

THE IMPACT OF THE CHANGE OF COAL CARBONIZATION

AND TAR DISTILLATION TECHNOLOGY ON THE PROPERTIES OF INDUSTRIAL PITCHES

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Summary

Two types of ovens are used for the production of coke. In nonrecovery ovens, all volatiles are burned to generate heat. These ovens were replaced by by-product ovens yielding tar and coke oven gas in addition to coke. Due to the different design of coke ovens and operational practices aiming at the increased productivity, the tar vapors in American coke ovens, compared with those in Europe and Japan, are more cracked and consequently, more aromatized and contain higher concentrations of QI. Tar was originally distilled in batch stills, where secondary QI was formed. The original binder specifications were based on pitches produced from these units. When petroleum type stills were accepted by tar distillers, no secondary QI was formed during the distillation. Therefore, a heat treating step was added in Europe and in Japan to meet the specification for the old style binder pitches. For the American tars with high concentration of QI, no heat treatment is necessary.

Coal Carbonization

In order to convert coal into coke, the coal charge has to be heated to temperatures on the order of 850 to 1100°C. Some 50-70 years ago, such coal carbonization in America was carried out either in beehive or in by-product ovens. (The trend in production of coke by these two methods in America is illustrated in fig. 1.)

The characteristic feature of beehive coking is direct heating. All heat necessary for the process is generated by combustion of carbonization by-products (tar and gas) within the oven.

In by-product coking, on the other hand, the production of the necessary heat for coking occurs in flues adjacent to the chamber holding the coal. In this "indirect heating" method, no air is permitted to enter the by-product carbonization chamber. All volatile products are withdrawn from the chamber, collected within the collecting main, and separated in the by-product train in either gaseous, liquid, or solid phase by scrubbing, cooling, chemical reactions, or other methods.

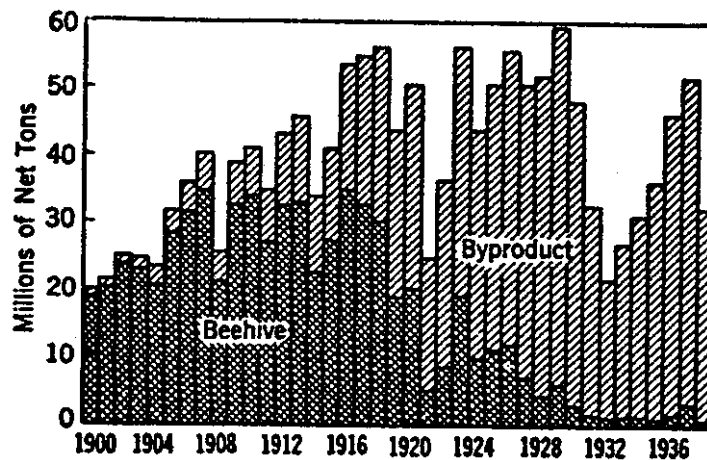


Figure 1 - Production of beehive and by-product coke in the United States, 1900-38.

Beehive Ovens

In the beehive oven, illustrated in fig. 2, coal is charged at the top through a charging hole, and the charge is leveled off through the side door. Gases are driven off by the sensible heat remaining in the floor, oven walls, and roof from the previous charge. Air is admitted through openings in the side door, and combustion takes place largely above the bed of coal; combustion gases are vented through the charging hole.

While beehive ovens are still considered appropriate standby carbonization equipment of low capital cost in the event of future excess demand for coke, in today's climate, only the modern nonrecovery process, which satisfies strict environmental regulations, is the process of choice.

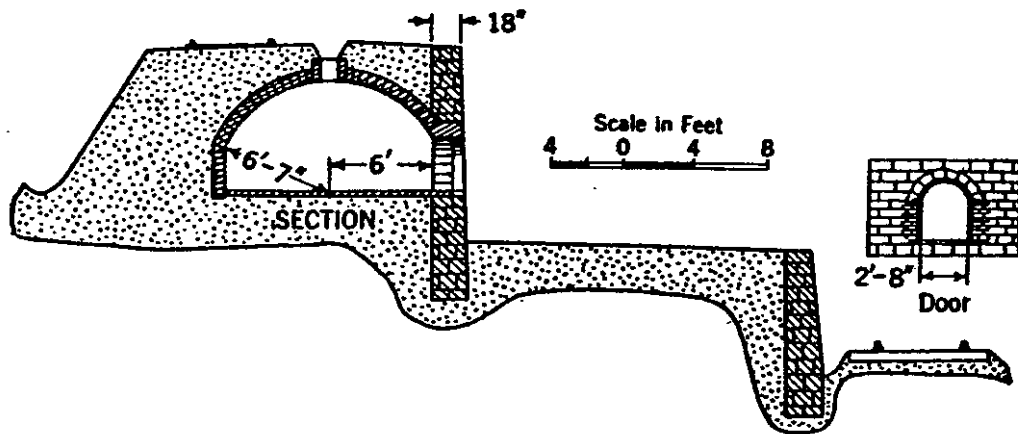


Figure 2 - Beehive oven.

