

CHEMISCH WEEKBLAD

ORGAAN VAN DE NEDERLANDSCHE CHEMISCHE VEREENIGING EN VAN
DE VEREENIGING VAN DE NEDERLANDSCHE CHEMISCHE INDUSTRIE

Hoofdredacteur: Dr. W. P. JORISSEN, Leiden, 11 Hooge Rijndijk, Telefoon 1449

Redactie-Commissie: Dr. A. van Rossem, scheik. ing., J. Rutten, scheik. ing., Dr. G. L. Voerman, D. van der Want, scheik. ing.

D. B. CENTEN's Uitgevers-Maatschappij, Amsterdam, O.Z. Voorburgwal 115, Telefoon 48695

INHOUD: Mededeelingen van het Algemeen Bestuur der Nederlandsche Chemische Vereeniging. — Gevraagde en aangeboden betrekkingen. — A. E. Dunstan and Robert Pilkethley, Recent development in the art of cracking. — Boekaankondigingen. — Ter bespreking ontvangen boeken. — Correspondentie, enz. — Vraag en aanbod.

MEDEDEELINGEN VAN HET ALGEMEEN BESTUUR DER NEDERLANDSCHE CHEMISCHE VEREENIGING.

Adresveranderingen:

A. Brzesowsky, scheik. ing., s.f. Delanggoe, Delanggoe (Java).
A. Bloemen, chem. docts., Soestdijk, Wald. Pyrmontlaan 14.
J. W. Döbken, scheik. ing., Groningen, Oostersingel 214, ing. aan de Gem. Gasfabriek.
O. Meulemans, scheik. ing., s.f. Redjo-agoeng, Madioen (Java).
Dr. J. F. L. Reudler, Zwolle, Heerenweg 24.
Dr. R. A. Weerman, scheik. ing., Amsterdam, Keizersgracht 526.

Rectificatie: In het Chem. Weekblad van 4 April komt onder de adresveranderingen voor: Dr. P. G. van de Vliet, IJmuiden, Schulpweg F 319. Het adres van Dr. P. G. van de Vliet blijft echter onveranderd: Helder, Zuidstraat 34.

* *

Op Zaterdag 4 April j.l. werd te Utrecht door den Voorzitter der Ned. Chemische Vereeniging de nieuw-benoemde Financieele Commissie, bestaande uit de Heeren: Prof. Dr. E. Cohen, Dr. F. G. Waller en Dr. G. L. Voerman, geïnstalleerd.

* *

De Penningmeester verzoekt den leden hunne contributie te willen voldoen door overschrijving op de postgiro-rekening 7680 der Ned. Chemische Vereeniging, Haarlem, of per postwissel.

Na medio April hoopt hij per postquitantie te beschikken over de nog niet betaalde contributies en abonnementsgelden. De inningskosten moeten dan echter op rekening van de desbetreffende leden worden gesteld.

Deze kosten bedragen:
voor Nederland f 0.30.
voor Ned. Indië f 1.50 à f 2.—.

De contributie zonder inningskosten bedraagt:
Voor leden in Nederland zonder abonn. „Recueil” f 15.—.
" " " " met " " " 21.—.
" " " Ned. Indië zonder " " " 16.—.
" " " " met " " " 22.—.
" " " het buitenl. zonder " " " 19.25.
" " " " met " " " 25.25.

* *

Gevraagde betrekkingen:

19. *Chemicus*, scheikundig ingenieur, diploma 1923, praktijk: diamantbedrijf en gasfabriek. Alle betrekkingen; ook in buitenland en koloniën.

20. *Chemicus*, dipl. scheik. ing. 1899, gepromoveerd 1920, met eenige fabriekskennis en 20-jarige laboratoriumervaring, zoekt werkkring.

21. *Chemicus*, dipl. scheik. ing. 1921, praktijk: 1 jaar ass. anal. scheik., 2 jaar ass. bedrijfsleider, in fabr. van org. chem. prod., zoekt betrekking.

22. *Chemicus*, chem. docts., biedt zich aan voor alle betrekkingen; ook bacteriologisch.

23. *Chemicus*, diploma scheik. ing. 1920; praktijk 1½ jaar fabriekslaboratorium, 4 jaar ass. anal. scheik. Alle betrekkingen.

24. *Chemicus*, diploma scheik. ing., 1922; 2 jaar fabriekspraktijk, zoekt betrekking, bij voorkeur organisch werk.

25. *Chemicus*, dipl. scheik. ing. 1922; praktijk: 2½ jaar assistent anal. scheik., org. scheik., colloïdchemie; laboratoriumervaring: biochemisch onderzoek, zoekt werkkring, alle richtingen (ook buitenland en koloniën).

26. *Chemicus*, doctor in de chemie, 23 jaar, 2½ jaar organische assistentspraktijk, zoekt werkkring. Alle betrekkingen.

27. *Chemicus*, 4 jaar laboratorium en 5 jaar fabriekspraktijk als leider huidverffabriek; specialiteit verf, lak en asphalt, in het bezit van eigen recepten, zoekt werkkring.

* *

Secties.

In een gecombineerde vergadering van het Alg. Bestuur met de Besturen van de Secties op 14 Maart j.l. werd betreffende de kwestie van de Secties afgesproken, dat voorloopig niets statutair zal worden vastgelegd, terwijl dienaangaande ook nog geen bepalingen in het Huish. Regl. zullen worden opgenomen. Bij aanneming van buitengewone leden, waarvan bij iedere Sectie het aantal niet te groot zal worden, zullen de Sectie-Besturen er op wijzen, dat ze volgens een voorloopige regeling worden opgenomen.

Deze regeling omvat de volgende punten, waaraan de Sectiebesturen en het Algemeen Bestuur zich zullen houden en die ook bindend zijn voor eventueel nieuw op te richten secties.

I. De Secties kunnen desgewenscht buitengewone leden aannemen. De Besturen der Secties en het Alg. Bestuur komen voorloopig overeen, zonder dat zulks nog in de Statuten of het Huish. Reglement is vastgelegd, de volgende punten in acht te nemen.

II. Uitgezonderd de Huish. Vergaderingen zijn alle vergaderingen der Secties toegankelijk voor alle leden der Ned. Chemische Vereeniging. De Secties bepalen zelf, welke vergaderingen „huishoudelijk” zijn. Tijdens de Algemeene Vergaderingen van de Vereeniging zijn ze dat niet.

III. De Secties nemen alleen hen tot buitengewone leden aan, die geen gewoon lid van de Vereeniging kunnen worden. De aanneming van een buitengewoon lid geschiedt alleen na toestemming van het Algemeen Bestuur.

IV. De Secties kunnen eigen contributies heffen.

V. De Secties trachten niet voor hunne financiën donaties te verkrijgen; de mogelijkheid van geldelijken steun uit de algemeene kas blijft bestaan.

VI. De Secties beheeren verder echter hunne eigen financiën.

VII. Tot de Bestuursfuncties der Secties worden alleen gewone leden gekozen.

VIII. In het Bestuur van iedere Sectie wordt een lid van het Algemeen Bestuur gekozen.

Dr. A. D. DONK, *secretaris-penningmeester*,
Verspronckweg 100, Haarlem.
telef. 12928.

665.5

RECENT DEVELOPMENT IN THE ART
OF CRACKING ¹⁾

by

A. E. DUNSTAN and ROBERT PILKETHLEY.

It is now eight years since Dr. Thole, Mr. Lomax and one of the present authors surveyed the problems incident to cracking. Much oil has flowed through the pipe-lines since then, and the present moment is a convenient one for a general consideration of the situation, seeing that the art is in process of being standardised.

Surveying the typical examples of cracking processes dealt with in the sequel and the subject in general, there are certain outstanding points of interest. In the first place, vapour phase processes working under practically atmospheric pressure have not been particularly successful; losses are high and the products are poor in quality. On the other hand, exceedingly high pressure processes have not advanced far beyond the development stage. Most of the processes which have been utilised to any extent operate under comparative moderate pressures. General observations appear to point to the conclusion that, provided the pressure is sufficient to maintain the oil under operation mainly in the liquid phase, there is no particular advantage in extremely high pressure, as far as the quality of the product is concerned, as oils converted at pressures between 350 and 700 lb. appear to have similar characteristics. Considering extremely high pressure processes like that of Bergius, it is apparent that hydrogen disappears in certain cases, but it is questionable if the hydrogen is contained in the liquid products of lower boiling point. Waterman's work on this subject is particularly interesting.

The question of temperature in liquid phase cracking is decided by the particular oil under treatment and the amount of spirit desired, as there appears to be a definite relationship between the three variables—time, temperature and yield. The percentage of spirit obtained after the oil has reached definite cracking temperature appears to double itself, within limits, for an increase of temperature in the neighbourhood of 10° C. In the same way, when the rate of pumping is halved, or the time of reaction doubled, the same increase in spirit content is noted.

There has not been a great advance in our knowledge of cracking from a chemical point of view during the last few years, and the problems connected with it have been more of an engineering quality. The most urgent problem to the majority of refiners is the elimination—or at any rate the diminution in quantity—of coke in order to allow plant to run continuously without having to close down periodically. Bergius claims to have successfully overcome this problem, but to the majority of others the question is definite, and it is questionable if coke can be eliminated without hydrogenation brought about by one method or another.

¹⁾ Voordracht door Dr. A. E. Dunstan gehouden op 30 Oct. 1924 voor het Technologisch Gezelschap te Delft.

Surprisingly little progress has been made in the examination of the residues left after the cracked gasoline has been removed from the synthetic crude oil. The work of Brownlee (v. i.) may be instanced as an attempt to explore the possibilities of this material, and investigators will do well to bear in mind that there is a raw material of unknown constitution, the knowledge of which would probably amply repay intensive research.

Nothing has arisen in the interim to cause us to modify the views discussed in the previous paper to which reference has been made. The kinetics of pyrolysis still remains in a sketchy and unsatisfactory condition, and it is not surprising that this should be so when it is realised what little exact knowledge we have of the decomposition of even the simplest hydrocarbons.

We now proceed to discuss a few processes which we have personally investigated, and these have been selected, firstly, because they exhibit interesting difference in procedure, and secondly, because they show promise of leading to a cracking technique and process which shall be as standardised and simple as a still or any other piece of familiar refinery plant.

A. Vapour Phase. Atmospheric Pressure.

Ramage's method of cracking is a typical vapour phase process. It consists of passing the vapour of the hydrocarbon over a reducible metallic oxide such as iron oxide, regulating the temperature and the time of contact in order to oxidise a part of the hydrocarbon with incomplete reduction of the oxide whereby separation of carbon is substantially prevented.

Ramage uses the following equations to illustrate his description of the process:—

1. $\text{CH}_{2n} + 2 + \text{Fe}_2\text{O}_3 = \text{C}_n\text{H}_{2n} + 2\text{FeO} + \text{H}_2\text{O}$.
2. $\text{C}_8\text{H}_{18} \rightleftharpoons \text{C}_6\text{H}_{10} \rightleftharpoons 4\text{C}_4\text{H}_8 \rightleftharpoons 8\text{C}_2\text{H}_4$.
3. $\text{C}_2\text{H}_4 + 2\text{Fe}_2\text{O}_3 = 2\text{C} + 4\text{FeO} + \text{H}_2\text{O}$.
4. $\text{C} + \text{Fe}_2\text{O}_3 = 2\text{FeO} + \text{CO}$ (550° C.).
5. $\text{CO} + \text{Fe}_2\text{O}_3 = 2\text{FeO} + \text{CO}_2$ (550° C.).
6. $\text{H}_2\text{O} + 2\text{FeO} = \text{Fe}_2\text{O}_3 + \text{H}_2$ (500–600° C.).

The hydrogen eliminated in (6) is alleged to be responsible for the hydrogenation of the unsaturated hydrocarbons which are produced in the main operations (1) and (2).

In Patent No. 1,365,849 Ramage claims further use for his process in treating aromatic hydrocarbons containing one or more alkyl groups, for the replacement of the alkyl group by hydrogen, thus converting toluene and xylene into benzene at a temperature approximating 700° C. in presence of a catalyst comprising a lower oxide of iron, and he claims particularly that whatever the source of the gas oil operated on, there is a consistency in the properties of the product.

In 1922 the process had developed on a reasonable scale and was past the experimental stage. Gas Oil from Persian and Mexican Crudes had been successfully cracked. The gas loss was by no means excessive compared with other vapour phase processes, but would more than suffice for the firing of the plant. The plant, however, could not handle oils other than distillates, and the product did not differ markedly from other cracked spirits. The same

refining losses were met with as are experienced with similar products. Considerable interest was attached to the condition of the cracking tubes. One tube which had been regularly used over eighteen months after opening up showed no signs of wear and tear.

An experimental plant operating at Detroit consisted of a horizontal gas fired still capable of working up to 50 lbs. pressure per square inch. The oil was introduced into the still and kept boiling at a pressure of 4—5 lbs., the vapours being led to the cracking tube, which consisted of 20 ft. of 4-in. iron pipe filled two-thirds with powdered hæmatite. Dry steam supplied by a small vertical gas fire boiler of 5-gallons capacity and at 6 and 7 lbs. pressure was led into the same end of the cracking tube as the oil vapours, the flow of each being regulated by gate valves pierced with holes of known diameter so that the orifices were as 4 : 1 oil to steam.

The cracking tube was heated electrically in 2 × 10 ft. sections and insulated with asbestos powder. A blind tube 3 ft. long was fitted through each of the flanged ends for pyrometers. After passing through the cracking tube the vapours passed through a short 1 in. tube to an air cooled catch-pot, where heavy uncracked oil was trapped and thence through a water-cooled condenser to gas-tight receivers fitted with gauge glasses and drain cocks. The uncondensed gases were scrubbed with gas oil and passed through a meter. The heating of still, boiler and cracking tube are commenced simultaneously with control valves closed. When the pressure of still and boiler reach 6 and 4 lbs. respectively and temperature along the whole cracking tube is at 550° C. the control valves of still and boiler are opened wide and the flow is automatically controlled by the pierced gate-valves. The flow of oil amounted to about three gallons per hour. On first introducing the vapours into the cracking tube the temperature of the first half drops to 450° C., then rises slowly to about 480° as the boiling temperature of the oil goes up. In the second half of the tube the temperature commences to rise at once, going up to 650° C., and the external heating is discontinued since the temperature maintains itself by means of exothermic reactions occurring within the tube. Uncondensable gas amounts to about 20 per cent. of the oil, and the reactions take place at practically atmospheric pressure so that obstruction can be detected at once by the pressure gauges.

On the commercial plant at Tulsa each furnace comprises a nest of 63 cracking tubes, 20 ft. by 6 in., arranged in rows of seven tubes, and the nest is fed by headers from the vapour line. Air blowing for a few minutes every 24 hours kept the hæmatite free from sulphur.

The life of the hæmatite seems to be indefinite, the experimental tube at Detroit having worked for over twelve months without being opened. During this period all sorts and conditions of oil had been run, but on opening the tube no trace of coking could be seen.

