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THE CONTRIBUTION OF CHROMATOGRAPHY TO THE PETROCHEMICAL INDUSTRY

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Even today the size of a petroleum-refinery is estimated by its crude oil distillation capacity, despite the fact that around 1948 the second phase in the development of refineries was almost completed. Thermal cracking, catalytic cracking, isomerization, polymerization and alkylation constituted at that time the major operations of every large refinery.

In the first and second phases of development the modern methods of analysis played practically no role in the refineries, although the mass spectrometer came into general use for the analysis of the cracking gases and this introduced the third phase in refinery development, the petrochemical industry. It is in this development that the modern methods of analysis and especially gas chromatography appeared to be indispensable. The interplay between classical refinery and modern petrochemistry is illustrated among other things by the dewaxing of lubricating oil, the production of paraffin wax, the thermal cracking of wax, quality improvement of wax, production of highly pure straight chain olefins and their applications.

At the end of World War II almost the total refining capacity of the occupied part of Europe was destroyed. When rebuilding the refineries a number of important U.S.A. developments, like for instance catalytic cracking, could be taken into account. It was in 1948 that the large Shell Refinery at Rotterdam could be put into full operation.
It would not be proper to pretend that the modern methods of instrumental analysis, more in particular chromatography, up till 1948 had played a role of any significance in the research and developed of the petroleum processes. The conversion of a classical refinery into a modern refinery largely took place in the years 1930-1950. During this period the refineries were extended with installations for catalytic cracking, polymerization (or rather condensation) of \( \text{C}_3 \) and \( \text{C}_4 \) into high octane engine fuel, alkylation isomerization, reforming and later the so called platforming or power forming. All these processes were developed with the aid of classical methods of analysis.

One important exception is worth mentioning. The pre war refinery laboratories had an alien attitude against new instruments. This attitude changed drastically when the Mass Spectrometer was introduced into the refinery, even before it was seriously considered for the research laboratories.

The introduction of the M.S. was made necessary in order to obtain a more reliable and more rapid method of analysis for the complex mixture of the gases obtained on catalytic cracking. The first mass spectrometers in a refinery were equipped with an extremely simple manually operated computer for matrix inversion enabling the simultaneous analysis of 12 components in the cracking gases.

Another important change in mentality should be mentioned. During the pre war period the use of petroleum as base material for the chemical industry was often discussed but had hardly been given a serious consideration. Again however with a few exceptions from which one will be discussed in some detail because it exemplifies the development of the petrochemical industry as an integral part of the refinery.

Lubrication oil has always been an important product of any refinery. As compared to other petroleum fractions it is very expensive and usually the range of lub oils have to fulfill a number of stringent specifications. One important specification is the so called pour point a measure of the n paraffin content.
Most crudes contain a large proportion of paraffins over the whole boiling range. As a consequence luboils when cooled below a certain temperature arrive at a structure where the oil suddenly stops to flow.

Since the oil, as a rule, must operate under extreme conditions of temperature, even as low as $-60^\circ C$ it is necessary to remove the major portion of the n paraffins. This is done in one of the "dewaxing" processes which require cooling to low temperature and filtering off the crystalline part. It is this step that is the most expensive. Reduction of cost would be possible if a proper outlet could be found for the byproduct "WAX" or paraffinwax, slack wax etc.

Among the many cost reducing outlets the so called thermal steam cracking of paraffinwax appeared to become rewarding. Wax and steam are passed through long hot tubes ($560^\circ C$ and more) and about 20% is converted into mainly $\alpha$-olefins. The fraction $C_5^c - C_{18}^c$ about is distilled off and the unconverted wax is recycled. The wax cracker olefins appeared among other things to be an excellent base material for detergents by treating them with sulfuric acid and sodalime. The Shell Marketing Department in London decided to market the product, The Subdivision Techn. Products (T.P) gave it the name T.P. ol or Teepol. It is here that the oil industry enters the "soap" market and meets another giant industry namely "Unilever". Results is a severe competition and from this moment nearly all major chemical industries discover the important market of the synthetic detergents and in relatively short time the pro's and contra's of the new products tend to be recognized. A very important factor appears to be the "biodegradibility" which appears to depend upon the absence of branched chains.