By-Product Ovens

The design of the modern coke oven battery was basically realized about the time of World War I. The main objective of both its design and operation is to achieve maximum yield and optimum properties of metallurgical coke and recovered by-products.

The chambers holding the charge were designed thin and high due to the small thermal conductivity of coal to be carbonized. The difficult problem of how to achieve even distribution of heat along the heated wall was finally resolved and excessive heat loss reduced by building the carbonization chambers adjacent to each other in a block ("battery"). The width of the chamber was standardized at an average 18 inches, the length at 40 feet, and the height at 12 feet. With experience in enhancing heat distribution, the height of the chamber has been increased up to 20 feet, and the length to 50 feet.

Two basic principles govern the design of the flues for heating the carbonization chamber. In the systems typically in use in the United States and Canada, the flues within one heating wall are connected to crossover flues, which transport the combustion gases over the top to the flue system in the other heating wall (fig. 3). This system, developed in 1920, is based on an invention of Joe Becker of the Koppers Company, Pittsburgh. In fact, most by-product oven plants in the USA and Canada have been built by Koppers.

In the system used for heating coke ovens in Europe and Japan, and, until World War I, on the American continent, there are no crossover flues (fig. 4).

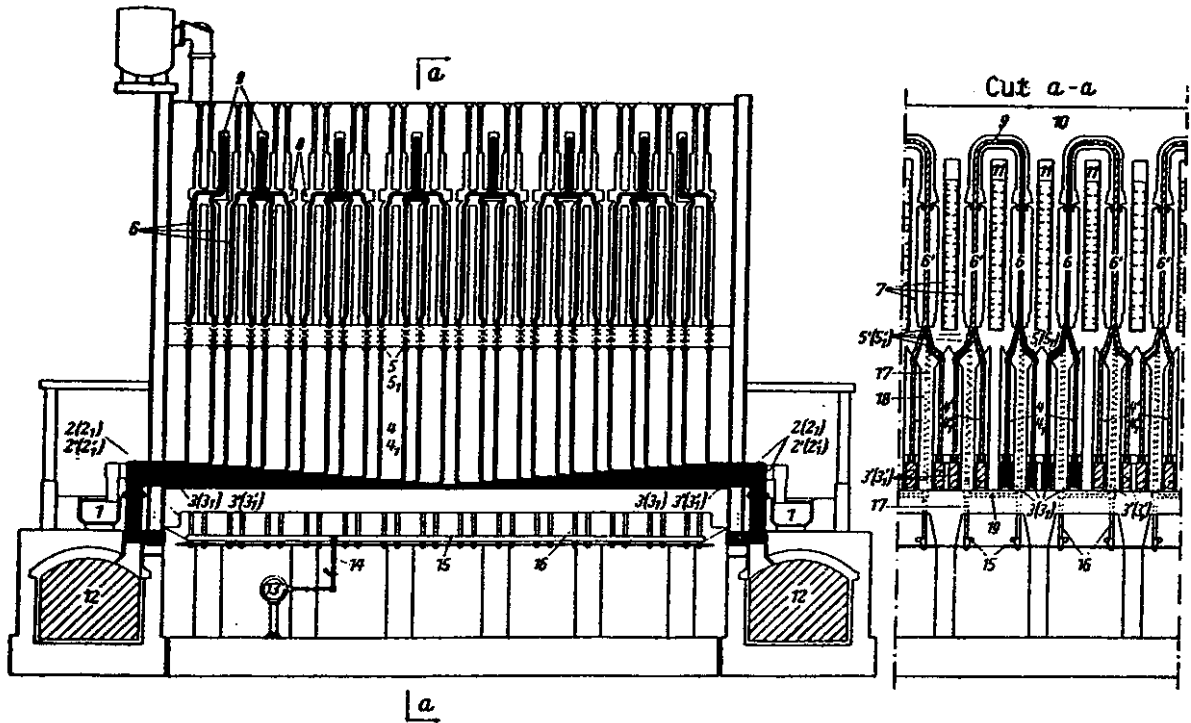


Figure 3 - American design of coke oven with crossover channels.