As a whole the plant appeared easy to run and working costs should be low.

A typical run conducted with heavy fuel oil on the Detroit plant gave the following figures:—

K.W. for heating = 8 per hour.

Temperature. — 1st half of tube, maximum 680° C., minimum 500°.

“ 2nd half of tube, maximum 710° C., minimum 600° C.

Oil possessed = 13.8 gallons.

Condensate = 8.15 gallons.

Condensate boiling below 200° C. = 13.8 gallons = 39 per cent.

Spirit from scrubbers = 2.0 gallons.

Volume of gas produced = 363 cubic feet.

Grand total of motor spirit below 200° C. = 3.18 + 2 = 5.18 gallons.

- Oil converted into motor spirit + 8.08 gallons.

Per cent. conversion to motor spirit = 64 per cent.

Loss of oil in cracking is 19.8 per cent. (includes

“ “ washing is 0.8 “ gas).

“ “ redistilling is 2.0 “

Total loss .. 22.6 per cent.

Analysis of the packing in the tube appeared to vitiate the claim that ferrous oxide was the chief component.

The spirit prepared by this process had the characteristic smell of cracked spirit and on slow evaporation yielded a gummy residue. Specific gravity, boiling range and degree of unsaturation compare closely with those of spirit made by other vapour cracking processes. Ramage claimed that he obtained a new class of cyclo-paraffin, but when compared with other cracked spirits his contention appeared to have no foundation. Chemical analysis points to the conclusion that instead of being a spirit largely composed of saturated compounds the proportion of unsaturated bodies exceeded 50 per cent.

A minimum of 70 per cent. recovery should be obtained with efficient scrubbing of the gas.

Further tests were carried out later, and the claim that oil in presence of steam passing over a contact mass of hæmatite converts it into ferrous oxide has not been substantiated, and in fact a contact mass of metallic iron under the same conditions produces identical results, for clearly the equilibrium attained will be the same whether one starts with the metal, any of its three oxides, or its carbonate.

The Dubbs process²⁾ has been developed from several basic patents and is one of the most successful processes of the twophase type wherein the oil is cracked in tubes in the liquid phase compare Fig. 1. At the moment there are 113 units of the plant in operation or under construction.

The process is simple in that the oil to be cracked is pumped through a heating coil in a furnace and passes into a hammer welded reaction chamber, wherein all coke is collected and from which the residuum produced is continuously withdrawn. The vapours pass from the reaction chamber into the dephlegmator, which separates the heavier oil from the lighter cracked vapours. The light vapours are condensed and the heavier fractions return to the heating tubes. The model which has been lent by the proprietors for this lecture shows the layout of the plant, and the flow chart shows in diagrammatic form the arrangement of the equipment.

²⁾ J. Ind. Eng. Chem. 15, 580 (1923).

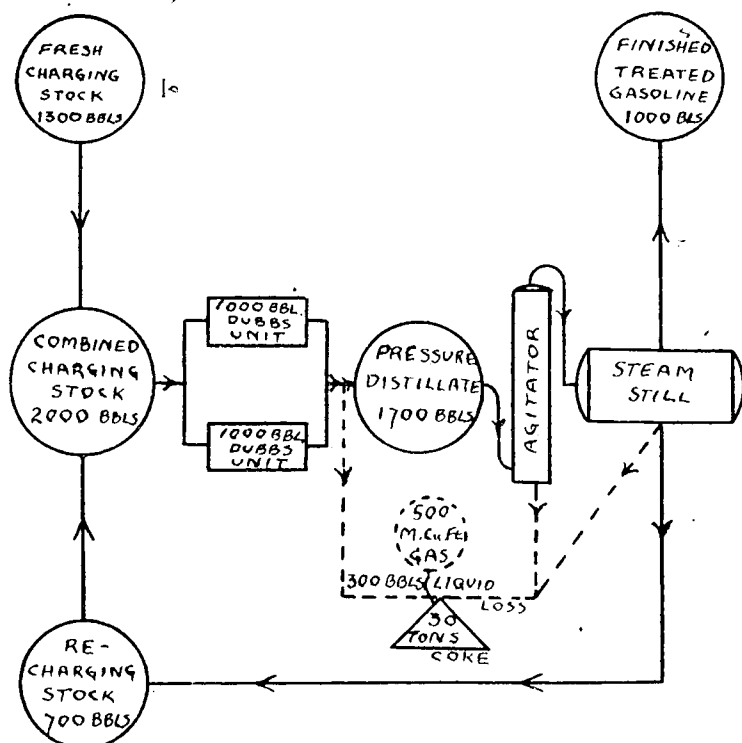


Fig. 1. Dubbs cracking process operation on Mid-Continent fuel Oil. No residuum run with re-cycle.

In the Standard Dubbs unit of 500 bbls. capacity per day the charging stock is pumped continuously and at a uniform rate by the feed pump, and is discharged either directly into the heating coil in the furnace or through the overhead line to the top of the dephlegmator, wherein it is preheated by the condensing vapours. The feed may be split by means of control valves, part of it going through the dephlegmator and the remainder direct through the heating coils. The oil enters at the bottom of the heating coil and flows upward, passing through fifty 4-inch tubes 30 feet long, connected in series by return bends. The furnace is side fired and has two compartments, a combustion chamber and a heating chamber. The hot gases from the combustion chamber pass into the chamber containing the heating coil at the top and flow downwards counter current to the flow of oil. The double chamber is designed to protect the tubes from the direct flame of the furnace. The oil is heated to the required cracking temperature, about 450° C., before it is discharged into the reaction chamber.

Cracking is completed in the reaction chamber without additional heat, heavy lagging being sufficient to maintain the temperature.

The oil separates into vapour and residuum fuel oil and the carbon liberated by the cracking is deposited in the chamber to form coke. The residuum is withdrawn continuously through a cooler to fuel storage.

The reaction chamber is 10 feet in diameter by 15 feet high and 1½ inches thick, and is provided with run-off pipes, for successive use as the coke level rises. The capacity for coke of each chamber is about 30 tons. The vapours from the reaction chamber are transferred by a vapour line into the dephlegmator, which also acts as a heat exchanger as the temperature in the dephlegmator is mainly controlled by the quantity of cold raw oil introduced.

The average temperature at the bottom of the dephlegmator is about 395° C. The condensed heavy oil and the raw oil, preheated to about 300° C., pass from the dephlegmator down the reflux leg via the feed line to cracking tubes.

The light vapours rise to the top of the dephlegmator and are discharged through a line into the condenser. The condensate and the uncondensable vapours flow into the pressure distillate receiver. Up to this point the entire system is under a uniform pressure of about 140 lbs./sq. in.; thereafter the gas separates at atmospheric pressure from the distillate and is used as fuel. In the process control temperature recording instruments are placed in the furnace, in the transfer liquid to the reaction chamber, in the cracked vapour as it leaves the dephlegmator, and in the residuum leaving the reaction chamber. Pressure is recorded by a gauge on the pressure distillate receiver. Oil meters measure the raw oil and a gas meter measures the amount of gas produced. It is claimed for the Dubbs Process that it has the ability to crack any liquid hydrocarbon from kerosene distillates to heavy residues such as Panuco Residue. There is no appreciable formation of carbon in the heating coil, and the length of the run is determined by the capacity of the reaction chamber to store coke. In the light of many serious results which have ensued from the operation of cracking plants the safety of the process is claimed. In a 500-bbls. unit only 10 to 20 bbls. of oil are in the coil subjected to heat, but not to direct flame, and a limited quantity (about 20 bbls.) is maintained in the reaction chamber which is outside the heating zone.

Due to the moderate pressure, average 150 lbs., there is no undue danger such as is present at substantially higher pressures.

The Dubbs process is the only process which is successfully cracking commercial fuel or topped crude direct without pretreatment or distillation.

Distilling fuel oil and cracking the distillate is not the same as cracking fuel direct, as the residue on distillation is pitchy, with only 50 to 60 per cent. distillate suitable for cracking, whereas running the fuel oil direct yields 40 to 50 per cent. Navy gasoline, 25 to 50 per cent. gas oil and the balance coke and gas. If residuum is desired this can be produced from the reaction chamber and is suitable for fuel.

The coke is dry and hard and a good commercial fuel. It is suitable for briquetting, and in most instances without a binder.

The one unit standard plant is estimated to cost about £15,000, without tanks, steam and water auxiliaries, etc.

The control of the plant is simple, and two or three men per shift are capable of operating two units with total capacity of 1000 bbls. per day. Once the operating conditions are fixed there is little or nothing to do until the run comes to a finish.

As an example of the work done by the plant we quote the cracking of Mid-continent fuel oil in a number of typical commercial runs. The fuel used was the residue after distilling off the gasoline, kerosene and gas oil, and ranged in specific gravity from 0.900 to 0.912.

The pressure distillate received represented 61 to 69 per cent., having a specific gravity 0.760 to 0.778. This pressure distillate on treatment with acid and

soda and redistillation gave 40 to 42 per cent. of American Navy Specification gasoline, the remainder being kerosene and gas oil suitable for further cracking. The residuum fuel was an excellent fuel, having a lower viscosity than the original, and amounted to between 25 and 36 per cent. of the raw stock. The specific gravity ranged from 0.959 to 0.979. The coke produced varied between 16 and 26 tons per run. The gas and coke together amount-

temperature in the reaction chamber until the reaction is complete.

The reaction chamber is a horizontal steel cylinder 40 feet long by 38 inches internal diameter and 3 inches thick. No heat is applied to the chamber, but it is heavily lagged to prevent loss of heat, and the oil is held in this chamber long enough to establish equilibrium between liquid and vapour phases; this period is estimated to be about fifteen minutes, and

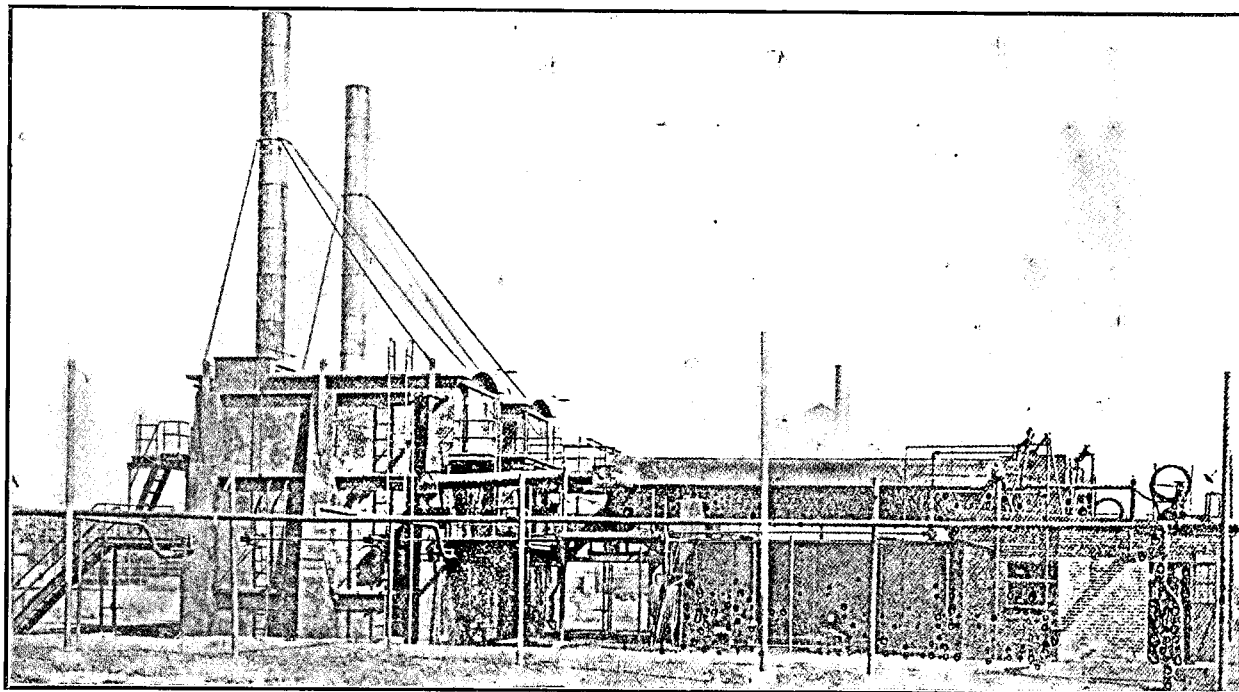


Fig. 2. A complete two unit installation of the Cross Process.

ed to $4\frac{1}{2}$ to 6 per cent. Fuel consumption about 2 per cent. of liquid fuel and the uncondensable gas produced and burned about 4 per cent. = total 6 per cent. The plant ran continuously for about five days on stream.

The Cross process was originally a vapour phase cracking process which developed into the present method when the advantages of liquid phase cracking became known.³⁾ Fig. 2.

It differs from the Dubbs process in the form of the apparatus, the pressure and temperature conditions, and the proprietors do not advise the use of heavy fuel residues without a preliminary distillation. It resembles the Dubbs process in so far as the heating and reaction zones are separate, and no heat is applied to the reaction vessel.

In the commercial operation of the plant heat is applied to the oil in the tubes placed horizontally in series. These tubes are 24 feet long, 3 inches internal, and 4 inches external diameter. They are arranged in two banks, containing 45 tubes each, above the furnace, and form a continuous coil. The upper bank of tubes acts as a preheater and the lower is the cracking coil. The oil is pumped downward through the preheating coil and upwards through the cracking coil; then passes directly into the reaction chamber at a temperature of about 470° C. Sufficient heat is applied to the oil to maintain its

results in a drop in temperature of about 50° C. between the inlet and outlet. It is stated that coke is not deposited to any extent in the cracking tubes, and the deposition is mainly confined to the reaction vessel.

Under normal conditions the amount of coke produced is less than 1 per cent. The discharge line from the reaction vessel is set at the liquid level and controls this level without any automatic device other than an ordinary relief valve. A pressure of 600 to 700 lb. per square inch is maintained on the system in order to prevent distillation and to keep the oil in the liquid phase. The oil from the reaction vessel is discharged to a vapour separator wherein a certain amount of fuel oil is collected. The vapours then pass to the dephlegmator, where the temperature is regulated to yield the required specification petrol, and the condensed fractions are withdrawn for further cracking along with raw oil stock. A condenser liquefies the gasoline and a gas separator removes the permanent gas formed in the process.

Sufficient gas is produced to provide fuel for the operation of the plant; an additional 1 per cent. of fuel oil is necessary to bring the plant up to the cracking temperature. The plant will operate on kerosene, gas oil or any distillate, but heavy fuel oils are not recommended on account of the excessive amount of coke deposited in the reaction vessel. By combining a simple type of pipe still with the main plant residue may be processed.

³⁾ Oil and Gas J. 20.

The plant can run continuously on gas oil for about a week, or on kerosene for about three weeks, without cleaning.

The throughput of a modern double unit Cross plant is 2000 bbls. per day, and it is stated that a yield of 33 per cent. of Navy gasoline can be obtained in one cycle from gas oil, 40 per cent. of the same quality from kerosene distillates, and 20 to 25 per cent. from fuel oil.