If we now revert to the dewaxing process with paraffins wax as byproduct it was observed that it contains only between 50-80% of n paraffins the remainder being branched and even n aftenes with a relatively long side chain. New specifications for the wax are required and soon instead of a byproduct wax must be produced as base material for a range of chemical products.
Soap research soon showed that a superior and competitive product could be obtained when only the \( C_{14}^{=} - C_{18}^{=} \) fraction was processed and when the wax contained over 95% of straight chain paraffins.

About 1952 the situation has developed as follows. The cracked destillate \( C_5^{=} - C_{18}^{=} \) is split into three main portions:

\[
C_6^{=} - C_8^{=} , \quad C_9^{=} - C_{13}^{=} \quad \text{and} \quad C_{14}^{=} - C_{18}^{=}. 
\]

The \( C_6^{=} - C_8^{=} \) fraction is sold to ICI where the material is converted into primary alcohols by means of the OXO process. In its turn the alcohols are esterified to produce all sorts of plasticizers. The \( C_9^{=} - C_{13}^{=} \) is used for alkylation with aromatics and appears to be an attractive improver of lub oil and lub oil dope. The \( C_{14}^{=} - C_{18}^{=} \) fraction is used for the manufacture of detergents.

We have arrived at a situation that through long lasting contracts with other giant industries some of the processes in a refinery are conducted to fulfill specifications (set up by others) of what earlier was a byproduct. The differences between main- and byproduct tend to disappear. Wax is produced not only for refining of lub oil but as a main product.

It will soon appear that the extending cooperation between giant industries calls for careful consideration of the methods of analysis. It also appeared that the oil industry had to go through a period of teething troubles. One important example will be mentioned.

The conversion of olefins into primary alcohols takes place through the OXO process, the simultaneous addition of CO and \( H_2 \) to an olefine double bond to form an aldehyde which in a subsequent step is then hydrogenated to produce the alcohol.

\[
\text{H} \quad \text{---C-C=C=+CO+H}_2 \rightarrow \text{---C-C-C-C-COH+CH}_2\text{OH} \quad \text{H} \\
\text{cobalt catalyst} \quad \text{---C-C-C-C} 
\]

The reaction is clean with a yield of more than 90% and some 10% condensation products as a byproduct.
Boiling point of olefins and alcohols

| C₅= | C₆OH | 157.2 |
| C₆= | C₇OH | 176   |
| C₇= | C₈OH | 195   |
| C₈= | C₉OH | 213   | about 100°C |
| C₉= | C₁₀OH |

Through the OXO reaction an alcohol is formed with one C atom more resulting in a boiling point increase of

From this it follows that only a relatively narrow olefin range can be processed in order to make separation of inconverted material from the alcohol possible.

An important specification, therefore, is the content of "heavy ends", the distillation residue C₈⁺.

It should be known that any product leaving the refinery is subjected to severe specification tests. So after a fair number of shippings from Shell-Rotterdam to ICI-Billingham all at once a large cargo was refused because the "heavy ends" were too far above specification. Such events tend to penetrate P.D.Q. (Pretty Damned Quick) to the top management, in this case the very Shell Board of Directors in the Hague Head Quarters. These gentlemen then take recourse to their research institutes and so the problem arrived on my desk.

This occurred a few after I had met A.J.P. Martin, who had just published with Tony James their first paper on G.L.C. The cooperation of ICI Billingham should be gratefully acknowledged here. As a result the Shell research Laboratories Amsterdam happened to be the first outside U.K. with a homebuilt Gas Chromatograph.

From the Gas Chromatogram (Dec. 1952) of a sample of the cargo refused by ICI it is immediately clear that we have to do with a main product C₆=, C₇=, C₈= contaminated with about equal amounts of the homologues C₉=, C₁₀=, C₁₁= etc. It is obvious that
this phenomenon cannot be ascribed to improper distillation, in which case there would be a gradual decrease in $C_9^-$, $C_{10}^-$, $C_{11}^-$ etc.