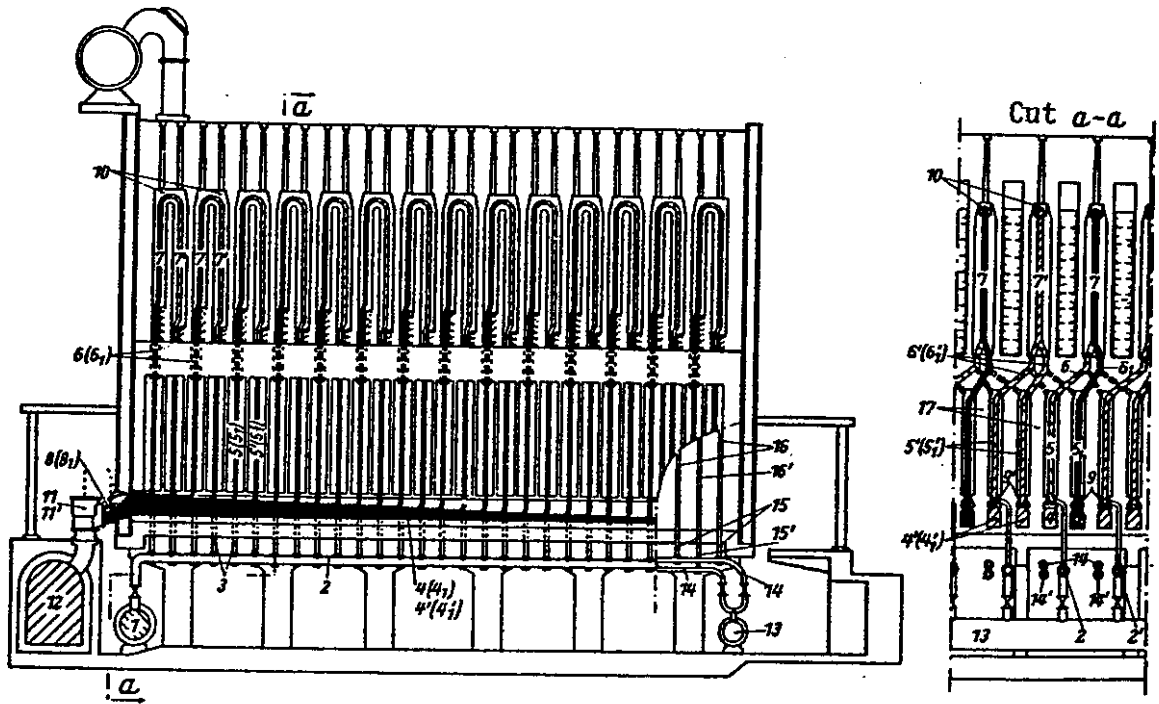


Figure 4 - European design of coke oven.

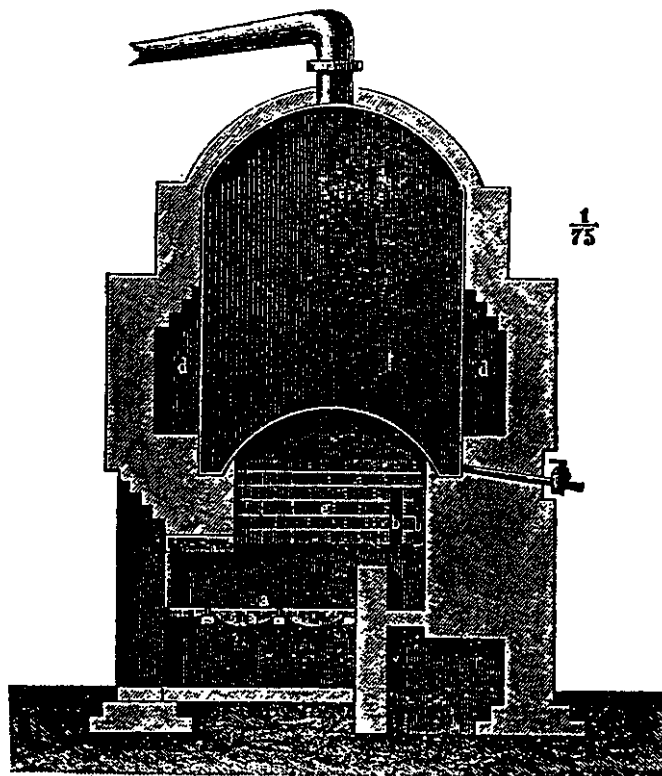


Figure 5 - Batch tar still.