The total yields in running gas oil and recycling the residue, without the addition of fresh oil, are recorded by Cross as follows:—

Gasoline (Navy)	46.8 per cent.
Fuel Oil	24.8 "
Loss	10.4 "

But as usually operated the production is of the order already stated, and the yield on recycling the oil is about equivalent to the cracking of an equal quantity of original oil.

Dr. Roy Cross accentuates the factor of safety in cracking plant, and is of the opinion that cracking problems are not so much chemical as engineering problems, and for this reason he has taken care as far as possible that his plant should be able to withstand the conditions of temperature and pressure under which the operation is conducted.

The latest development in the well-known Carleton Ellis cracking method is an instance of a parallel development by experience and observation towards the same object, for it is our opinion that vertical reactors will be more the rule than the exception in the future, Fig. 3. The process is licensed by the

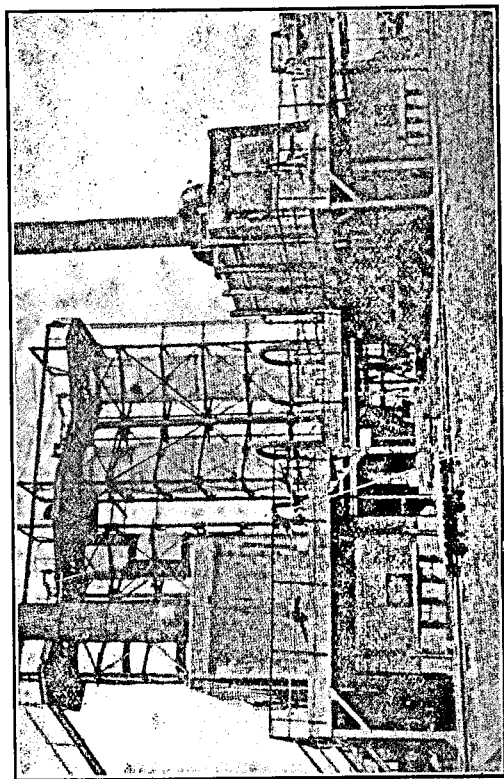


Fig. 3. Carleton-Ellis Plant.
The cracking coils are enclosed within the vault-like construction behind the steel doors of each unit. The upright cylinders in the rear are the soaking drums. Stills and fractionating equipment are not in view.

Standard Oil Company (N.J.), and is similar to other plants using the process, but the Invincible Oil Company has taken into account the different classes of crude or topped oil it will use, and has constructed a plant sufficiently flexible to allow any of these

oils to be treated for the production of commercial gasoline. The plant is in two units, each of which is capable of a daily throughput of 2000 barrels.

The oil is fed into coils under a pressure of 350 lb., and natural gas is used as fuel. The oil usually passes through the coils at a rate of 5000 gallons per hour into the "soaking drums", which are upright cylindrical reaction vessels. The quality of the crude stock determines how long the oil must remain in these drums, but it is held long enough to allow the time factor to have its effect, and is then released steadily, passing into horizontal vaporising stills, where the cracked products vaporise and pass overhead into the fractionating columns. The gasoline produced can be treated as straight run spirit and does not require blending to bring it to commercial specification. It is claimed that a residuum fuel oil is obtained, after the gasoline has been removed, which is free from suspended carbon, of excellent quality as a fuel oil.

There are two cracking coils each with a capacity of 2000 barrels per day, and the flexibility of the equipment is due to the "soaking drums" or upright reaction chambers, of which there are two to each system. They can be operated singly, in pairs, or can be omitted, according to the treatment necessary. On raw material which gives considerable quantities of coke the system can work on one chamber while the other is being cleaned, or the amount of coke can be divided by using both. On stocks requiring less time for cracking one drum is sufficient, and when it is desired to lower the viscosity of a fuel oil only, the drums may be by-passed, without coming into action. The length of the running period varies with the crude stock and the products desired, but the average is six days on gas oil or crude. Likewise the field of gasoline will vary, but can be easily controlled.

This particular plant departs from the common practice of carrying pressure throughout the system, and is practically a combination of a cracking still and a crude still, and it is possible to see the quantity of oil that each still is running without relying on mechanical measurements.

The plant has been designed to give the utmost from an economical, as well as a safety in working, point of view. Heat economisers are used wherever possible, resulting in the ingoing oil entering the heating coil at a temperature of about 250° C.

The A. D. H. cracking process.

The Auld, Dunstan and Herring Process, fig 4, is the direct result of several years work which started when the author observed that the Selling property of Persian residue was to a great extent destroyed by heat treatment under pressure.

The object of research work at that time was the rendering of the residue available as a fuel which would pass the standard tests.

It was found that heat treatment of oil at a temperature of 400° under a pressure of 200 lbs. per square inch, for a determined period reduced the solid hydrocarbon content without materially affecting the boiling point of the liquid treated.⁴⁾ When acted on as above for one hour, the solid paraffin in a Persian residuum fuel oil was reduced from 4 %

⁴⁾ Brit Pat. No. 156, 284 (1924).

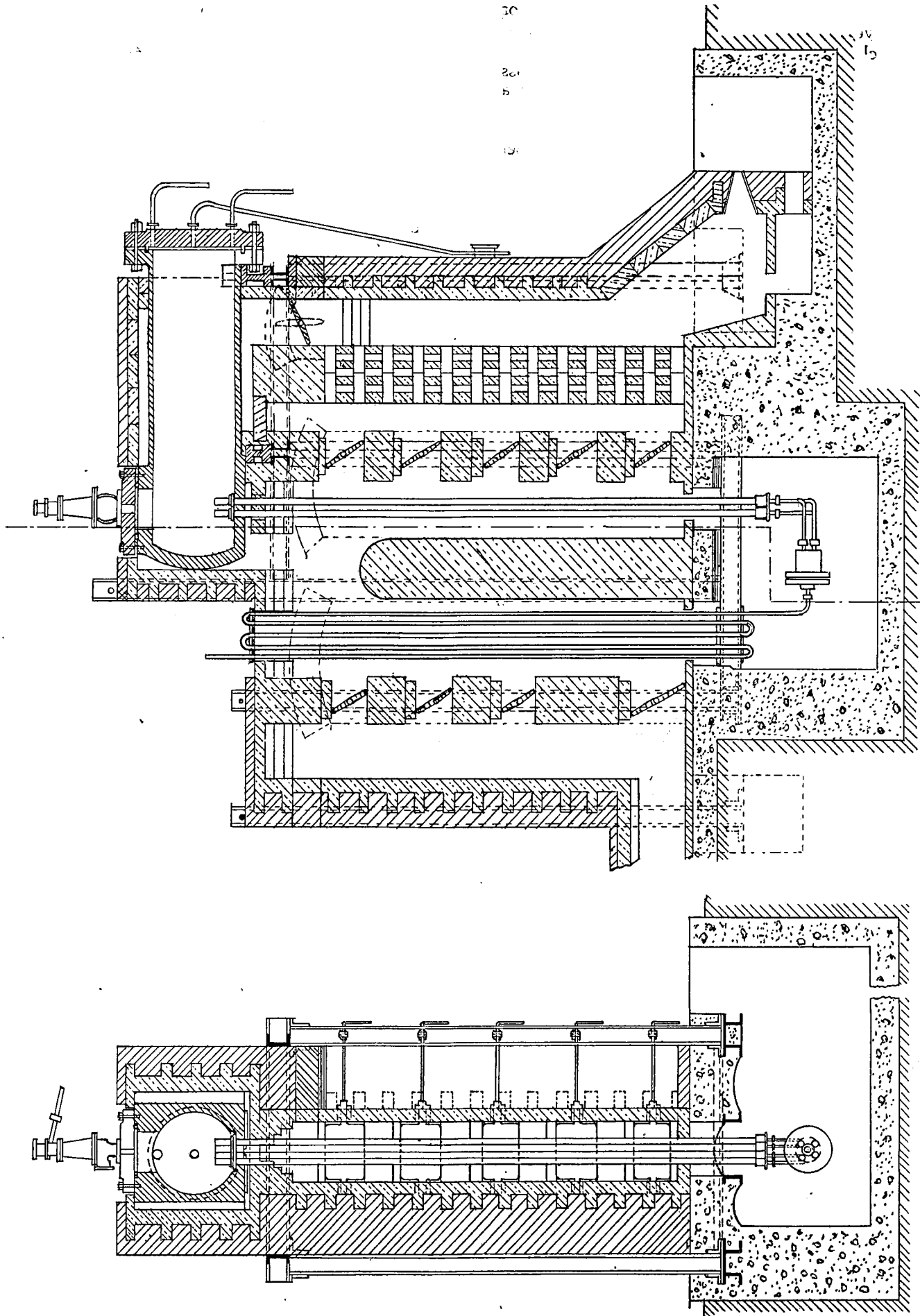


Fig. 4. Auld-Dunstan-Herring Plant.

to 0.25 %. Later the production of Petrol along with liquid residue was required, and further investigations led to the erection of a small plant which was altered and modified until it bore no resemblance to the original and thus the present Auld, Dunstan and Herring plant, for which a patent⁵⁾ has just been granted, was evolved.

The process is a liquid phase operation throughout and has advantages over the vapour or dual phase systems.

The quality and yield of spirit is better, temperatures are lower, the plant is easier to control and less gas is formed. The development of the plant has been governed almost entirely by the following points as basic principles.

(1). The pressure should be sufficiently high substantially to maintain the oil passing through the plant in the liquid condition for all but the lightest products; this can be attained by using pressures of the order of 25 to 30 atmospheres. This high pressure also directs molecular scission towards the middle of the molecule thus limiting the amount of gas and carbon formed.

(2). The yield of light spirit should be deliberately restricted. This for two reasons:—

(a). The retention of a considerable mass of the heavier oil helps to hold up the carbon formed and to move it forward to the point most suitable for its deposition, this is especially important when cracking asphaltic residues.

(b). The greater the extent of decomposition the lower the quality of light spirit or the greater the amount of gas and carbon formed. The reason for this is that the thermolytic decomposition of a paraffin hydrocarbon appears to proceed along definite lines and at the best, successive disruption of the paraffin molecules must increase the percentage of unsaturated compounds or at the worst produce gas and carbon. This explains why a cracked spirit is not so suitable as an uncracked one for the production of light products and why the number of times an oil can be cracked is limited.

(3). For each oil there is a definite and fairly well defined narrow range of temperature at which appreciable decomposition occurs. Above that temperature decomposition rapidly increases.

(4). There appears to be a marked time factor, which is a function of the temperature, governing the spirit. There is an appreciable lag between the moment of attaining the thermolytic temperature and the formation of the products, and the temperature must be maintained for a considerable time if the disruption is to proceed to the maximum extent corresponding to that temperature.

(5). It follows that the rate of flow of the oil must be a direct function of the temperature and controlled correspondingly.

(6). It is impossible to prevent the formation of carbon and this difficulty must be met by inducing the deposition of carbon in places suitable for its removal. The plant must, therefore, be of the simplest type with as few bends and corners as possible

where carbon can accumulate. Each part must be readily accessible for taking down or for cleaning. Local overheating, which must tend to produce highly undesirable conditions must be avoided.

On the basis of the above principles a general procedure has been developed.

Procedure.

The thermolysis of the heavy oil is carried out in three distinct stages, which in effect, are zones of temperature and rate of flow. In the first or preheating stage, the oil is carefully heated to a point, preferably not more than 250° C. below what we defined as its "Optimum temperature" which is the temperature at which the specific extent of decomposition occurs, once the molecular inertia has been overcome. In this stage the rate of flow is immaterial and the preheater can be of any form compatible with efficient temperature control.

In the second stage the oil is quickly raised to a temperature about twenty degrees above the optimum. This stage is very important and must be carefully controlled. It is here that advantage is taken of the time lag, to give the oil its impetus towards disruption without materially effecting decomposition. This portion of the plant termed the "Thermolyser" consists of a number of pipes in parallel of such a bore that the oil can be rapidly heated throughout its bulk and of such a length that the oil has passed through with minimum amount of actual decomposition or at any rate, of separation of carbon.

After leaving the thermolyser the oil passes forthwith to the "Reactor" (the third stage). This is a vessel of such dimensions that in passing through it the oil remains for at least the amount of time necessary to obtain equilibrium as regards the specific extent of decomposition required. By suitable means the reactor is maintained at or above optimum temperature. Owing to the endothermic nature of the reactions involved a certain amount of external heat must be supplied to do this. The position of the reactor is determined by the need of avoiding gas locks and shape by the accessibility necessary for cleaning. Since most of the carbon is actually formed in the reactor and since it is of considerable size and the oil in it fairly quiescent the bulk of the carbon produced in the process is deposited here. The cracked oil is drawn from the highest point of the reactor cooled or dephlegmated and discharged into a gas separator.

In order to carry out the process as specified the furnace and flues are so designed that control of the temperature is obtained in the three different heat zones. In the preheater the oil is raised to the desired temperature by means of waste gases from the thermolyser and reactor and controlled by means of flue dampers or by varying the rate of pumping the oil. In the thermolyser flue the temperature is controlled by dampers which regulate the supply of hot gases from the furnace. The temperature at this point in the process must be carefully controlled. Lastly the temperature of the reactor is maintained by admitting a regulated proportion of the furnace gases into the flue surrounding that vessel. The combined flue gases from the reactor and the thermolyser pass to the preheater. In this way the temperature of the heating

⁵⁾ Brit. Pat. No. 220, 664 (1924).

gases may be little higher than the oil temperature.

By reason of the manner in which the heat is applied the interval between the acquisition of the cracking temperature and the consequent reaction is prolonged and advantage is taken of this prolongation to raise the temperature above the mean cracking temperature. The lower the determined temperature of cracking the longer will be the interval between the acquisition of that temperature and the actual decomposition and the smaller the yield. Thus when using the same apparatus for different oils with different determined cracking temperatures, but approximately the same time factor, the yield of light spirit will vary by reason of the difference of temperature employed as well as by difference in the character of the oil. It is possible to vary the time factor by varying the rate of flow. Where the final temperature within the thermolyser is higher than the determined temperature, increase in the rate of flow prevents decomposition and deposition of carbon in the thermolysing tubes.

The process has among its objects to avoid secondary reactions, to reduce the amount of incondensable gas, secure light products of good quality, to restrict the quantity of light products whereby the vapours and gases are in a large measure dissolved in the treated oil in which part of the carbon deposited is relatively small in quantity and is not deposited in the thermolysing tubes where it would hinder the operation but is exclusively deposited in the reactor when it can be easily removed.

The capacity of the reactor is determined having regard to the rate of flow and to the maintenance of the liquid in the reactor for such a length of time that cracking to the desired extent is completed. This is usually effected within two hours when the yield of spirit is relatively moderate.

