
3.	Anonymous	Perfect Permanent Organization for Hydro Patents Company Oil and Gas J. 31 (11) 28,38 (1932)
4.	Burrell, G.A.	Hydrogenation Commercially Applied Oil and Gas J. 28 (21) 134-6,245 (1929)
5.	Haslam, R.T. and Russell, R.D.	Hydrogenation of Petroleum Ind. Eng. Chem. 22 1030-7 (1930)
6.	Haslam, R.T. and Russell, R.D.	Some Aspects of Hydrogenation in Oil Refining Bul. Am. Pet. Inst. 11 (3) 80-9 (1930)
7.	Mockler, A.E.	To License Hydrogenation Process Oil and Gas J. 28 (3) 42,74 (1929)
8.	Truesdell, Paul	Hydrogenation to Be Used First in Conversion of Heavy Fuel Oil Nat. Pet. N. 21 (28) 27-9 (1929)

Additives for Lubricants

Three interrelated factors have tended to inhibit petroleum companies from producing seminal innovations in lubricants. First, lubricants are used to lubricate machines and machine design determines the need for new lubricants. Even if it could be done it would hardly be worthwhile to develop some new lubricant without having a specific application in mind.

Secondly, the phenomena relevant to lubrication are so frightfully complex that even minor advances are difficult to make and require extensive peformance testing since bench scale testing is usually good for little more than preliminary screening. And just to close the vicious circle machine design is constrained by the properties of available lubricants. It is largely an economic constraint because mechanical engineers can often "design out" the need for special lubricants although it may be costly to do so. Lubricant formulators claim that mechanical engineers often use lubricants the way architects use ivy - to hide mistakes.

Finally petroleum companies have had little incentive to innovate, because they enjoyed, at least until recently a strong position. Some of them have been supplying technical service to bearing manufacturing, machine builders and lubricant customers since the last part of the nineteenth century. These suppliers knew (and know) more about lubricants and lubrication than anyone else. Petroleum products dominate lubrication. They are cheap of course, but perhaps more important petroleum lubricants and modern machinery grew up together & machine design has evolved around properties of petroleum lubricants in many subtle ways. Finding a substitute would be difficult. The fact that petroleum companies had access to many base stocks put them in the best position to change formulations and evaluate the consequences. Naturally they were secretive about their findings.

Machine builders have incentive to innovate to the extent they are constrained by lubricant performance. They can't do much though without

developing considerable in-house expertise in lubrication. General Motors made this step and in 1931 informed the petroleum industry of what they had done. In that year they presented a paper dealing with lubrication under extreme presure at the annual meeting of the American Petroleum Institute. (5)

The paper said that the petroleum lubricants then available failed under extreme pressure and this inhibited advances in automobile design. General Motors contemplated introducing automobiles which required high pressure lubricants but would not do so until suitable lubricants were widely available. The technical sections of the paper described a machine for testing high pressure lubes and showed that addition of certain compounds to petroleum oils led to adequate lubricant performance. The improved performance was ascribed to formation of tough self-healing films on the metal surfaces.

The following year they presented a second paper which showed that their test was related to actual performance. It also described ways to obtain adequate performance without using specially formulated lubricants. (6)

These two papers publicized the idea of using added chemicals to compensate for deficiencies in petroleum oils coupled with the use of relatively simple screening tests. This innovation lessened the advantages accruing to experience in formulating lubricants. They also promised a large market for extreme pressure lubricants and stimulated their development.

There was an implied threat to lubricant suppliers that if they did not produce satisfactory products General Motors would. The papers demonstrated technical capability and General Motors also had wide marketing outlets. One wonders whether another company could have had as much impact.

During the next decade there was a tremendous burst of activity in developing additives.(8) Leading petroleum companies were Standard of New Jersey, Standard of Indiana, Socony Vacuum and Texaco. (3,7)

General Motors worked its magic again in 1940. They described the need for a heavy duty crankcase oil for automobiles which required a number of additives.(4) Very soon thereafter Jersey announced their Essolube HD engine oil. (2)

Some oil companies notably Standard of New Jersey and Standard of California produce additives for sale. The company which developed this business to the greatest extent is Lubrizol. It was founded in 1928 as a compounder of specialty lubricants but withdrew from this business in 1942. (1)

1. Anonymous — Barrons 45 24 (Dec. 6, 1965)

2. Anonymous — Essolube HD New Type of Engine Lubricant Chem. Eng. N. 19 282,4 (1941)

3. Byers, J. H. — The Patent Structure on Pour Point Inhibitors Nat. Pet. N. 28 (49) 83-89 (1936)
Patents Show Trend In Extreme Pressure Lube Technology Ibid 28 (51) 79-84 (1936)
Patent Literature in Refining Technology Oiliness Agents Ibid 29 R3-R8 (1937)
Organic Amines, Hydroxy Compounds Lead Among Antioxidants for Lubricants Ibid 29 (6) 67-70 (1937)