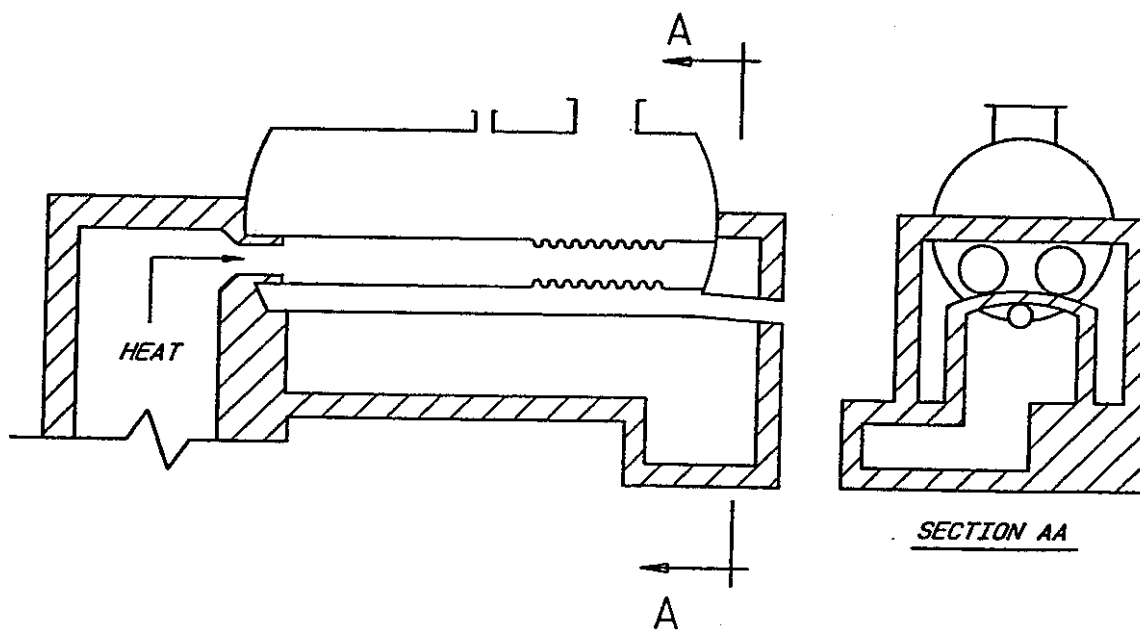


Figure 6a - Batch still - detail.

Carbonization Conditions and Tar Properties

It is generally recognized that the operating conditions during carbonization (temperature, carbonization time) have a more profound impact on the tar properties than the nature of the carbonized coal. The volatiles distilled from coal are severely thermally cracked when exposed to the environment of the carbonization chamber. This pyrolysis occurs mainly in the open space above the carbonization charge: the higher the temperature in the open space above the coke, the more aromatic tar, containing more quinoline insolubles, is formed.

With advances in combustion technology, it became possible to generate progressively higher carbonization temperatures and to reduce the time required for devolatilization of coal, that is, to increase the productivity of coke production. What we see, therefore, is that, increasingly, more aromatic tars were available, with higher concentrations of QI.

This trend was especially evident in the USA, Canada, and Australia, where the design of the coke oven batteries with crossovers contributed to overheated tops. Additional factors contributing in recent times to such overheating and to severe cracking conditions are: 1) preheating of the coal charge; 2) leaking walls and spot combustion caused by air sucked into the chamber when lower pressure is maintained in the carbonization chamber in order to eliminate the emissions of carbonization products into the environment; and 3) pipe-line charging, which results very often in a large, empty space above the coke.

This trend toward higher aromaticity tars with high concentrations of QI is not evident in Europe and Japan. There, the tops of carbonization chambers are maintained at lower temperatures due to the design of their ovens (no crossovers), and due, sometimes, to the special operational practices aimed at avoiding overheating the oven top and preventing cracking of some desirable chemicals, for example, toluene.