The process is continuous and is advantageously carried out under such conditions that a relatively moderate amount of gasoline is produced for the process was originally developed and the plant devised for dealing with Persian residues. Different kinds of oil, however, have been experimented with, for example, gas oil, which is a less difficult problem than residue, on account of the lower amounts of coke and gas formed although the temperatures required are higher. The oil used in this case was a typical gas oil of Specific Gravity .857 and initial boiling point 195° C. Yields of spirit varying from 10 to 30 % (200° end point) can readily be obtained, the yield varying with the temperature and rate of flow of the oil.

The cracking of Persian residue proceeded on similar lines and it is questionable if equally good results with asphaltic residues had previously been obtained at that date. In the cracking of heavy asphaltic residues the temperatures employed are lower than in the treatment of gas oil.

In the treatment of a viscous asphaltic residue in the plant, its temperature is slowly raised in the preheater to about 370° C. thence through the thermolyser where the oil is uniformly and gradually heated under precise temperature control to between 400 and 410° C. The oil then passes into the reactor where the temperature is maintained at about 390° C. The pressure is held at 400 lbs. per square inch and by this treatment 10 % gasoline is

produced together with a proportionate amount of kerosene. The residue has a viscosity of 340 seconds Redwood No. 2 at 30° F. The original oil had a viscosity of over 2,000 seconds under the same conditions. The coke amounts to less than 0.5 % and gas about 1.5 %.

In the treatment of gas oil the determined temperature within the reactor is 400° C. and in the thermolysing tubes 420° to 430° C. with the same rate of flow and pressure as in the cracking of oil. The gasoline produced amounts to over 20 %.

Scottish Shale Gas Oil in the same plant produces 24 % of gasoline at a temperature of 380° C. in the reactor, and 410° in the thermolyser. Coke amounting to 2.3 % and gas 5.5 %.

Heavy Mexican residue 0.931 Specific Gravity gives an 9 % yield of gasoline, at 370° C. in the reactor and 410° C. in the thermolyser. In this case cracking is maintained particularly low to avoid undue deposition of carbon. The coke amounts to 1.3 % and gas 1.2 %.

A test of Persian Gas Oil, on a 206-hours run, yielded 20.5 % gasoline, 2.8 % gas and 0.47 % coke. The operation in this case was brought to a conclusion, only through shortage of raw stock.

Under slightly different conditions of temperature and pressure kerosene and wax sweats have been cracked in the apparatus, the former yielding 41 % boiling below 175° C., and the latter 26 % boiling below 200° C.

This plant has thus successfully cracked kerosene, gas oil Scottish Shale oil, paraffin sweats, Persian and Mexican fuels, but like other plants it will not give a high yield of spirit from heavy residues and at the same time run for an indefinite period. The length of time it can operate is limited by the size of the reactor.

Yields of light spirit, of Engler distillation up to 200° C., can readily be obtained varying from 10 to 30 %. It will treat heavy residues, which will not pass the Admiralty test, producing a limited quantity of Spirit and a liquid fuel which does not gel on standing for a considerable time.

The *Bergius process* has attracted considerable attention, particularly in countries possessing much coal but little or no oil. The early work of Bergius led to the formation of artificial coal from cellulose, wood, etc.; these experiments were intended to reproduce the natural methods of coal formation by variations in temperature and pressure. He was successful in producing a black powder, the carbon content of which was 84 per cent. under a temperature of 349° C. and 160 atmospheres pressure. This substance possessed the properties of ordinary bituminous coal, and on further heating under pressure it passed to the anthracitic type. Bergius discovered that this substance was susceptible to hydrogenation by heating to 400° C. in the presence of hydrogen for some hours, and 70 per cent. of the product was soluble in benzene. In later experiments coal was mixed with oil, and it was found that natural coal was converted up to a 90 per cent. yield of oil, provided that the carbon content of the coal did not exceed 85 per cent.

The products were of the consistency of thin coal-tar which yielded fractions suitable as fuel oil.

In the cracking of oil by the usual methods gas

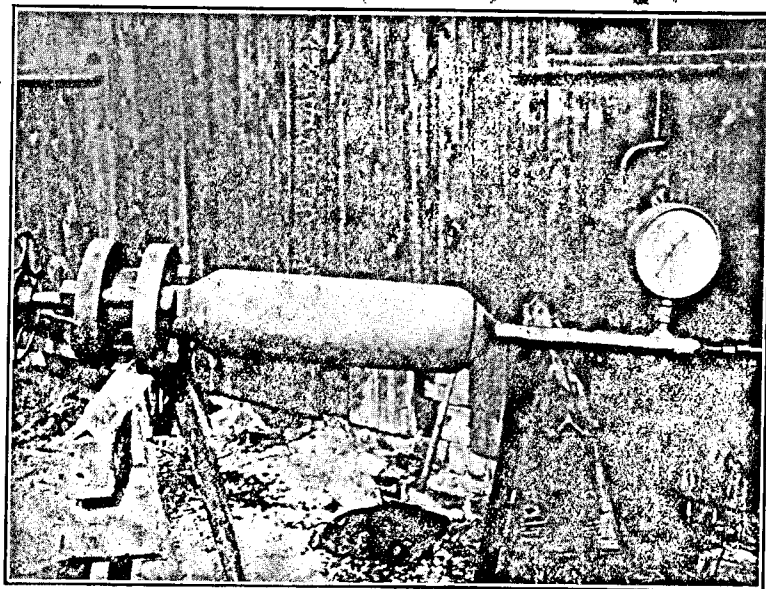


Fig. 5. Bergius experimental autoclave.

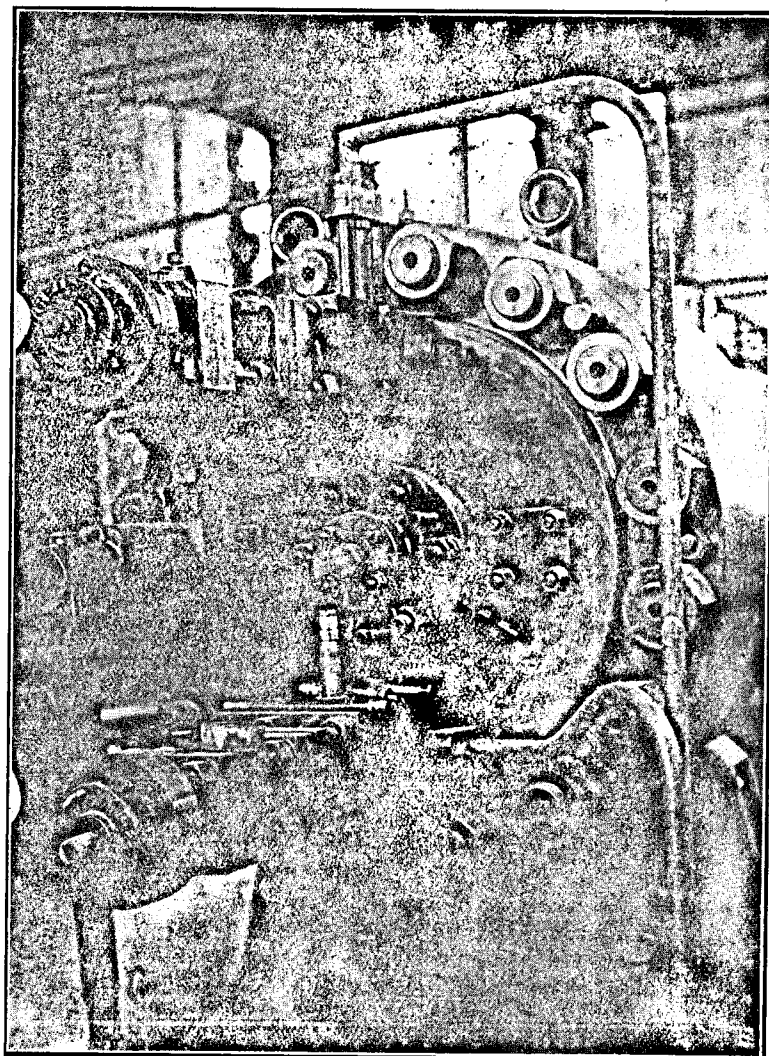


Fig. 6. End view of reaction chamber, Bergius large-scale plant.

and coke are produced, the latter being a great hindrance to the continuity of working, and, further, the higher the carbon content of the raw oil the greater is the amount of coke deposited in the cracking plant, and for this reason it is not commercially possible to crack heavy asphaltic oils or residues to give a high spirit yield. Bergius took up the problem, and by applying heat in the presence of hydrogen under great pressure stated that practically no coke and very little gas were produced when he cracked heavy oils at a temperature of about 450°C . and 100 atmospheres initial pressure.

Bergius developed a laboratory apparatus capable of withstanding very high pressures (fig. 5). The essential part of the plant being a simple linear joint, a double cone, making a metal to metal connection, was found to be efficient under the conditions of working.

The commercial unit differs little from the experimental plant. The apparatus employed consists of a heavy horizontal steel cylinder (fig. 6, 7 and 8). Inside the cylinder there is a cast-iron vessel and between them a current of highly-heated inert gas, CO_2 or nitrogen, at the same pressure is thus maintained by the outer shell.

Oil and hydrogen are preheated and sprayed into the autoclave continuously and the light products are removed as rapidly as they are formed, the high boiling fractions dropping back for further hydrogenation. The heavy residue is continuously withdrawn from the bottom of the vessel.

Heat exchangers are arranged for both the out-flowing products and the outer heating nitrogen.

The system of heating by means of inert nitrogen reduces the risk of accident and maintains a temperature which varies not more than 5°C . for weeks. Control is operated from a central switchboard placed some distance away. Safety of the operators is thus assured.

In the commercial working of the plant at Rheinau the preliminary laboratory experiment determines the best conditions for rapid and efficient hydrogenation. The autoclave is of 5 litres capacity and is charged with a weighed quantity of oil, hydrogen is pumped into a definite pressure and the vessel is heated for about an hour by gas jets and rotated in a horizontal position at about 60 revolutions per minute.

The pressure increases at first, but as hydrogenation proceeds it gradually falls off and eventually becomes more or less constant, thereby differing from the ordinary cracking process, where the pressure steadily increases, even when the temperature becomes constant (fig. 9). The apparatus is allowed to cool, and samples of gas are withdrawn for analysis, the amount of hydrogen absorbed being thus ascertained. The autoclave is finally opened and the contents weighed and distilled.

In the commercial unit the autoclave is thirty feet long and three feet in diameter, placed on concrete slabs sloping towards the closed end. It is fitted inside with a stirring device which penetrates to the far end. The heating is effected by passing nitrogen through coils, heated in a furnace, then through the annular space between inner chamber and the heavy steel wall of the autoclave.

The plant can deal with fifty tons per day, and as no carbonisation occurs continuous working for an indefinite period is practicable. The hydrogenation is in most cases accompanied by very little thermal change, but on the whole the reaction is believed to be slightly endothermic. The final pressure reached in some cases is as high as 280 atmospheres.

With regard to the hydrogenation of coal the continuity of the process is brought about by grinding the coal to pass a 400 per inch mesh sieve and mixing with oil. This mixture can be circulated by pump.

Bergius claims that any coal containing less than 84 per cent. carbon, on an ash free dry basis, can be successfully hydrogenated at a temperature of about 400° C. and pressure up to 200 atmospheres, with the production of hydrocarbons similar to petroleum distillates.

The hydrogenation of coals containing more than 84 per cent. of carbon has not been successful.

As an example of the work done by the Bergius plant a test made on a heavy residue may be quoted:—

The Properties of the ingoing oil were—

Specific gravity at 15° C. .896
 Viscosity at 20° C. .812 Engler
 = 237 Redwood.
 Flash point 77° C. = 171° F.
 Hard asphalt .84 per cent.
 Sulphur 1.02 per cent.

Engler Distillation—

I.B.P. 198° C.
 210° 1 per cent. by vol.
 250 6.5 " "
 Distillate p.c. = 23.7
 270 13.0 per cent. by vol.
 Distillate S.G. = .821
 300 27.5 per cent. by vol.
 Residue 75.7 per cent. by lot. sp.
 Loss .6. gr. .921.

The apparatus was run continuously and 4650 kilos. of oil were put through.

The yields were:—

Distillate 84 per cent.
 Residue 8 " "
 Gas 8 " "

The distillate contained:—

Benzine 30 per cent.
 Kerosene 25 " "
 Gas oil and fuel 37 " "
 Gas and loss 8 " "

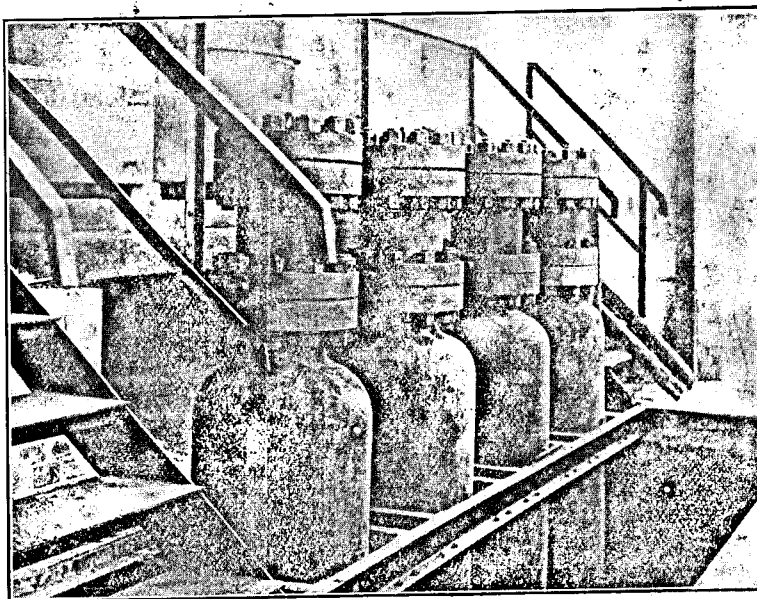


Fig. 7. Bergius commercial unit, showing joints.

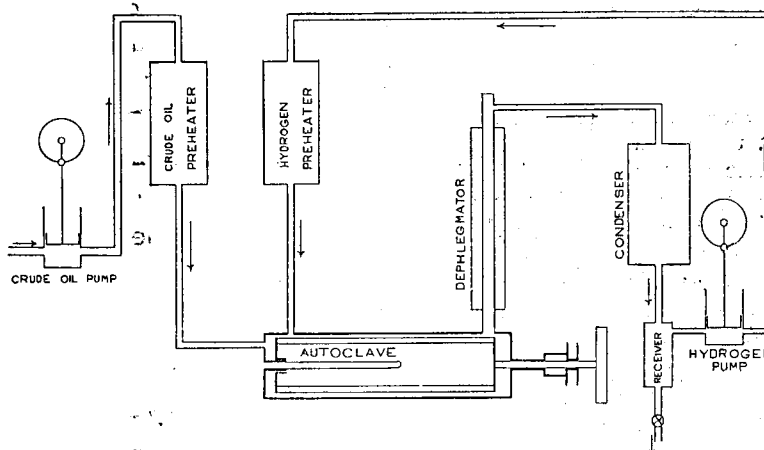


Fig. 8. Bergius commercial plant.