The solution was relatively simple. Wax cracking was done at two refineries, Shell Rotterdam and Shell Stanlow and any excess cracked distillate was shipped from one refinery to another. Two telexes confirmed that the ship used for the ICI cargo, was previously used to ship total $C_5-C_{18}$ cracked distillate from Stanlow to Rotterdam. According to Petroleum standards the ship had been properly cleaned. Obviously according to the standards of the chemical industry a better cleaning procedure is required. To make a long story short, 48 hours after receipt of the sample we could inform H.Q. the name of the ship and its previous cargo's. This event immediately paved the way for GC. But luck seldom comes alone. It was only one week later that Shell Research Lab Amsterdam were asked to find out what anti icing dope was used in a competitor product. Again I will make the story short. The chromatogram of the gasoline in question taken on a polar column showed a marked peak retained more than any of the H.C. It immediately could be identified as Isopropanol.

H.Q. had given Amsterdam 6 months for the solution of the problem and the answer arrived within 24 hours. Result: Immediate visit of the president of Shell to the Amsterdam Laboratories, and important for every research institute a generous research budget.

In the above it has been told how gas-liquid chromatography came to the oil industry. It also has been mentioned how from the oil industry the petrochemical industry was born and finally how giant industries like ICI, Unilever and Shell started to cooperate in many fields. These developments changed the climate in the analytical laboratories and the interest in modern instrumental methods of analysis grew rapidly. Where as formerly samples from the plant were brought to the laboratories, we gradually see analytical instruments move into the plant. This had a tremendous effect upon the plant operators since now they could see the quality of the product they made which resulted in more steady operation of the installations and improved quality at lower production costs.
It is remarkable that it took a few years before GLC got a firm footing in the U.S.A. This changed rapidly when Perkin Elmer marketed about 1955 a simple, reliable and robust instrument, a real workhorse. In many laboratories one can see these 18 year old instruments still in operation.

In the period of 1955-1960 the registered number of instrument firms, manufacturing G.L.C. instruments grew to over 120. In the 5 years following only 20 survived, most of these were bought by firms like Perkin Elmer, Beckman, Hewlett Packard and later Varian.

Also in this period G.L.C. appears to have developed into the largest single analytical technique and today it is impossible to see how most of today's petrochemicals could have developed or could be produced without the aid of G.L.C.

Sometimes the borderline between oil industry and Petrochemical industry is somewhat diffuse. In the years after the war Universal Oil Products, directed by Vladimir Haenzel, developed the very important Platforming Process. As we know it is a reforming process with a bifunctional catalyst Pt on SiO₂, operating under mild (20-50 atm) H₂ pressure and e.g. enabling to convert in one pass cyclopentane derivatives in aromatics. The process was intended to produce high octane components for aviation fuels. Soon however it become also an important process for pure or nearly pure aromatics.

For instance the rapidly growing production of Nylon caused a world shortage for benzene (C₆H₆). This raw material occurs only in traces in crude oil and its main source was from coal tar.

To day it is obtained by subjected the C₆ fraction of light gasoline to the platforming process yielding a fairly pure benzene. The benzene is then hydrogenated to cyclohexane which is then oxidized to adipic acid. The products must have a high purity, because impuritis tend to affect the colour of the Nylon fibers. It should be observed that the platforming process here acts as a sort of purification process.
Cyclohexane (impure) — Benzene + impurities the impurities in benzene can be removed by distillation and the pure benzene is converted into pure cyclohexane. G.L.C. with an apolar column will detect traces of benzene in cyclohexane. When using a polar column G.L.C. will detect traces of cyclohexane in benzene.

A second example may be taken form the production of paraxylene. Along with Nylon the fibres derived from paraxylene (Terylene etc.) have become of extreme impotence. The normal way of obtaining the xylenes is by extractive distillation from a 130-145°C fraction preferably rich in aromatics. If one considers that the boiling point of toluene is 110°C and that of ethylbenzene 136°C it is obvious that by careful distillation the fraction 115-128°C is virtually free of aromatics and contains almost exclusively C-saturates.

If this fraction is subjected to the platform process xylenes are formed boiling above 140°C and a simple but good distillation will yield the desired xylenes. Since extractive distillation is about 15 times as expensive distillations, it follows that the above process results in a tremendous cost saving. Unnecessary to mention the important role of G.L.C. in processing and quality control.

With these few historical examples I hope to have shown the contribution of chromatography to the petrochemical industry. It
would be easy to add numerous examples, but at an anniversary it may be as well to move from the past to present.