Tar Distillation

The original tar stills operated by a batch method. These tar batch stills went into operation around the turn of the century, and, until about 1940, accounted for most pitch production. They were fabricated from wrought iron or cast iron (figs. 5, 6a, 6b) and were heated directly with flue gas from combusted fuel -- coal, oil, or gas.

In order to devolatilize tar and reach the required consistency of pitches, the distilled material was severely overheated due to insufficient flow of poorly heat conductive material. Sometimes steam was introduced to agitate and strip off the residual volatiles at the end of the run.

These tar stills were prone to frequent fires because of high temperature and large volumes of oil distilled.

To increase the productivity of tar distillation and decrease the fire hazards by reducing the volume of heated oil, the batch operating stills were converted into continuous units (fig. 6c). (An example of an old continuous tar still with multiplicity of reboilers fired with solid fuel is given in fig 7.)

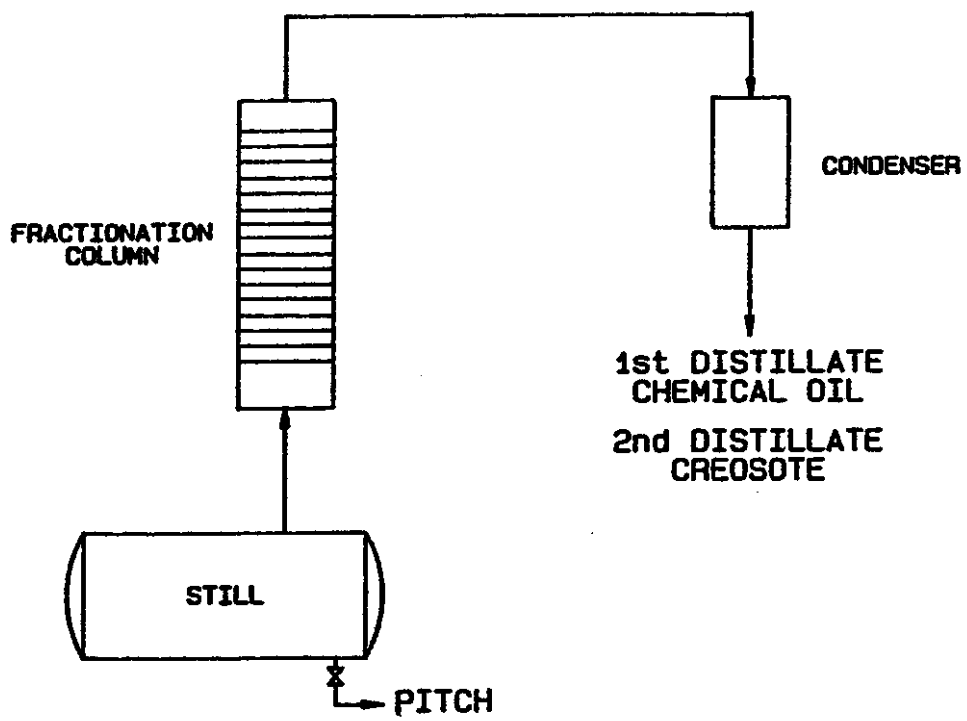


Figure 6b - Batch still distillation.