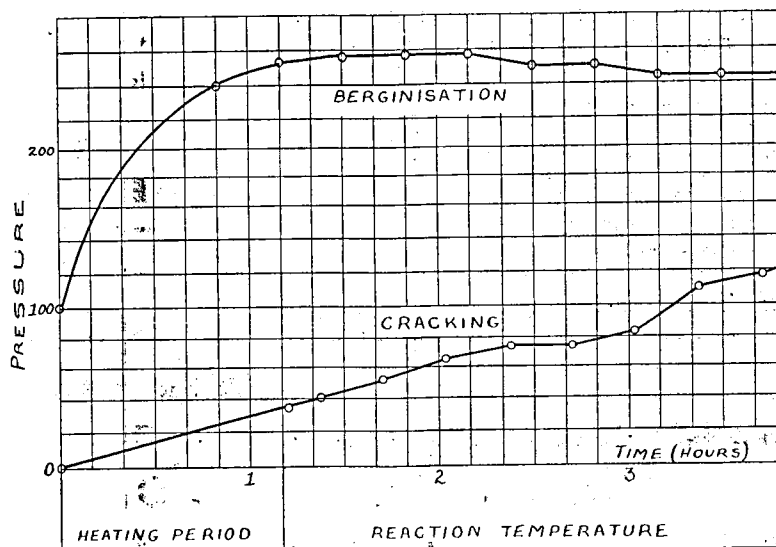


Fig. 9. Comparison of pressure curves for berginisation and cracking.

The hydrogen consumption was about 1 per cent. and the benzene after refining with less than 1 per cent. acid and soda was water white and contained .07 per cent. sulphur. The kerosene was slightly coloured and both benzene and kerosene had a pleasant colour. Fuel consumption was about 6.5 per cent. and the gas produced contained about as much free hydrogen as is required for the Berginisation of the oil.

Opinions differ as to Bergius's claims regarding hydrogenation of the liquid products produced by this process, and different investigators have been working on his method.

H. I. Waterman and J. N. J. Perquin are investigating the Bergius process from a chemical standpoint and their results published up to date lead to interesting conclusions.

They remark on the complexity of the subject and complain of the difficulty in comparing the unsaturation of products, the iodine and bromine values being vitiated by substitution effects.

Experiments on a fraction of Borneo oil and on Mexican asphalt at various temperatures and pressures with and without hydrogen showed no definite advantage in hydrogenation, although hydrogen disappears as shown by the falling pressure curve and the residues show a lower specific gravity than those of cracked products. For Borneo oil 403 to 410° C., for Mexican asphalt 385 to 390° proved to be the best temperatures.

The results of Berginisation do not differ greatly from those of cracking, the chief difference being the difference of gravity in the residue after distillation. The solid paraffin can be almost entirely converted into liquid and gas if time is given. The colour of the Berginised oil is red or yellow, whereas the cracked oil is opaque and very small in amount. Hydrogen is absorbed, the final pressure in the cold being less than the initial pressure and hydrogen has disappeared from the gas. The bromine value is somewhat lower in the Berginised oil.

Comparing experiments with hydrogen under high pressure, under low pressure, and in the nascent state with inert gas and with simple heating under autogenous pressure, it appears that the yield of oil is the same, and that very high pressures are required before hydrogenation takes place (fig. 10).

The pressure curves show that the pressure increases even after the temperature becomes constant in all cases except in hydrogenation experiments, so that hydrogen is evidently consumed, although the course of the pressure curves cannot be explained, as the nature of the reaction products or the chemical reactions taking place are not clearly understood.

Franz Fisher attributes hydrogenation of coal, by means of sodium formate and with carbon monoxide and steam, to the nascent condition of the hydrogen. This work was repeated with Mexican asphalt, but without material effect on the yield, distillation curves, or bromine value, as compared with simple cracking. No hydrogenation of paraffin wax was observed with water and carbon monoxide at a temperature of 420° and 113.5 atmospheres pressure. P. Bruylants states that asphalt at 50 atmospheres pressure gave 31 per cent. of spirit boiling between 35 and 150° C. All the hydrogen fixed was found in the gases.

Investigations have been made by ourselves com-

paring the effect of hydrogen and nitrogen in an autoclave similar to that of Bergius on both gas oil and fuel oil under pressure up to 135 atmospheres for three hours at a temperature of 410° C. The final pressures cold were higher in the tests with nitrogen,

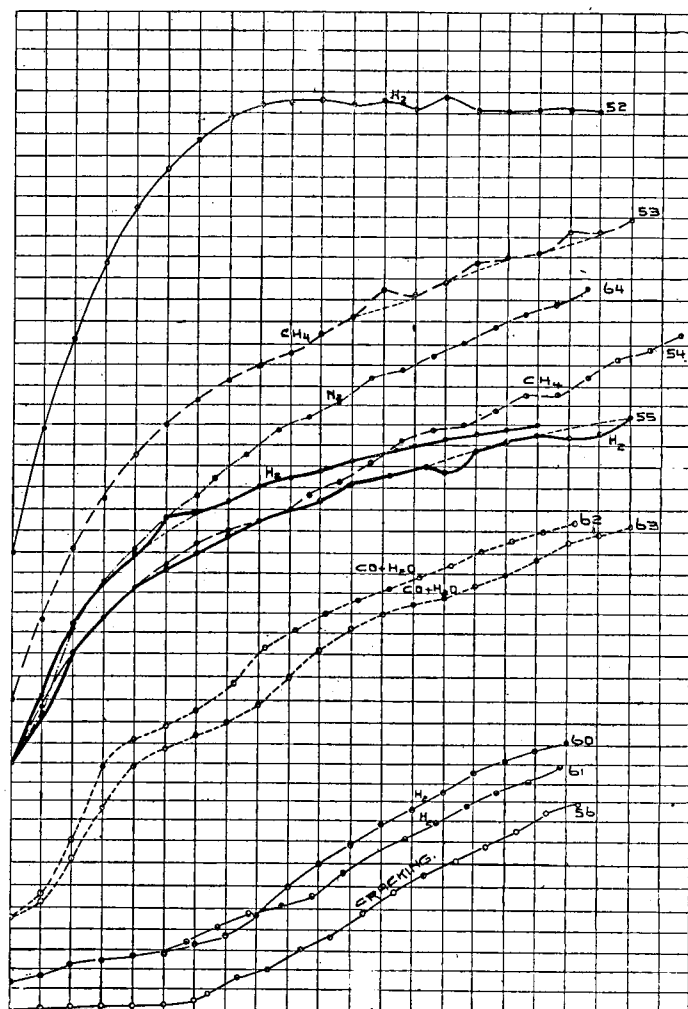


Fig. 10.

Curves illustrating the experiments of Waterman and Perquin.

the sulphuric acid value of the liquid product showed little difference, and ultimate analysis of the carbon and hydrogen gave the same result for both. The analysis of the gas showed very low unsaturated content, in the neighbourhood of 1 per cent., in both cases. The specific gravity of the residue after distilling to 200° C. was generally slightly lower in the hydrogenation experiments but not sufficiently definite as to rule out experimental error. It is evident, therefore, that hydrogenation of the liquid products is not definitely proved for pressures under 150 atmospheres, but it is possible that hydrogenation takes place at much higher pressures such as 300 atmospheres as indicated in Waterman's experiment, where the pressure curve becomes horizontal at about 280 atmospheres.

Recent work of an experimental nature has been conducted in the investigation of effects of temperature, pressure and rate of flow on cracking and in order to study closely these effects it has been necessary to construct special apparatus to obtain accurate control of the variables.

For this purpose a continuous working model, which can put through from three to twelve gallons

per hour, is in use (fig. 11). In this model the pressure can be maintained at a constant point and the temperature can be controlled to within $\pm 1^\circ \text{C}$. The oil is pumped through a coil heated by gas to a certain point below cracking temperature then passes

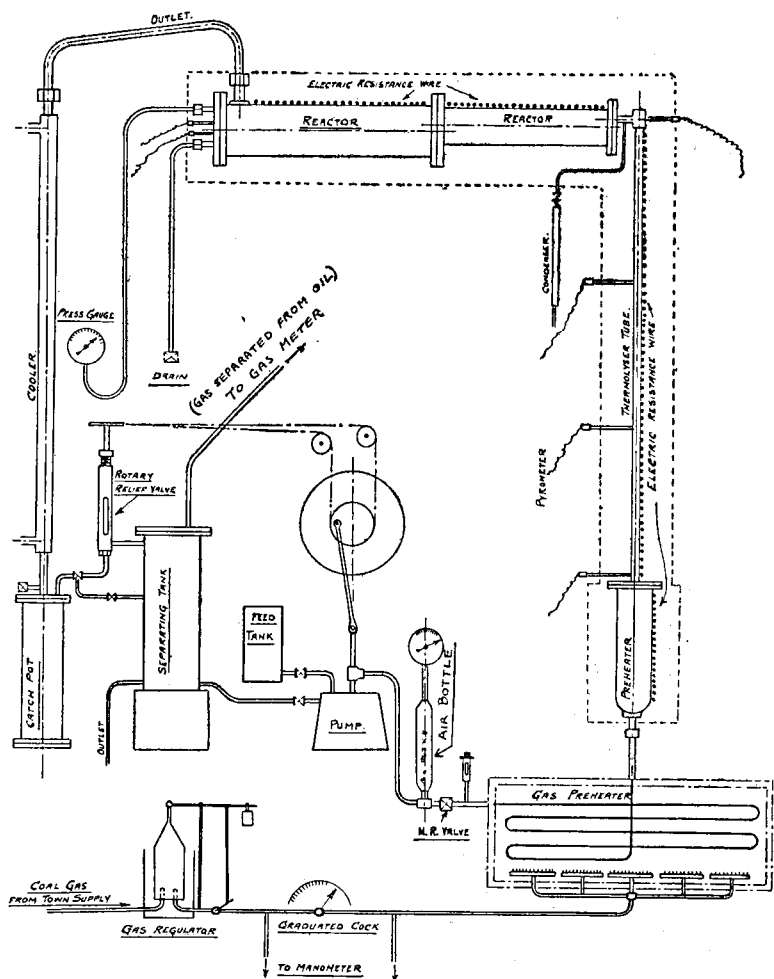


Fig. 11. Diagram of Anglo-Persian model plant.

into an electrically heated preheater thence to the thermolyser tube where the oil is heated above the mean cracking temperature. The oil is discharged into the reactor where the time factor has its effect. The reactor is in two parts, cylindrical in shape. The first is of smaller diameter than the second; and they are fitted together so that the smaller is on a higher level than the larger. The heating of the thermolyser and reactor is accomplished by electric windings in sections, two circuits to each section and each controlled by thermostat so that the plant has great flexibility. The oil, after leaving the reactor passes through a cooling tube and catch pot, then expanded into a gas separator. The oil flows to a stock tank and the gas passes through a meter to a gasometer.

A rotary relief valve of special design maintains the pressure, constantly at the desired point throughout the run of the plant. Pyrometers register the temperatures at five points (fig. 12) between the gas preheater and the top of the thermolyser tube, and two sliding pyrometers can explore the reactors from end to end.

A gas regulator maintains the heating gas supply at a constant pressure, in order to prevent fluctuations in the heat applied to the primary heating coil. The electrically heated parts of the plant are heavily

lagged to prevent radiation, and it is possible to set the working temperatures by means of the rheostats.

At present the plant is in use to determine more accurately the effect the temperature on the petrol yield, the effect of pressure, the effect of time and

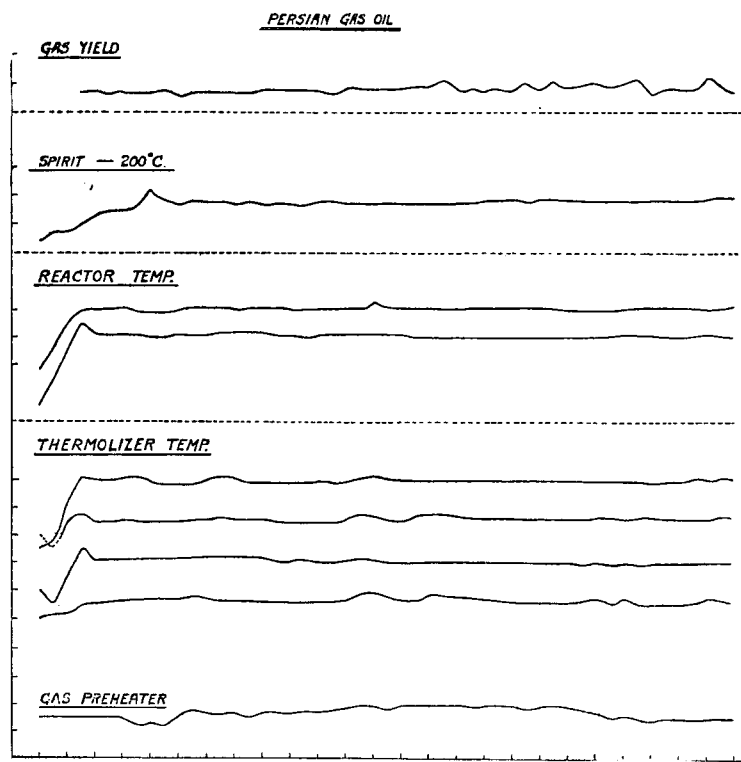


Fig. 12. Temperature curves, Anglo Persian model plant.

rate of flow and the manner in which coke is formed during the continuous cracking of different classes of oil.

Although results are by no means complete, certain progress has been made in these determinations.

The original oil for these experiments was Persian Gas Oil of specific gravity .850.

In the first series of experiments general observations were made on temperature and time effects on the petrol yield and in the quantity of coke and gas produced. A noticeable feature was the condition of the coke at the junction between the small and large sections of the reactor, where there is a straight drop of 3 inches. Evidently the coke had been thrown out of the liquid in the reactor, firstly as a liquid pitch which had flowed from the smaller reactor into the larger, decomposing as it flowed, and the coke at this point assumed the form of a cascade, and below that level the main body of coke had filled up the reactor to a certain level with a horizontal smooth surface. Above this surface no deposition to mention had taken place.

Again, on pyrometer pockets or other tubes projecting into the reactor deposition of coke had taken place on the upper surfaces and practically none on the under surfaces.

The temperature of the reactor in these series of experiments ranged from 410° to 440° and it appears that for the same oil at constant pressure and rate of flow there is a definite increase in the quantity of petrol produced per degree rise in temperature. For the range of temperatures examined it appears that for every 10°C . rise in cracking temperature this increase amounts to double the percentage yield of

spirit. On the other hand when the temperature and pressure remain constant the production of petrol varies inversely as the rate of flow. Double the rate of pumping reduces the percentage yield of spirit by fifty per cent. This again is with reference to the particular range of temperatures investigated. I am not yet prepared to state that the action proceeds regularly to the complete conversion of the heavy oil.