4. Mougey, H. C. — Heavy Duty Motor Oils Proc. Am. Pet. Inst. 21 (3) 63-75 (1940)

5. Mougey, H. C. and Almen, J. O. — Extreme Pressure Lubricants Ibid 12 (3) 76-81 (1931)

6. Mougey, H. C. and Wolf, H. R. — Extreme Pressure Lubricants, Correlation of Service Data with Laboratory Testing Methods Ibid 13 (3) (1932)

7. VanVoorhis, M. G. 200 Lubricant Additive Patents Issued in 1938 and 1939
Nat. Pet. N. 32 R64-R77 (1940)

8. Wright, W. A. Survey of Past and Present Trends in Lubricating Oil Additives
Ibid 37 R34-R38 (1945)

Polymerization

Gasolines must have appreciable volatility at ambient temperatures and are therefore formulated with some gaseous and low-boiling liquid hydrocarbons. Refiners often used the liquids condensed from natural gas to "pressurize" gasoline but with advent of thermal reforming, normal refinery operations produced much larger quantities of gases than could be used in gasoline. The excess was burned as refinery fuel which was wasteful. Of course this depressed the demand for natural gasoline which was already suffering because it has low octane rating.

In 1935, Pure Oil Company and Phillips Petroleum Company announced thermal processes and Universal Oil Products Company announced a catalytic process for polymerizing olefinic gases to liquid products. Suitable feeds were olefin containing off-gases from thermal cracking and reforming units. (3,5,6) Polymerization was immediately considered to be an important advance.(2)

Pure Oil claimed to have the first process and their first unit went on stream in a Pure refinery sometime before 1935. It was called the Alco process because it was licensed and built throught the American Locomotive Company.(7,8)

Phillips Petroleum formed the Polymer Process Company (Polyco) to exploit their process and designated M. W. Kellogg as licensing agent. The Texas Company, Standard of Indiana and Standard of New Jersey all of which held patents on polymerization were part owners of the new company. The first Polyco unit went on stream at the Phillips refinery in Borger, Texas in 1933.(1,4)

Univeral Oil Products invented a process using solid phosphoric acid catalyst which made thermal processes obsolete. The first UOP unit went on stream at Shell's East Chicago refinery in 1935.

By 1937 Atlantic and Humble had licensed the Polyco process, Atlas Pipe Line and Tidewater had licensed the Alco process. Six companies (Pan American, Shamrock, Shell, Sinclair, Texas and Wilshire) had licensed the UOP process.(8) Both thermal processes are now obsolete but the UOP catalytic process is still being used.

Universal Oil Products developed a process using solid phosphoric acid catalyst which was [illegible]. The first unit went on stream at Shell [illegible] 1935.

By 1937 Atlantic [illegible] the [illegible] process, [illegible] Pipe Line and [illegible] (Pan American [illegible]) and [illegible] the UOP process [illegible] and UOP catalytic process [illegible]

1.	Anonymous	Phillips Forms Company to Handle Their New Polymerization Process Oil and Gas J. 34 (16) 26 (1935)
2.	Anonymous	Polymerization Refiner 14 (10) 455-6 (1935)
3.	Cooke, M.B. Swanson, H.R. and Wagner, C.R.	Thermal Conversion of Hydrocarbon Gases Proc. Am. Pet. Inst. 16 (111) 129-129 (1935)
4.	Foster, A.L.	Imposing Patent Structure Already Developed to Cover Polymerization Nat. Pet. News 27 (47) 45 (1935)
5.	Ipatieff, V.N. Corson, B.B. Egloff, Gustav	Polymerization, A New Source of Gasoline Ind. Eng. Chem. 27 1077-81 (1935)
6.	Keith, P.D. and Ward, T.J.	Thermal Conversion of Hydrocarbon Gases. Proc. Am. Pet. Inst. 16 (111) 129-39 (1935)
7.	Wagner, C. R.	Pure Oil Outlines Position Regarding Use of Polymerization Oil and Gas J. 34 (29) 41 (1935)
8.	Willson, C.V.	Manufacture of Gasoline from Gases Spreading Oil and Gas J. 35 (40) 21 (1937)

Alkylation

Alkylation is the process of reacting an olefin with isobutane in the presence of an acid catalyst to form highly branched paraffins which have high octane ratings. The process was developed prior to World War II to produce high octane aviation gasoline. Performance of piston driven aircraft - range, rate of climb, etc. - is very sensitive to octane number of the gasoline used and by the late thirties refiners were hard pressed to produce high octane gasoline which met other specifications for aviation fuels. Alkylation was an advance because it used reactive olefins more efficiently than polymerization, by using a paraffin which would not polymerize. Then too alkylate unlike polymerizate does not need to be hydrogenated. The use in aviation fuel has become less important but alkylate is used in automotive fuels now that automobile engines require 90+ octane gasoline.