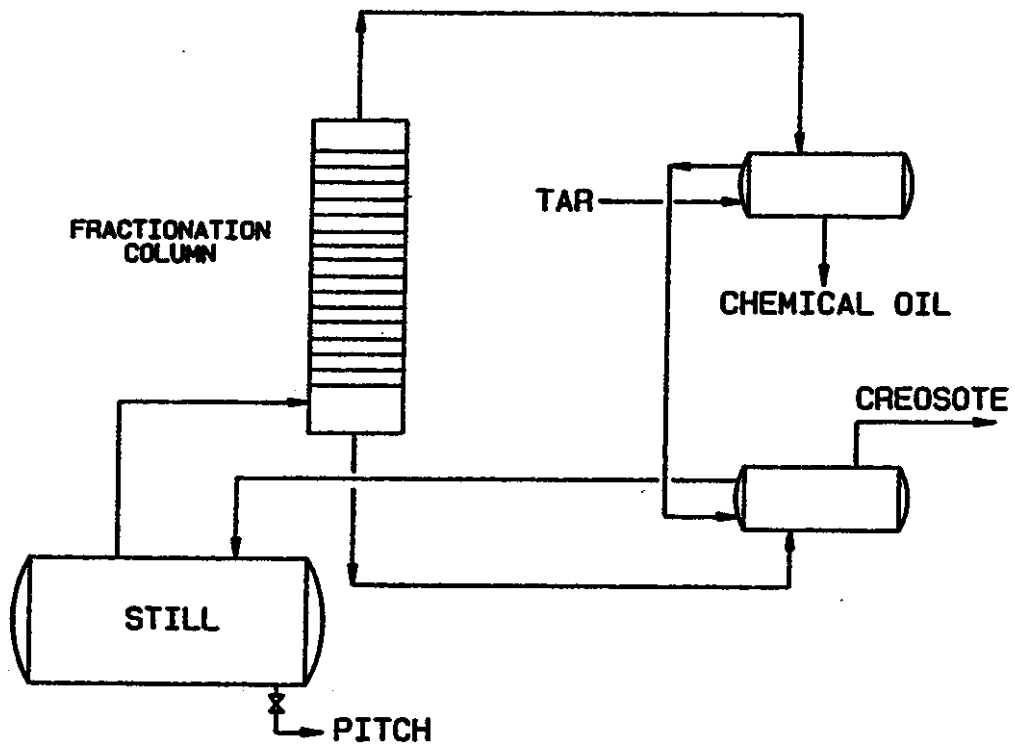


Figure 6c - Batch still revised for continuous operation.

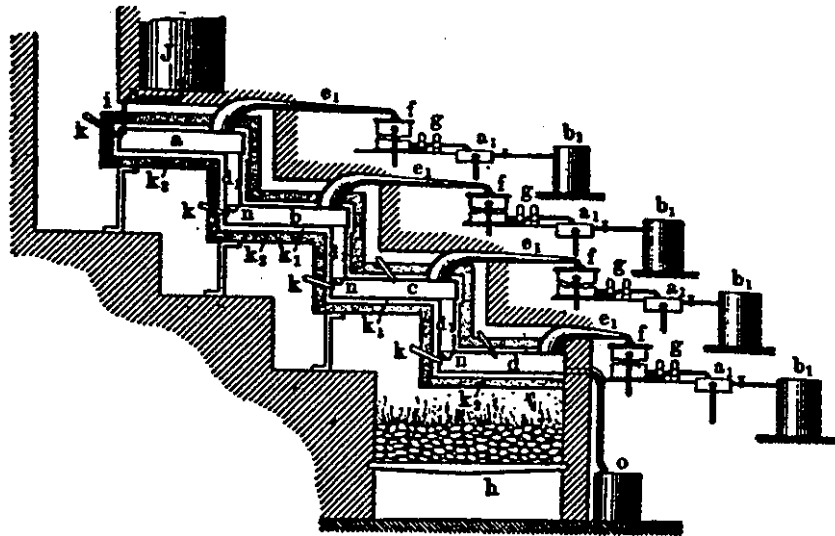


Figure 7 - Continuous tar still.

It was the petroleum industry which deserves credit for the fast improvement of distilling units and development of better distillation procedures.

The design of a pipe still was a major breakthrough (fig. 8). In this unit, only a small volume of turbulently flowing (to prevent coking) oil is rapidly heated to temperatures high enough for very fast evaporation of lighter fractions from oil maintained at lower pressure by efficient vacuum pumps (fig. 9).

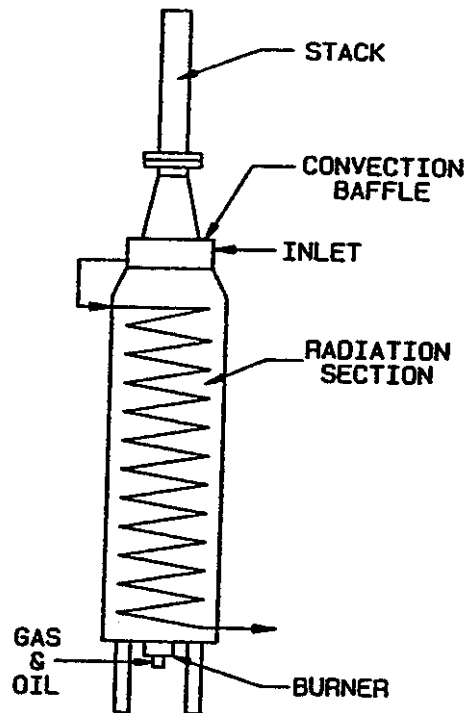


Figure 8 - Tubular heater.