The manner in which the deposition of coke took place between the sections of the reactor is very interesting as it leads to the theory which has not previously been published, that in the course of cracking, asphaltic compounds are produced which are insoluble in the cracked oil and are, therefore, thrown out of solution, naturally as a liquid pitch of high specific gravity at the high temperature of the reactor. The temperature of the walls of the vessel is sufficiently high to continue the decomposition of this liquid pitch, with the evolution of gas and the formation of solid carbonaceous coke, which will contain a percentage of free carbon depending on the time in which it remains in contact with the sides of the vessel, for it is noticeable that the coke removed from the reactor after an experiment is more dense at the contact surface.

This decomposition of pitch and liberation of gas at the higher temperatures of cracking is more evident, in other words, with a low production of petrol there is a lower percentage of coke formed.

With regard to the temperature and time effect, in these experiments the rate of pumping was doubled and doubled again, with constant pressure and temperature maintained to the same degree, with the result that in each case the quantity of spirit was approximately 50 % of the amount for the lower pumping rate. But it appears to be more beneficial to pump at a higher rate, as at the higher rate of flow less carbon is produced than with a higher percentage of petrol at a lower pumping rate, and the total quantity of spirit per hour is at least equal, if not greater, at the lower pumping rate. This effect will be limited of course by the quantity of heat which can be transmitted to the oil.

Following up the observations of the first series of experiments a second series was conducted with especial attention to the question of coke formation and its possible elimination.

In one experiment where the temperatures of the heating elements of the reactor were particularly high it was observed that the heat was not transmitted throughout the oil but had only a surface effect and in order to correct this a stirring device was inserted into the reactor. This stirring device brought the contents to the same temperature throughout, but also had the effect of stirring the deposit of coke and caused choking at the outlet.

At a certain temperature and rate of flow it was observed that the outflowing liquid from the plant was muddy, as if it contained suspended matter. If the temperature were increased or the rate of flow decreased the outflowing liquid became clear and often of better colour than the original. When the latter happened it was understood that coke was in process of being deposited in quantity within the reactor, but if the former, it was estimated that only a small percentage of deposit was produced, and experiments were conducted to find if possible a

critical temperature of deposition.

The temperature of deposition, however, varied with the cracking temperature and the time factor.

Further experiments were carried out under the same pressure and at the same rate of flow but the reactor part of the plant was removed so that the thermolyser tube became the cracking zone and the preheater became a "segregator" for pitchy matter. The time factor was, therefore, different; and the essential parts of the plant were all in a vertical position.

The first results confirmed the observation that the pitchy substance was produced and flowed to the lowest level, for the coke formed in the plant had concentrated in the segregator, immediately beneath the thermolyser tube, to a depth of 12 inches, with practically no coke above that level, although there was clear evidence that it had run down the thermolyser tube into the segregator.

In view of this settling of the pitch or coke, means were provided for examining the oil at different points in the apparatus and samples taken from top middle and bottom showed different amounts of asphalt. (Estimated by precipitation with petroleum ether).

The original oil contained19 %
" outlet " " " " " " "	.4 "
" middle " " " " " "	1.5 "
" bottom " " " " " "	1.2 "

The bottom sample contained inflowing oil. Further results showed that with increasing temperature, the outlet oil became lighter in specific gravity while samples from the Segregator became heavier, thus:—

Temperature	Outlet Sample	Bottom Sample
390.	.850	.852
400.	.847	.852
410.	.845	.854
420.	.843	.869
430.	.836	.876

Samples drawn before choking took place .916
Asphalt 6.13 %

Samples drawn before choking took place .929
Asphalt 8.20 %

This result led to an attempt, under the same conditions, to keep the segregator clean by removing the heavy residue as fast as it was formed, to prevent its conversion into coke. The lower part of the segregator was kept comparatively cool in this experiment.

In the earlier stages of the trial similar results were obtained as before, and at the same temperature the same rise in Specific Gravity was observed. By drawing off the heavy residue the plant continued operating for a much longer period and the heavy residue did not attain the same density as in previous work.

With a temperature which yielded 30 % of Spirit the increase of Specific Gravity was noticeable at once, in the samples from the segregator. This effect steadily increased until specific gravity .926 was obtained. For the first time, a deposit of hard pitch, small in amount, was obtained, without coke, from the bottom of the segregator.

In this series of experiments an endeavour was made (1) to find if there is any critical conditions at which coke is deposited (2) to observe the manner in which coke is formed and deposited (3) to prevent the formation of coke in the plant by withdrawing heavy residue from the plant before carbonisation took place.

(1). There appears to be a critical stage at which the outflow becomes clear, and the most important factors which decide the occurrence of this phenomenon, appear to be percentage of spirit in the outflow, temperature in the reactor and a rapid reduction of pressure.

In comparison with small variations of pressure the mean absolute pressure has very little effect.

It seems probable that the evolution of gas from the body of the liquid, which steadily increases as the percentage of spirit and the temperature increase, assumes such proportions, particularly if the pressure is reduced, as to carry over a considerable proportion of the liquid in the reactor, resulting in a two-phase system. From this point high pressure distillation proceeds, giving a pale clear outflow, until the gas is forced out of the system by incoming oil when the outflow again becomes highly coloured and muddy from suspended asphaltic matter produced in the residue from the previous distillation. In this connection the relationship between the specific gravity and percentage of spirit in the product has been investigated and it appears that for normal heat treatment in the liquid phase, the relationship is best represented by a straight line of constant slope, passing through the point representing the original oil.

(2). Further confirmation was obtained that an intermediate product is formed of the nature of liquid insoluble pitch which ultimately cokes on continued heating but before carbonisation tends to flow downwards, owing to its high density. There is evidently a connection between the appearance of clear oil at the outlet and the heavy asphaltic residue at the bottom of the segregator. This only begins seriously to concentrate simultaneously with the clearing of the product. The residue contained a considerable amount of dissolved or suspended asphalt and, in one case, concentration by distillation yielded a residue of 16% soft pitch which contained 2% of sulphur and was almost completely soluble in carbon disulphide.

(3). The plant was altered for the purpose and efforts made to run off pitchy residue as it formed and before it had time to decompose into solid coke, and in the last experiment, the plant continued operating for six hours after the appearance of the heavy compounds and during this period the asphaltic residue was withdrawn completely from the bottom of the segregator.

The Refining of Cracked Products.

The difference between straight run spirit and the product from cracking processes entails a different method of refining, and in order to find a suitable economical process there has been a considerable amount of investigation during the last few years.

The nature of cracked spirit varies, on account of the varying composition of the raw materials and the different conditions under which it is formed. The conditions appear to have more effect than the raw material, and there is one outstanding fact which is impressive, and that is, the difference in the composition of the products obtained by vapour phase and liquid phase processes.

In vapour phase cracking, usually carried out under atmospheric pressure, the product is highly unsatu-

rated and contains compounds which render it most difficult to refine with ordinary refining agents.

Much of the earlier work, of course, was concerned with vapour phase spirit. Much of such spirit is very poor in quality and deposits large amounts of gum on standing. Refining methods for this spirit must be drastic; losses are great, and the final products are as a rule of inferior quality. The treatment of liquid phase cracked spirit is more simple and numerous methods have been devised which result in the production of water white gasoline of inoffensive smell.

As most of the cracked gasoline produced at present is more or less liquid phase the experiments carried out have been mainly concerned with products of that type, and it is noticeable that the spirit is similar in general behaviour, whatever the original stock employed, except in the sulphur content, which is to a great extent directly proportional to that of the raw stock.

The freshly distilled spirit is almost white, but goes off colour on standing, becoming brown and slowly depositing a reddish-brown gum. This gum is different in character from the typical gum of a vapour cracked oil. It is granular instead of liquid, the quantity is less, and in appearance is similar to the polymerised product formed when kerosene is exposed to light and air. The colour is different, having none of the light yellow shade so characteristic of vapour cracked spirit.

The total loss to sulphuric acid (100 per cent.) in the case of a liquid phase spirit from Persian residue was 22 per cent., and from an American gas oil 25 per cent. A vapour phase cracked spirit lost over 70 per cent. with the same treatment.

Various refining agents have been proposed for the purification of cracked oil such as silica gel, aluminium chloride, bauxite, fuller's earth, etc.

Plain filtration through contact agents such as bauxite, silica gel, etc., does not give a satisfactory result.

When cracked spirit is slowly distilled over small quantities of crushed anhydrous aluminium chloride the distillate, after washing with soda to remove hydrochloric acid, is of good smell, water white and stable. The process is simple and effective. Unfortunately the non-volatile polymerised bodies formed in quantity in the still are very resinous and deposit on the walls as a sticky mass difficult to remove and involving loss of aluminium chloride. So far these inherent difficulties have not been overcome. Recovery of aluminium chloride is also difficult (compare the cracking processes involving its use), and the operation therefore likely to be expensive.

The use of anhydrous zinc chloride for refining cracked spirits has also been patented, and its action is similar to aluminium chloride, much less drastic, but the problem of refluxing or distilling over this solid is the same.

A modification of this process wherein the zinc chloride was mixed with an equal quantity of zinc dust showed a limited saturation effect and considerable mechanical advantage, for the mixture remained dry and could be handled with an ease impossible with the zinc chloride above. Polymerisation is slower and more even. The distillates were colourless and of good smell.

When cracked spirit at ordinary room temperature

is mixed with bauxite, floridin, activated charcoal, or other porous materials of a similar nature, polymerisation of the most unsaturated compounds present takes place with evolution of heat. The reaction proceeds more vigorously if the contact material is maintained at an elevated temperature, and if kept at a few degrees above the final boiling point of the liquid so that the reaction takes place in the vapour phase the products of polymerisation are retained in the contact material and a colourless, sweet-smelling condensate is obtained which has lost its tendency to form gums. In this operation the contact material becomes clogged with the polymerised gum, which is difficult to remove and may cause choking of the filters. It has been found that by working at about 100° C., and thus maintaining the spirit substantially in the liquid phase, polymerisation takes place equally as well as in the vapour phase. The polymerised products, however, are washed out by the oncoming material, and by this means the contact material is kept clean and free to continue work for a longer period than would otherwise be the case. On issuing from the filters the spirit is of a much darker colour than originally, since it contains the original volatile gum-forming constituents dissolved in the form of non-volatile gums. By means of a simple distillation, therefore, the latter are left behind in the still, and a colourless, sweet-smelling and non-gumming product is obtained.

The contact material can be steamed out and roasted, and is then ready for further use. This part of the process is identical with that in use for recovering bauxite after kerosene filtration and presents no difficulties.

The result of the treatment is to lower the amount boiling below 100° C. by about 2 per cent., as compared with the untreated material, but otherwise the boiling points are identical. The sulphur content is reduced from about 0.3 per cent. to about 0.15 per cent., but the product remains quite stable in bright sunlight for many months without gum formation or reversion in colour. A sample made from a vapour phase gasoline has already successfully withstood twelve months' exposure in a window with a south aspect.

Cracked spirits treated with strong sulphuric acid give acid tars in quantity varying with the unsaturation of the spirit and the amount and concentration of the acid used. The spirit undergoes loss both by actual removal of unsaturated and polymerisable bodies and by the raising of its boiling point by polymerisation of some of the compounds present. The residual spirit can be obtained water white and non-gumming and with a lower sulphur content. The smell is altered and is peculiarly terpenic in character. The ordinary American practice is to use 1 per cent. or 2 per cent. of C.O.V., but with bad cracked products as much as 4 per cent. or 5 per cent. is sometimes needed to give the desired results. The losses are then proportionately greater and the peculiar smell of the spirit more marked.

During the acid treatment alkyl sulphates are apparently formed, and these cannot be removed by soda washing, and, if left in, may cause the subsequent reversion of the spirit. They must be removed by distillation, but during distillation they generally decompose and sulphur dioxide is formed.

The effect of different proportions of acid have been investigated and samples have been treated with ½ per cent., 1 per cent. and 2 per cent. of acid.

The sulphur content was reduced in direct proportion to the amount of acid used, the original being .102, ½ per cent. .06, 1 per cent. .04, 2 per cent. .02. Sulphur dioxide is formed in the redistillation of the treated spirit, and the greater the treatment the greater the amount of SO₂ evolved. This effect takes place about 130° to 140° C. and is accompanied by darkening of the liquid due to the separation of a finely divided carbonaceous solid.

A combined treatment with acid and bauxite has been investigated and petrol obtained by methods involving a hot bauxite treatment, 1 per cent. acid and soda, bauxite filtration and redistillation has good stability showing no signs of reversion, and the smell is more like straight run spirit than any hitherto handled.

Of all the methods tried the sulphuric acid and soda, redistillation, and a final soda wash is probably the most economical.

Another method of treating cracked products has been patented by R. H. Brownlee, whereby oil of high flash point, high viscosity and low cold test is obtained by polymerisation of a light unsaturated oil, such as gas oil from synthetic crude, by agitating it with a catalyst at 200° to 400° F. AlCl₃, HCl, or a halide, or reagents which will produce a halide, in its vapour state.

The light hydrocarbon is purified by treatment with sulphuric acid and then acted on by the catalyst in a vessel provided with an agitator and a heating coil. In about 1½ hours the action is complete and the sludge is allowed to settle off. The oil is cooled, soda treated to precipitate colouring matter and washed with water, then distilled with the aid of steam.

The distillate includes products having the flash points of naphtha and kerosene and a number of lubricating oils which have a very low cold test.

Anglo-Persian Oil Co., Ltd., Research Department,
Meadhurst, Sunbury-on-Thames, England.

BOEKAANKONDIGINGEN.

631.15(022)

Emil Aberhalden, Handbuch der biologischen Arbeitsmethoden, Abt. XI, Methoden zur Erforschung der Leistungen des Pflanzenorganismus, Teil 3, Heft 1.: Methoden zur biochemischen Untersuchung des Bodens, von J. Stoklasa (Lieferung 145); Urban & Schwarzenberg, Berlin/Wien, 1924; 262 blz.; Mk. 9.60.

In de inleiding (14 pp.) neemt Stoklasa o.a. stelling tegen sommige Russische onderzoekers, die meer nadruk leggen op chemische en fysieke processen bij de voedselopname door gewassen, terwijl hij wijst op het belang der bacterieele processen. In een later gedeelte heeft hij nog een polemiekje over de prioriteit van deze laatste meening, waar hij zich deze tegenover Hesselink van Suchtelen toekent.

Afdeeling I behandelt het biophysisch en biochemisch bodemonderzoek (105 pp.).

Afdeeling II behandelt het bacteriologisch bodemonderzoek (77 pp.).

Een afzonderlijk hoofdstuk hiervan is gewijd aan de biologische absorptie, een, volgens S., miskend onderdeel,

waaronder hij verstaat de assimilatie van ionen door levende micro-organismen, en wél te onderscheiden van chemische absorptie.

Afd. III behandelt eigenschappen en aard der organische stoffen in den bodem (60 pp.), waarin veel eigen werk wordt beschreven.

Afd. IV wijdt enkele p.p. aan een biochemische bepalingmethode van P_2O_5 en K_2O , welke in een zoodanigen toestand in den bodem voorkomen, dat ze opgenomen kunnen worden.