In 1937, Gustav Egloff of Universal Oil Products discussed several ways including alkylation which could in principle produce high octane gasoline and described the large body of scientific work that had been done.(6) At the annual meeting of the American Chemical Society in September 1938, personnel from Anglo-Iranian Oil described alkylation with sulfuric acid.(5) Early in 1939 C.F. Braun Co. announced they were offering licenses for sulfuric acid alkylation and were building several plants.(2)

The process was covered by patents owned by Anglo-Iranian Oil, Humble Oil and Refining, Shell Development Co., Standard Oil Development Co., and Texaco Development Co.* These companies had been working independently on closely similar processes and pooled their efforts in joint development. M. W. Kellogg and UOP contributed to later development. (2,7,8)

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By late 1939 six alkylation units were on stream; Shell refineries had two, Humble, Texaco, Standard of New Jersey and Anglo-Iranian each had one. Eight more were being built.(7) Royalty on the process was 43¢/barrel of alkylate in 1941 and was to fall to 15¢/barrel on alkylate used by the government by 1943.(8)

Phillips Petroleum developed thermal alkylation of ethylene about the same time as sulfuric acid alkylation was being developed; the first unit went on stream in 1940. The process was never widely used even though the early sulfuric acid process could not alkylate ethylene and propylene efficiently.(1,9) Phillips was one of the first companies to use anhydrous hydrogen fluroide as an alklation catalyst.(4) This process which UOP announced in 1942 could alkylate ethylene and propylene. (3)

*The chemistry of alkylation is closely realted to polymerization which was a "hot" area in the mid-thirties which may explain why several companies had pertinent patents. But why did they not exploit them? One suspects that the patents were obtained for strategic reasons - to have bargaining counters in the event of successful innovation. elsewhere.

1. Alden, R.C. — Neohexane Plant Operating at Record High Pressures. Nat. Pet. N.32 R234-40 (1940)

2. Anonymous — Alkylation Process to be Offered for License Nat. Pet. N.31 (18) 17 (1939)

3. Anonymous — See Supply of Aviation Gasoline Enlarged Through Hydrofluoric Acid Alkylation Nat. Pet. N.34 R131-2 (1942)

4. Anonymous — Special Catalyst Handling Equipment Provided in HF Alkylation Plant Nat. Pet. N.35 243-4 (1943)

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5. Birch, S.F., Dunstan, A.E., Fidler, F.A., Pim, F.B. and Tart, T. — High Octane Fuel Production (Abstract) Nat. Pet. N.30 R454 (1938) High Octane Isoparaffinic Fuel, Ind. Eng. Chem. 31 884-91 (1939) Ibid. 31 1079-83 (1939)

6. Egloff, Gustav — Synthetic Products from Petroleum. J. Inst. Pet. Tech. 23 645-668 (1937)

7. McAllister, S.H. — High Octane Aviation Fuel by Sulfuric Acid Alkylation Process Trans. Am. Pet. Inst. 20 (3) 89-100 (1939)

8. Murphy, G.B. — Alkylation, Oil Industry's Contribution to War Requirements of Aviation Fuel Nat. Pet. N.34 R4 (1942)

9. Oberfeld, GG and Frey — Thermal Alkylation and Neohexane. Trans. Am. Pet. Inst. 20 (3) 78-88 (1939)

Isomerization

The paraffinic hydrocarbons of petroleum which are predominately straight chain compounds can be converted in part to branched chain isomers by a strongly acidic catalyst like anhydrous aluminum chloride. This conversion is called isomerization.

While isomerization can greatly increase octane ratings of paraffinic naphthas, the process is used almost exclusively to convert normal butane to isobutane for alkylation. Heavier hydrocarbons tend to crack and form sludge which leads to low yields and high catalyst consumption.