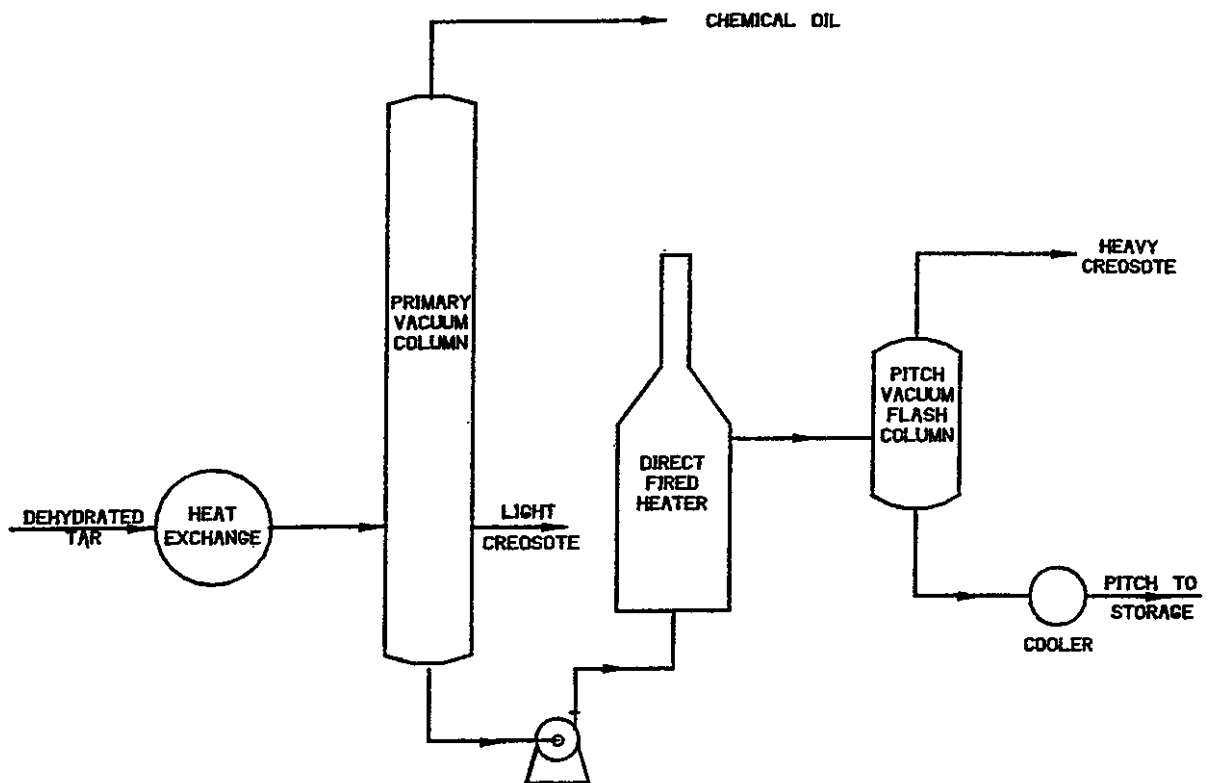


Figure 9 - Modern continuous distillation.

The distillation practices of the petroleum industry were adopted by tar distillers about 30 to 40 years ago.

Unlike in the older continuous tar stills, no heat treatment of the distilled material occurs in modern continuous tar stills due to good vacuum and consequently low temperatures, and due to the short residence time.

Aluminum and Pitch

The commercial production of aluminum started around the end of the 19th century, that is, about the time when the first by-product ovens were developed and the first tar still came on stream.

The first specifications for pitches used for making anodes for the aluminum industry reflected the properties of pitches produced at that time. These pitches were produced in batch stills from low aromaticity and low QI tars. Large volumes of pitch remaining in the bottom of the batch still were exposed to high temperatures in order to strip off the residual low boilers and to prepare a pitch with the required softening point. Therefore, the QI in this "old style" pitch consisted of considerable portions of QI formed by liquid phase cracking of hot oil, i.e., of secondary QI.

In the old tar still, which was not equipped for distillation under reduced pressure, it was not possible to produce high softening point pitches (i.e., with softening point above 100°C). At that time, aluminum was produced by the Soderberg process and additional stripping of low boilers from pitch was accomplished in the potlines.

In fact, up to about 1950, the only specification for binder pitch was its softening point.