Het geheele werk door wordt met een zeer uitgebreide literatuur voeling gehouden, terwijl de werkzaamheid van den schrijver op het behandelde gebied gedurende eenige tientallen van jaren een waarborg biedt, dat de behandeling bij den schrijver in goede handen is geweest.

Bij vele onderzoekingsmethoden die beschreven worden zal men wel andere „Lieferungen" van dit standaardwerk der „biologischen Arbeitsmethoden" moeten raadplegen of andere boeken, wanneer men zelf aan het onderzoeken gaat. Deze korthed in sommige opzichten is intusschen eerder een voordeel voor het besproken boek dan een nadeel: een „receptenboek" is het niet geworden.

A. Massink.

* * *

663.6(022)

Allan A. Pollitt, *The Technology of Water* (Chemical Engineering Series); London, Benn Ltd., 1924; 158 pgs. 16° geb. sh. 6.

Wie een aardig boekje wil hebben, keurig uitgevoerd en met een uitstekend (al is het dan ook betrekkelijk populair) overzicht over alles wat water betreft, kan dit boekje met vertrouwen aanschaffen. Het behandelt eerst de natuurlijke wateren, die voor de industrie (en voor drinkwater) in aanmerking komen, dan het water voor de belangrijke industriën, drinkwater en de behandeling van het water, om het voor de diverse toepassingen geschikt te maken. Het boekje heeft alles voor en niets tegen, behalve de prijs.

J. F. van Oss.

* * *

667.212(022)

E. Ristenpart, *Chemische Technologie der organischen Farbstoffe*; 2e verbesserte Auflage mit 21 Abb., analytische Tabelle und 12 Mustertafeln mit 81 Ausfärbungen; Leipzig, Barth, 1925, 299 pgs. 8° geb. Mrk. 15.

Voor velen, die iets willen weten over het groote gebied der kleurstoffen in den vollen omvang, zonder te kunnen beschikken over de speciale literatuur der onderdeelen, zal dit boek een welkome aanwinst zijn. In de eerste 10 pgs. wordt een kort overzicht gegeven over de teer en zijne bestanddeelen, waarin, ondanks het kleine bestek, reeds zeer veel behandeld is.

Van pg. 12 tot pg. 31 wordt behandeld het chloreeren, nitreeren, sulfoneeren en oxydeeren der grondstoffen. Naast schemata worden telkens afbeeldingen der te gebruiken apparaten gegeven. Daarna komt tot pg. 68 een stuk over de verdere tusschenproducten, verdeeld in de hoofdgroepen: de reductie der nitro- tot aminogroepen, de kalismelting der sulfonzuren tot phenolen, de vorming der naphtholen, invoering van hydroxylgroepen, vorming van aminen en amino-phenol, het alkyleeren, het ary-leeren, het azyleeren en de vorming van oxy-carbonzuren.

Hoofdstuk III loopt van pg. 68 tot 263 en begint met het geven der hoofdbegrippen en met een kort overzicht over de kleurentheorie van Ostwald, die in het korte bestek toch duidelijk uiteen is gezet en voorzien is van de juist voldoende kleurmonsters. De groote Duitse en Zwitsersche kleurstoffabrieken worden in het kort (tot den oorlog!) besproken met opgave der hoofdproducten; ook de statistiek loopt slechts tot 1913 en is dus tegenwoordig van geenerlei waarde meer.

In het algemeen beperkt dit hoofdstuk zich blijkbaar tot de vooroorlogsche periode en wordt het later niet-Duitsche werk genegeerd, hetgeen ook uit de bibliografie te zien is, terwijl de statistieken wanhopig achter zijn.

Na de behandeling der kleurstoffen, verdeeld in de gewone groepen, volgt een hoofdstuk over kleurstof-analyse volgens chemische en physische methoden en zoowel voor de kleurstoffen zelf als voor de gekleurde vezels. Alles is kort gehouden, maar in vele gevallen zullen de gegevens goed bruikbaar zijn. Zonder twijfel heeft ook de atlas van 12 kaarten met een aantal gekleurde monsters met inlichtingen er over (zelfs de fabrieken) zijn aangegeven) heeft waarde.

Het boek kan velen goed te pas komen en is voor onzen tijd niet duur te noemen.

J. F. van Oss.

* * *

621.72:658.2(021)

The Planning, Erection and Operation of Modern Open Hearth Steel Works, by Hubert Hermanns; Ernest Benn, Limited, London, 1924; 273 illustrations, 28 tabellen, 300 pag. Prijs: geb. 42 sh.

Een boek, geschreven door den Duitser Hermanns en in het Engels vertaald door Wesley Austin. In de ijzeren staalfabriceerende bedrijven, zowel uit een oogpunt van aanleg als van bedrijf, is het transportvraagstuk van primair belang. In een openhaard bedrijf, dat 250 ton grondstoffen per dag verwerkt, moeten deze quantiteiten op de meest economische wijze worden aangevoerd en de producten worden afgevoerd. Wanneer dit transportvraagstuk niet behoorlijk is opgelost, geeft het niets of de ovens zelf hun werk perfect verrichten. Het bedrijf zal dan toch stagneren. Het nieuwe in dit boek is, dat het de transportkwestie en daarmee samenhangend dus het ontwerpen van openhaardfabrieken in het middelpunt der beschouwing plaatst. Het mechanische en civiel-bouwkunstige deel neemt er dus de voornaamste plaats in. Een hoofdstuk over „details of equipment" behandelt de gebouwen, de constructies van verschillende types van openhaard ovens, generatoren en hulpmachines voor gieten, laden, lossen en transport. Een hoofdstuk over de inrichtingen voor het verminderen van warmteverliezen sluit zich daarbij aan.

Dit boek heeft ongetwijfeld grote kwaliteiten en menig vakman zal het grote aantal plattegronden en verticale doorsneden van staalfabrieken uit de werkelijkheid, met veel belangstelling bestuderen.

De schrijver richt zich en terecht, tot de staf van staalbedrijven en deze zal zonder twijfel van schrijvers zorgvuldige compilatie veel plezier beleven. De schrijver hoopt ook op succes bij studenten aan Technische Hogescholen. Dat ook zij er enig nut van zullen hebben is waarschijnlijk; toch komt het boek voor hen in menig opzicht tekort. Een compilatie toch heeft vooral zijn nut voor de vakman, die de hoofdzaken van het bedrijf reeds kent en in staat is de plattegronden en doorsneden met kritiek te beoordelen. Maar de student beschikt daarover nog niet en hem moet juist de kritiek gegeven worden. En om dat te kunnen, moet men leidende principes en axioma's aangeven, beginselen en methode. Dat alles zal men echter in dit boek tevergeefs zoeken en het nut er van voor studenten moet daarom, volgens mijn wijze van zien, gering zijn.

Om een voorbeeld te noemen. Ook het transport in de fabriek heeft haar theorie. Kruisingen moeten zoveel mogelijk worden vermeden, opdat verschillende transporten elkaar niet zullen kunnen ophouden. Een vraag is of vervoer in vele kleine eenheden voordeliger is dan in weinig grote. Verder is zo'n fabriek in zeker opzicht een gewoon spoorwegstation, dikwijls gecombineerd met een havenbedrijf. Ook daarvoor zijn algemene grondslagen van bedrijf. De overwegingen of zo'n fabriek als door-gaand of als kopstation moet worden gebouwd, spelen hier bijv. een rol. Over de voor- en nadelen van beide,

evenmin over de hiervoor genoemde vraagpunten, vindt men in dit boek iets.

De chemië-techniese beschouwingen in het boek dragen een kinderlijk karakter en verraden de werktuigkundige of civiel ingenieur, die hier op glad ijs is. Dit komt echter in de literatuur op het gebied van staal en ijzer meer voor.

Neen, een studieboek is dit niet. Wel een goede aanwinst voor de bibliotheek van de vakman.

De uitgave is uitstekend verzorgd; papier, druk en inbinden laten niets te wensen over. Een bibliografie en index besluiten het werk.

A. Korevaar.

* *

Chemie der Zelle und Gewebe, Zeitschrift für die Probleme der Gärung, Atmung und Vitaminforschung, neue Folge der Zeitschrift für technische Biologie, herausgegeben von Hugo Haehn — Berlin; Bd. XII Heft 1, November 1924; Borntraeger; Berlin; Subskriptionspreis 6.— Goldmark.

In 1912 verscheen het eerste nummer van het Zeitschrift für Gärungsphysiologie, allgemeine, landwirtschaftliche und technische Mykologie. Na eenige jaren van bloei begon dit tijdschrift te kwijnen wat er toe leidde, dat Band VIII in 1919 verscheen onder den nieuwen titel van Zeitschrift für technische Biologie, waarmede uiteraard een wijziging in de strekking van het tijdschrift gepaard ging. Deze wijziging bleek intusschen geen verbetering te zijn, want ondanks het feit, dat er een aantal belangrijke technisch-biologische verhandelingen in verschenen, verraadden de laatste afleveringen een onmiskenbaar gebrek aan copie. De uitgevers zijn thans overgegaan tot een nieuwe reorganisatie, tengevolge waarvan thans Bd. XII onder den bovenvermelden nieuwen titel verschijnt. Eensdeels is men dus tot den aanvankelijken opzet teruggekeerd, maar daarnaast heeft men het uitermate gelukkige denkbeeld gehad het tijdschrift tevens dienstbaar te maken aan het onderzoek op het gebied van de stofwisseling der hoogere organismen. Aangezien er geen twijfel mogelijk is omtrent het bestaan van een gemeenschappelijke kern in de stofwisseling van zoowel lagere als hoogere organismen, is het ongetwijfeld van groot belang, dat de chemische physiologen van alle richtingen door het nieuwe tijdschrift er toe zullen worden gebracht, onderling meer dan tot nu toe nauwe voeling te houden. De namen van de medewerkers, waarvan hier slechts H. von Euler, W. Küster, O. Meyerhof, L. Michaelis, S. P. L. Sørensen en O. Warburg mogen worden genoemd, doen de beste verwachtingen koesteren aangaande het welslagen van dit nieuwe periodiek.

A. J. Kluyver.

* *

Allgemeine Technische Mikrobiologie I Teil: Die Mikroorganismen; von Prof. Dr. Alexander Janke, Technische Hochschule Wien. Mit 10 Abbildungen und einer Tafel. Verlag von Theodor Steinkopff, Dresden und Leipzig, 1924; 342 pag. Prijs ingen. Mk. 12.—.

Dit boek vormt Band IV van de „Fortschritte der Chemischen Technologie in Einzeldarstellungen“, welke onder redactie van Prof. Dr. B. Rassow te Leipzig bij den bekenden uitgever Steinkopff verschijnen. Deze omstandigheid zou doen verwachten, dat het de bedoeling van den schrijver zou zijn geweest een overzicht van de „microbiologische technologie“ te geven, iets waaraan zeker groote behoefte bestaat, daar de laatste deugdelijke samenvattingen op dit gebied reeds van 1913 dateeren. Uitdrukkelijk zij daarom vermeld, dat bij den titel van dit boek de nadruk geheel moet vallen op de woorden „Allgemeine Mikrobiologie“, terwijl de opneming van het woord „technische“ alleen gerechtvaardigd wordt door het feit, dat de meerdere of mindere betekenis der verschillende organismen voor de techniek van invloed is geweest op de keuze, welke organismen meer of minder diepgaand

zouden worden behandeld. Het thans verschenen eerste deel behandelt de morphologie en systematiek der microben, benevens de physiologie der voortplanting en de prikkelwerkingen. In een later uit te geven tweede deel zullen de stofwisselingsprocessen worden behandeld, terwijl ook nog een afzonderlijk werkje over sterilisatie en conserveringstechniek in uitzicht wordt gesteld.

De stof is in drie onderdeelen gesplitst: Het eerste behandelt de bacteriën en Actinomyceten (81 blz.), het tweede de eigenlijke schimmels (190 blz.), het derde geeft een beknopt overzicht van enkele belangrijke algen, korstmossen, slijmzwammen, protozoa en ultramicroben (32 blz.). Zooals uit de gegeven cijfers blijkt, valt het zwaartepunt geheel op de behandeling der schimmels, terwijl de uit technisch oogpunt toch zeker belangrijker bacteriën vrij stiefmoederlijk zijn bedeed. Dit geldt in het bijzonder voor de systematiek dier organismen, waarbij in hoofdzaak aan het verouderde systeem van Migula is vastgehouden, dat, wat de belangrijkste reeks der Eubacteria aangaat, op zuiver morphologische kenmerken is gebaseerd. Men had mogen verwachten, dat een dergelijke primitieve en eenzijdige indeeling in 1924 als overwonnen zou zijn beschouwd. Om deze reden kan dit boek als inleiding tot de studie der technische bacteriologie niet worden aanbevolen. De hoofdstukken over den vorm, de voortplanting en de inhoudsbestanddeelen van de bacteriën, alsmede het geheele onderdeel, dat de eigenlijke schimmels behandelt, zijn daarentegen als zeer geslaagde samenvattingen te beschouwen. In het bijzonder moge worden gewezen op de uiterst groote hoeveelheid literatuur, vooral van de laatste tien jaren, welke in het boek is verwerkt, waardoor het voor iederen microbioloog een betrouwbare gids bij verdere studie zal kunnen zijn.

A. J. Kluyver.

* *

Michel Petrovitch, Durées physiques indépendantes des dimensions spatiales; Zurich, Jean Frey; Paris, Blanchard, 1924; 28 blz.

Op blz. 9—20 bespreekt de schrijver een zeer mooie, zuiver elektrische methode, door G. Lippmann in 1887 aangegeven, om de tijdseenheid vast te stellen. Daarbij komt hij tot het besluit dat de zoo experimenteel gedefiniëerde tijdseenheid even lang uitvalt voor alle laboratoria die t. o. v. elkaar een eenparige beweging hebben. Heeft de schrijver gelijk, dan is de bijzondere relativiteitstheorie fout, want een vergelijk van zijn tijdseenheid met het trillingsgetal van de natriumvlam zou ons de gelegenheid geven om uit te maken, hoe snel de aarde in verschillende jaargetijden door de lichtaether vliegt. Merkwaardig genoeg vermijdt de schrijver het conflict met de relativiteitstheorie te onderstrepen.

P. Ehrenfest.

* *

A. Henderson, A. W. Hobbs and J. W. Lasley Jr., The Theory of Relativity, Studies and Contributions of the Department of Mathematics in the University of North Carolina. Chapel Hill, N. C., U. S. A.; The University of North Carolina Press; London: Humphrey Milford; Oxford University Press; 98 blz., 6 fig., Prijs 11/6 sh.

Na een inleiding over de experimenteele grondslagen en de kinematica van de bijzondere relativiteitstheorie geeft dit aardige boekje voornamelijk een uiteenzetting van de wiskundige hulpmiddelen van de algemeene relativiteitstheorie en een vergelijking van de daarin optredende „krommingstensoren“ met de overeenkomstige grootheden in de gewone oppervlaktentheorie. — Men vindt in dit boekje echter ook een zeer zorgvuldige bespreking van de experimenteele bewijzen van Einsteins theorie.