The first butane isomerization process was developed by Shell Development Company and their first unit apparently went on stream in 1941.(1,2) Immediately after Shell's process was announced both Standard Oil of Indiana and Universal Oil Products announced isomerization processes which like Shell's used aluminum chloride catalyst but which were to operate on debutanized light naphtha. Neither company had a commercial unit operating.(4)

Butane isomerization was apparently widely used in conjunction with alkylation by 1943, while isomerization of higher paraffin was little used.(3)

1. Anonymous	Shell Isomerization Process for Producing Isobutane Nat. Pet. N. 33 P 403-6 (1941)
2. Coulthurst, L.J.	Isomerization of Feed Stocks Charged to Alkylatin Unit Oil and Gas J. 39 (37) 37 (1941)

3. Foster, A.L.
Isomerization a Useful But as Yet Little Used Tool for the Refiner
Oil and Gas. J. 41 (42) 66-72 (1943)
Facts About Possibilities of Alkylation and Isomerization Processes
Ibid 41 (49) 77-88 (1943)

4. Murphy, G. B.
Catalytic Isomerization Will Put Nation Far in Lead in Aviation Gasoline Supply
Nat. Pet. N. 33 R401-3 (1941)

Catalytic Reforming

Straight run gasolines i.e. gasoline distilled without further processing, have low octane ratings and knock badly in automobile engines. During the twenties it was customary to blend straight run with cracked gasolines which have higher ratings. By the early thirties the compression ratio of automobiles was so high that straight run gasolines couldn't be used at all.(3) The solution was to reform thermally i.e. pyrolize straight run naphthas, which converted them in part to olefins and aromatics which have high octane ratings. Thermal refining was generally considered to be just a special case of cracking. It evolved from vapor phase cracking which was used by Gulf Oil and General Petroleum to produce aromatics especially toluene during World War I (2).

Thermal reforming produces large amounts of gas and tars so that gasoline yields were 70% or so of the feed. The light gases could be polymerized to high octane gasoline or used as chemical feed stocks.(10)

By the late thirties thermal reforming was very widely used but pertroleum technologists saw the need for (and forecast) the development of a catalytic reforming process.(4,5) The first such process was developed by Houdry Process Corp. and installed by Sun Oil in 1939. It was essentially the Houdry fixed-bed catalytic cracking process using a hydrated silica catalyst.(7)

The next process to be perfected was Hydroforming which was developed jointly by M.W. Kellogg, Standard Oil Development Company and Standard Oil of Indiana. The first unit went on stream in 1940 at Pan American's Texas

City refinery. The catalyst was supported molybdenum oxide which was licensed from Standard Catalytic Company, a subsidiary of Standard Oil of New Jersey (9). When operating on a very narrow cut, the process efficiently converted straight chain hydrocarbons to aromatics. It was less successful with gasoline and in addition was a complicated process requiring high capital investment.(5,8)

Writing in 1948, Sachanen suggested that the then available catalytic reforming processes did not offer enough advantage to replace thermal reforming.(8)

In 1949 Dr. Vladimir Haensel at Universal Oil Products invented a process using supported platinum catalysts. The first unit went on stream in October 1949 at the Old Dutch Refining Company plant in Muskegon, Michigan. The process called platforming was capable of producing 100+ octane gasoline.(6) By 1951 UOP had issued 21 licenses and six units had been built.(1)

Four catalytic reforming processes were announced in 1951, Catforming (Atlantic Oil), Houdriforming (Houdry), TCR (Socony Vacuum) and Fluid Hydroforming (M.W. Kellogg).(1) Of these, only Catforming used a platinum catalyst. The first unit went on stream in 1952 at McBride Oil and Gas.

1.	Anonymous	Many New Catalytic Reforming Processes Now Available Pet. Ref. <u>30</u> No. 9 183-193 (1951)
2.	Brooks, B.T.	A Brief History of Petroleum Cracking. In Dunstan, W.E., Nash, A.W., Brooks, B.T. and Tizard, Henry, (Eds.) <u>Science of Petroleum</u>, Oxford 1938 Vol.III Pp.2078-86
3.	Foster, A.L.	From Pot Still to Cat Still Pet. Eng. <u>26</u> No. 10 C7-20 (1954)
4.	Howes, D. A.	Catalytic Reforming in <u>Science of Petroleum</u> Vol. III Pp. 2119-22
5.	Ipatief, V.N.	The Problem of Rational Utilization of Petroleum and Petroleum Distillates Proc. Am. Pet. Inst. <u>17</u> (111) 13-16 (1936)
6.	Kastens, M.L. and Sutherland, Robert	Platinum Reforming of Gasoline Ind. Eng. Chem. <u>42</u> 582-593 (1950)
7.	Peterkin, A.G. Bates, J.R. and Brown, H. P.	Catalytic Reforming for the Production of Aviation Gasoline Proc. Am. Pet. Inst. <u>20</u> (111) 101-9 (1939)
8.	Sachanen, A. N.	<u>Conversion of Petroleum</u> 2nd Ed. Reinhold New York 1948 Pp. 344-5
9.	Smith, D.J. and Moore, L. [illegible]	First Commercial Hydroforming Plant Now in Operation Oil and Gas J. <u>3[illegible]</u> No. [illegible] 87-[illegible] (1941)
10.	[illegible]	Vapor Phase Cracking in <u>Science of Petroleum</u> Vol. III Pp. [illegible]