Pitch was regarded almost as an industrial waste and most of it was burned to generate heat for distillation and for many heat deficient processes in the steel mills. Nevertheless, there were some nonfuel applications of pitch, for example, it was added to coal for carbonization and was used as core pitch for foundries, for roofing, road tars, briquetting of coal, impregnating of fiber pipe, and production of pitch coke.

After the Korean War, the aluminum industry put considerable emphasis on improving significantly the economy of the aluminum production, and it was at that time that the basic specification of pitch properties, such as QI, coking value, and BI, were defined and implemented by the aluminum industry.

As mentioned previously, the design of the European coke ovens and other operational practices eliminating excessive overheating of the carbonization oven tops resulted in lower aromaticity tars with low concentration of QI. These tars did not change very much over the years. However, the tars produced on the American continent and in Australia changed significantly with years, becoming highly aromatic and containing high concentrations of QI. After the stills and practices used by the petroleum industry were adopted by tar distillers, no heat treatment was needed for such highly aromatic, high QI tars during their distillation to pitches.

On the other hand, pitches produced from European or Japanese low QI tars did not reach QI levels found in "old style pitches" produced in out-of-date stills with considerable degree of heat treatment, or in the "new style" competitive pitches produced by distillation only, from high aromatic tars on the American continent. In order to meet the specifications of the aluminum industry, special heat treating units were added in Europe and in Japan to the modern vacuum tar stills with the objective to render the pitch a controlled degree of heat treatment (fig. 10), i.e., to form some secondary QI and to reach the QI levels requested by the aluminum industry.

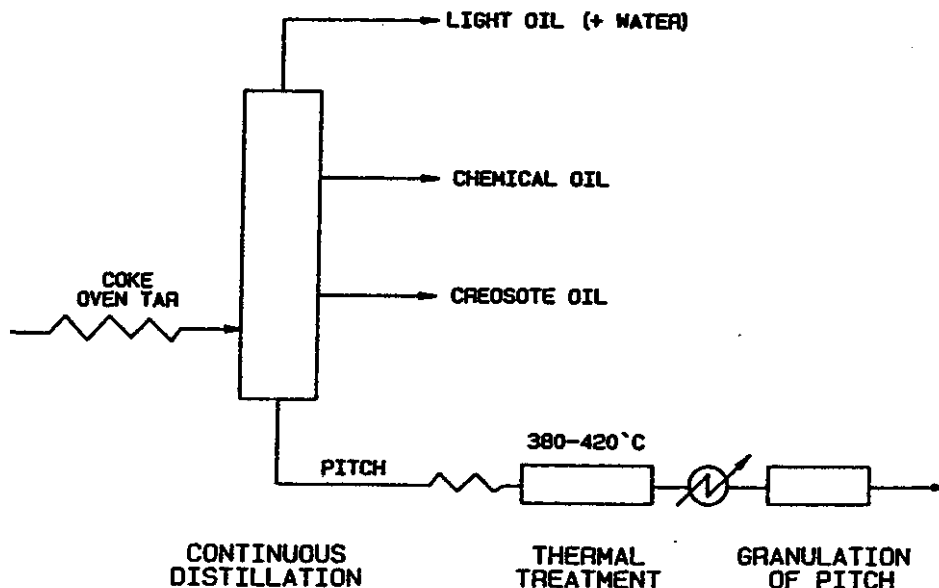


Figure 10 - Preparation of heat treated pitch.

As a consequence of this development, two types of pitches are available today on the market, both with comparable concentration but different quality of QI:

- A. "Old style pitches" (from Europe and Japan) containing secondary QI in addition to primary QI.
- B. "New style pitches" (from US, Canada, Australia) containing only primary QI and no secondary QI.

Before the discovery of mesophase by Brooks and Taylor in 1965, no difference was made between QI formed by vapor phase cracking and liquid phase heat treatment (secondary QI).

As long as the users were using pitches from the same tar plants, the conditions of the anode preparation got adjusted by the operators to either the "old style" (heat treated) or "new style" (not heat treated) pitch.

The situation started to become more complicated when the operators of anode plants, tuned originally, to "new style" pitch, had to switch to "old style" pitch and visa versa. It was found that these two types of pitches do not perform exactly the same way.

In order that appropriate operational adjustments can be made in time when such a switch of binders occurs, there is a need for a sensitive analytical tool, which would add another value to the set of characterization data determined routinely in pitches. This value would reflect the degree of heat treatment given to pitches during their production. It would be used by the aluminum producers as a criterion for excluding pitches which would not perform in the operation as pitches yielding the desired operational parameters.