P. Ehrenfest.

* *

5301(022)

Vicomte de Güell, L'espace, la relation et la position, Essais sur le fondement de la géométrie; Paris, Gauthier Villars 1924; 139 blz.

De levendige discussies over ruimte en tijd die Einsteins werk in het leven geroepen heeft, brengen den schrijver er toe, beschouwingen die hij in 1900 reeds gehouden had, te publiceren. Op blz. 1-43 wordt nagegaan de ontwikkeling van de begrippen ruimte en tijd van af de Grieken tot aan Newton en Kant, op blz. 47-93 hun modificatie in de niet-Euclidische meetkunde en bij Einstein. Op blz. 94-139 wordt een poging geschetst tot nieuwe axiomatisering van de Euclidische meetkunde als wetenschap van positierelaties, waarbij bv. heelemaal in 't begin de rechte lijn ingevoerd wordt als „système de positions dans une direction inaltérable” en later twee evenwijdige lijnen als lijnen „qui ont la même relation de position par rapport à une troisième qui les coupe”. Zoo'n onuitgewerkte schets is natuurlijk moeilijk te beoordeelen.

P. Ehrenfest.

* * *

016: 5301(022)

Maurice Lecat, Bibliographie de la relativité suivie d'un appendice sur les déterminants à plus de deux dimensions, le calcul des variations, les séries trigonométriques et l'azéotropisme; Bruxelles, Larmartin, 1924; 290 + 40 blz.

In dit boek vindt men de nauwkeurige titel, benevens de plaats, waar ze verschenen zijn, van 3775 verhandelingen van 1175 schrijvers, eerst alfabetisch naar de auteurs en daarna chronologisch gerangschikt. Daarop volgen eenige zeer interessante statistieken omtrent de verdeling over de verschillende nationaliteiten (de schrijver betoont zich een warm voorstander van internationalisme in de wetenschap!) en van de lawine-achtige vermeerdering van de relativiteitsliteratuur.

Dit groote werk kon slechts met succes voltooid worden door een schrijver die reeds vroeger zijn sporen verdiend had in deze techniek, blijkens zijn andere groote bibliographische uitgaven.

P. Ehrenfest.

* * *

513.7(022)

L. Bergmann, Nomographische Tafeln. (Bibliothek des Radio-Amateurs, 8. Band) 75 blz., 47 fig. Berlin, Springer, 1925. Prijs 2.10 mark.

Dr. Ing. O. Lacmann, Die Herstellung gezeichneter Rechentafeln, Ein Lehrbuch der Nomographie. 100 blz., 68 fig. Berlin, Springer, 1925. Prijs 4 mark.

Heeft men op een of ander gebied b.v. in de techniek steeds weer met een bepaalde functie van twee, drie of meer veranderlijken te maken, dan zou men gaarne een grafische voorstelling bij de hand hebben, waarop $z = f(x_1, x_2, x_3)$ zoo gemakkelijk mogelijk en nauwkeurig genoeg af te lezen is, voor verschillende combinaties van x_1, x_2, x_3 -waarden; zoo'n grafische voorstelling heet dan „nomogram”. Zooals men weet, is het de verdienste van d'Ocagne, dat hij in zijn „Nomographie” zoo veelzijdig mogelijke hulpmiddelen hiertoe aangegeven heeft¹⁾, gerangschikt naar de verschillende klassen van functies en naar het aantal der veranderlijken. Heeft dus een ingenieur, chemicus, handelsman of medicus herhaaldelijk met een en dezelfde formule te maken, dan levert de nomographie hem reeds de types van nomogrammen die bijzonder geschikt voor deze formule zijn. Wil men eenigen kijk krijgen op karakter en nut van de nomographie, dan zal men haar het liefst toegepast zien op voorbeelden die den eigen werkkring toebehooren of er eenigszins verband mee houden. Het rijk verzorgde boek van Lacmann kiest zijn voorbeelden uit de hydraulica en

¹⁾ M. d'Ocagne, Traité de Nomographie, Paris, Gauthier-Villars 1921.

staat daardoor, uiterlijk beoordeeld, onze lezerskring misschien iets minder na als het aardige boekje van Bergmann, dat zijn voorbeelden haalt uit het zoo algemeen menselijke, huiselijke gebied van de „draadlooze”. Wie hier ziet, hoe men b.v. $\gamma = 2\pi \sqrt{LC}$ of de

formule voor de brug van Wheatstone $R = R_0 \frac{x}{1-x}$

voor alle mogelijke combinaties van de rechts voorkomende veranderlijken dadelijk kan aflezen door een draad te spannen over drie schaalverdelingen die eens vooral vast, naast elkaar, geteekend zijn — die heeft alleen daardoor al een goed idee gekregen van de schoonheid en vruchtbaarheid van de nomographie.

Langzaam en schuchter dringen de allereenvoudigste graphische voorstellingen in het wiskundeonderwijs binnen. Zouden de rekenliniaal en groote gedeelten van de nomographie pas volgen als de daarin niet geoefende volksstammen uitgestorven zijn?

P. Ehrenfest.

* * *

541.202: 537.101(022)

Marcel Boll, L'électron et les phénomènes chimiques; Publications de la Société de Chimie-Physique, IX; A Hermann et fils, Paris, 1919; 43 pp., 9 fig.

Dit boekje is een overdruk van een redevoering, gehouden in Maart 1914, bijgewerkt tot 1919. Het behandelt zeer in het kort eenige atoommodellen (J. J. Thomson, Rutherford) en bespreekt de verschillende wijzen, waarop electronen kunnen worden uitgezonden. Het grootste deel van het boekje wordt ingenomen door een gedetailleerde beschrijving van de proeven van Haber en Just, uitgevoerd om de uitzending van electronen tijdens een chemische reactie aan te toonen (1909-1911) en de bespreking van de resultaten en de overeenkomst met analoge verschijnselen. Een korte beschrijving van Perrin's stralingstheorie besluit het thans wel wat verouderde boekje.

J. Kalf.

* * *

54: 69(0712)

Dieckmann, Leitfaden der Chemie für Baugewerkschulen und andere technische Fachschulen, B. G. Teubner; Leipzig-Berlin, 1925, 65 pp. Prijs Mk. 1.20.

Voor een dergelijk werkje zal bij ons de belangstelling niet groot zijn. Het peil staat beneden dat van onze chemie-leerboekjes voor H. B. scholen. Heel beknopt worden de grondbegrippen behandeld, daarna volgen verschillende hoofdstukjes over de voornaamste grondstoffen, waarbij vooral de nadruk gelegd wordt op de technische toepassingen. Bij verbranden wordt b.v. besproken hoe men met de minste hoeveelheid water een brand moet blussen en waterschade vermeden kan worden. De organische chemie wordt in 5 bladzijden als aanhang afgehandeld; niettegenstaande dat wordt het Wiese-zout in structuurformule medegedeeld. De afwerking is netjes.

Hubert ter Meulen.

* * *

541.202(022)

L. Zehnder, Die Synthese des Stoffs: Ludwig Hofstetter Verlag, Halle a. S., 1924, 280 pgs., M. 12.

De structuur der materie is nog steeds een raadsel en biedt daarom gelegenheid tot de meest phantastische ideeën. Hier is getracht de opbouw der molekulen te verklaren door middel van een oeratoom. Het heelal zou opgebouwd zijn uit twee oerstoffen; de oeratoomstof en de aetheratoomstof, terwijl nog twee oerkrachten, elasticiteit en zwaartekracht, het geheel completeeren. Beide oeratoomsoorten hebben een bolvormig oppervlak, de oeratomen zijn massieve kogeltjes, de aetheratomen zijn nog kleiner, lineair misschien een honderdste of een duizendste van de oeratomen. Hieruit bouwt Zehnder alle atomen op, waarbij hij vooral het oog heeft op de meest stabiele formaties, nl. de tetraëdrische opstelling

van 4 oeratomen. Doorbouwende op deze theorie komt hij tot een symbool voor de paraffin-koolwaterstoffen, waaruit hij door weglating van de eindstandige waterstofatomen de olefinen construeert. Volgens zijn opvatting zouden dus de additiepunten bij de olefinen aan de eindpunten der keten liggen, wat absoluut niet het geval is.

Afwerking en druk is keurig. Hubert ter Meulen.

* *

532.74(022)

Progress in Absorption, Review of the papers presented at the symposium on absorption at the Ithaca Meeting of the American Chemical Society, September 11, 1924, by W. G. Whitman; publicatie van de Massachusetts Institute of Technology, Serial no. 111, 8 pg.

Dit boekje bevat de opsomming van een achttal verhandelingen, wier inhoud in het kort aangegeven wordt, t.w. de verhandelingen: Principles of Gas Absorption by W. K. Lewis and W. G. Whitman, die een bespreking geeft van de algemeene absorptieprincipes speciaal in verband met de oplosbaarheid van het gas en het gebruikte apparaat; The Mechanism of Absorption of moderately Soluble Gases in Water by H. G. Becker; A Study of the Mechanism of Absorption by R. T. Haslam R. L. Hershey and R. H. Kean; The Absorption of Carbon Dioxide and Ammonia From Gas Bubbles by P. G. Ledig en Comparative Absorption Rates for Various Gases by W. G. Whitman and D. S. Davis, welke vnl. experimenteele gegevens met verschillende gassen en verschillende toestellen bevatten en The absorption of Gasoline From Natural Gas by R. P. Anderson en The Absorption of Hydrogen Sulphide by F. W. Sperr Jr., respectievelijk de absorptie van Gasoline en H₂S behandelend en The analysis of Mists and Fogs by H. C. Weber, waarin de bepaling van zure dampen. Voor hen, die een kort overzicht willen hebben over de behandelde stof in bovengenoemde verhandelingen, is het boekje wel aan te bevelen. J. Al.

* *

675(021)

A. Wagner en Prof. Dr. J. Paessler, Handbuch für die gesambte Gerberei und Lederindustrie; Deutscher Verlag, Leipzig, 1924. Aflevering 1; 48 blz.

Wie het gerbereitechnisches Auskunftsbuch für die gesamte Lederindustrie van J. Schmidt en A. Wagner, in 1905 door den eerstgenoemde zelve uitgegeven, kent, zal het zeer zeker toejuichen, dat van dit boek een nieuwe uitgave verschijnt. Waar de heer Wagner zich de deskundige medewerking van Prof. Paessler verzekerd heeft, die sinds vele jaren directeur is van de Freiburger Versuchsanstalt voor de lederindustrie, kan het niet anders of dit werk zal wederom een vademecum worden voor iedereen, die met de lederindustrie te maken heeft.

In deze eerste aflevering worden o.a. afvalstoffen, afvalwater van looierijen, afwelkpersen, het kalken (aeschern) uitvoerig en duidelijk behandeld.

J. L. van Gijn.

* *

675(021)

A. Wagner und Prof. Dr. J. Paessler, Handbuch für die gesamte Gerberei und Lederindustrie. Deutscher Verlag, Leipzig 1924. Aflevering 2-3; 93 blz.

In deze afleveringen worden o.a. besproken: anhydaatleder, anilinekleurstoffen, aanleg van lederfabrieken en bontververijen (zeer aanbevelenswaardige wenken worden hier gegeven), antiekleder, antiseptische middelen, appretuur en appretuurmachines, het bleeken van leder, het uitloogen van looistoffen, uitzetmachines, automobielleder, bacteriën in de looierij, het beitsen (deze beide onderwerpen hadden gevoegelijk wat uitvoeriger behandeld

kunnen worden) en betonwerk in de looierij. Het geheel maakt ook door de goede illustraties van machines een welverzorgden indruk.

J. L. van Gijn.

* *

* *

548.7:535.4-6(022)

M. C. Neuburger, Kristallbau und Röntgenstrahlen, mit besonderer Berücksichtigung der experimentellen Ergebnisse der Kristallstrukturforschung; Enke, Stuttgart, 1924, 110 blz., ingen. Mk. 3.—.

Dit deeltje van de Sammlung chemischer und chemisch-technischer Vorträge behandelt zeer oppervlakkig de Röntgenanalyse (meer in het bijzonder de Laue- en de Debije-methode), de theorie van Born, de theorie der Röntgenstralen en de chemische toepassingen op deze gebieden. Het roert in een kort bestek (70 blz., de rest wordt ingenomen door een opsomming van de verkregen kristalstructuren) zeer veel onderwerpen aan, soms onnauwkeurig. Het is daardoor slechts geschikt voor hen, die zich tevreden willen stellen met een causerie op dit gebied.

A. Karssen.

TER BESPREKING ONTVANGEN BOEKEN.

- H. G. Wells, The Chemical Aspects of Immunity; Chem. Catal. Comp., New-York, 1925; 253 blz.
H. W. Gillett and E. L. Mack, Molybdenum, Cerium and Related Alloy Steels; Chem. Catal. Comp., New-York, 1925; 299 blz.
G. A. Burrell, The Recovery of Gasoline from Natural Gas; Chem. Catal. Comp., New-York, 1925; 600 blz.
W. H. Dovley, Textiles; Heath, London; 750 blz.

CORRESPONDENTIE, ENZ.

Hun, die zich schriftelijk wenden tot den hoofdredacteur (of de redactie in 't algemeen), wordt verzocht porto in te sluiten voor het antwoord per brief of wel voor de opzending naar den drukker of voor de inwinning van informaties.

VRAAG EN AANBOD.

De opneming in deze rubriek geschiedt gratis.

Bij elk antwoord dient echter porto voor doorzending aan aanbieder of aanvrager te worden ingesloten. Correspondentie over elk tijdschrift, boek, enz. op een afzonderlijk stukje papier te plaatsen en te richten tot den hoofdredacteur.

Ter overneming aangeboden:

- Bakhuis Roozeboom, Heterog. Gleichgewichte, Heft I (1903), geb., Heft II, Teil 2 (1918), Heft II, Teil 3 (1918), Heft III, Teil I (1911), Heft III, Teil 2 (1913).
Wi. Ostwald, Grundl. d. anorgan. Chem. 4. Aufl. (1919), geb.
Behrens-Kley, Mikrochem. Analyse. I (1921), II (1921), beide geb.
Tables Annuelles III (1912), uitg. 1914, geb.
Chem. Weekblad 1920, 1921, 1922 en 1923.
Rec. trav. chim. 1920, 1921, 1922 en 1923.
Winkler-Brunck, Massanalyse, 1920, geb.
Cannizzaro, Historische Notizen und Betracht. Atomtheorie.

Ter overneming gevraagd:

- Bakhuis Roozeboom, Heterogene Gleichgewichte, Heft II, Teil 1.
Zij, die nummers van Chem. Weekblad en Rec. trav. chim. wenschen te ontvangen, ter completeering van jaargangen, gelieven zich te wenden tot den hoofdredacteur.

Men wordt dringend verzocht bericht te zenden, zodra de plaatsing in deze rubriek door een ontvangen aanbieding of aanvraag niet meer noodig is.