The present:

Gas Liquid Chromatography has shown to be a method that from the theory point of view can be treated with the aid of fairly simplified models. The fundamental work by Glueckauf, van Deemter and Gidding should be mentioned. From simplified as well as from more involved theories a much better understanding of the mass transfer phenomena playing a role in chromatographic processes resulted. In its turn the knowledge gained has led with great success to the classic methods of column chromatography and to day we can be witness of the renaissance of liquid Chromatography in the form of High Performance Liquid Chromatography pioneered by among others Kirkland and Huber.

GLC in combination with mass spectrometry has, in spite of the high capital investment required, grown to the perhaps most powerful analytical tool, yielding pro unit time an abundancy of information. I recall that about 1960 it was believed that GLC would almost completely replace MS. It appeared however, on the contrary, to have stimulated research in MS instrumentation.

Not all the information produced by GLC-MS is equally relevant or some may show to be completely irrelevant. Anyhow the information produced by the combination of these two instruments comes to us in a heavily coded form and the appropriate decoding even to day constitutes a difficult problem. In the GC-MS combination the use of computers is a necessity, they can be used on line or off line from small electronic integrators, dedicated computers, to data crushers. At the Max Planck Institute in Mühlheim the complete set of GC-MS computer costs over one million dollar and the GC instrument only 1% of the total cost. Nevertheless the other 99% of the investment would be almost useless without the GC.

An interesting question comes up here: what size must an industry, a research institute, a medical institute etc. have, in
order to be able to run such costly equipment. It appears not only to require a high capital investment, it also needs a fairly large and skilled staff to run it; the running cost + depreciation must be estimated at least to be 25% of the investment per year. The lifetime? An optimistic estimate will be eight years. Who can afford it? What can be the return on investment.

The Future: It is easier to say a few words about what will be needed in the near future than to be speculative about what we may expect.

HPLC mill for some time to came develop further but unfortunately at a slow rate. The main reason being the lack of a series of suitable detection systems. It accurs to me that a high price for a real good detector is not prohibitive, compared for instance the MS in GC.

Huber’s estimate that by 1980 the number of liquid chromatographs may be on a par with the number of gas chromatographs can be criticized and may be ascribed to the great interest from the side of the pharmaceutical industries. However large an interest these industries represent, they must be considered small as compared to the oil and the Petrochemical Industry, and in these fields the demand for Gas Chromatographs will continue to dominate.

In spite of the growing interest in capillary columns the packed columns are expected to cover about 90% of the total demand. This is regretable.

There is a great need to make the powerful HC-MS combination available at a much lower cost. The development of MS instruments in the past decade has been geared to the requirements of packed columns. Now that capillary columns can easily be made by any skilled operator, it is hoped that development in MS will follow. It is our experience that this will reduce the total investment considerably.

I now would like to conclude with the following: GC, related and ancillary techniques have opened wide avenues for the whole chemical industry. They have enabled to make new product, to im-
prove products and to make them more economically. The forthcoming
time will put a heavy demand upon these techniques. The emphasis
is going to be on improved quality but above all we must learn to
produce our chemicals in a much cleaner way. We may be optimistic
in assuming that the modern analytical techniques will take an ac-
tive part in this aspect.

A last and more personal observation:

Man is a very complex chemical reactor, chemical, biochemical,
enzymatic reactions play an important but largely unknown role.

The analytical techniques could develop so will for economic
reasons. Now they are there they can be used to the benefit of
human life, to prevent illnesses to help in diagnosis and medical
treatment, not in the first place to prolong human life, but to
avoid unnecessary suffering.

Резюме

В первые два периода развития нефтеперерабатывающих устано-
вок практически не имели значения современные аналитические мето-
ды, хотя при анализе газов крекинга использование весового спек-
трометра было общепринято. Это уже третий период развития нефтепе-
рерабатывающих установок, причем это и есть основа появления неф-
технической промышленности. В этом периоде развития стали необхо-
димыми методы современного, особенно газохроматографического ана-
лиза.

О связи между обычными нефтеперерабатывающими установками и
современной нефтехимической промышленностью даём сведения в связи
с описанием извлечения парафина из смазочных материалов, произ-
водства парафина, крекинга парафина, улучшения качества парафина,
производства особенно чистых олефинов с прямой цепью.