F R I E D R I C H B E R G I U S

Chemical reactions under high pressure

Nobel Lecture, May 21, 1932

Since the Royal Swedisch Academy of Sciences has considered my work on the development of high pressure methods for chemical reactions, and in particular work on the hydrogenation of heavy hydrocarbons and coal, to be worthy of the Nobel Prize, I wish to combine my gratitude for the high honour bestowed upon me with a report on the development of these systematic investigations and chemical researches to which my academic and industrial activities have been mainly devoted for almost 20 years.

The success of the first experiments with the high-pressure hydrogenation of oil and coal in the years 1912 and 1913 was due to the fact that the laboratory which I directed at that time in Hannover had already developed a method which permitted the conduct of a wide range of reactions in relatively easily operated apparatus at pressures up to about 300 atm and temperatures up to 450°.

In 1908 and 1909 I was given an opportunity in the laboratories of Nernst and Haber to witness the use of the high-pressure methods in investigations into the ammonia equilibrium and ammonia synthesis, and I tried my hand, in these laboratories, at that time, at syntheses by high-pressure techniques, with the then imperfect apparatuses, and with little success.

When, in 1909, I joined the physical-chemical laboratory of Hanover Institute of Technology led by Bodenstein, I decided to take up work on this new field which appeared promising to me on a wider scale, and developed, first in the laboratory of the Institute, and then in my own, relatively well-equipped private laboratory, assisted by several colleagues, of whom I would specially mention Hugo Specht, the methods and apparatus for investigating a number of diverse high-pressure reactions in the course of the years.

The problems in most of the investigations were mainly of a technical nature. Purely theoretical research was also done, but, if only for material reasons, to provide an economical justification for the private research laboratory, the principle of practical applicability of the problems studied had to p r e d o m i n a t e .

In our work, high pressure was used as a means for carrying out chemical

reactions in very different senses of the term. I reported on this in a monograph in 1912 ("The Application of High Pressures to Chemical Processes and Simulation of the Genesis of Bituminous Coal")*. Ammonia synthesis had first availed itself of the possibility to influence *the position of the equilibrium* of a gas reaction in a certain direction by increasing the pressure. In our first detailed study into high-pressure reactions we applied the Le Chatelier principle to a heterogeneous system, i.e. to the study of *the dissociation of calcium peroxide,* whose dissociation pressure curve can, as a result of the slow rate of disintegration at low temperatures, only be measured in a temperature range at which the pressure of dissociation is already about 100 atm.

We made extensive use of the possibility, provided by high pressure methods, to conduct reactions between substances that are liquid at normal temperatures, i.e. at temperatures at which the vapour pressure of the substances concerned is very high, in other words to react liquids with one another at temperatures at which the substances concerned otherwise react only as gases and even then react very slowly or not at all with one another. This includes investigations into the *reactions of superheated water,* its influence on coal and iron and the *saponification of organic chlorides,* such as chlorobenzene and ethylene chloride with aqueous solutions of caustic alkali. In the end, we employed in the *hydrogenation of heavy petroleum and coal,* the increase in hydrogen concentration made possible by high pressure, and thus enabled acceleration of the rate of addition of hydrogen to the disintegrating oils and to coal.

Study of the dissociation of CaO₂

My main reason for mentioning the first series of experiments in 1910, the measurement of the *dissociation equilibrium of calcium peroxide,* is that it played a significant part in the development of our high-pressure work. The economical and technical starting-point of these researches was the interest which the production of peroxides and perborates had gained at the time. Production methods of hydrogen peroxide and its starting materials were anything but perfect. Engler and Becker had computed the dissociation conditions of calcium peroxide by means of Nernst's approximate formula and found that its dissociation pressure reaches 1 atm. at as little as 55°, and must rise to about

* Die Anwendung hoher Drucke bei chemischen Vorgängen und eine Nachbildung des Entstehungsprozesses der Steinkohle, Verlag Wilhelm Knapp, Halle, Germany.

100 atm at 170°. Our experiments showed that measurement of these disso-
ciation pressures was only possible when the calcium peroxide was examined
not in the solid state, but dissolved in the caustic potash-caustic soda eutectic.
After lengthy efforts, we succeeded in obtaining fairly accurate measurement
of dissociation pressures, starting both from the calcium peroxide decompo-
sition side, and from the formation of oxygen and lime. In the end we also
succeeded in converting lime in suspension in caustic alkali melt practically
completely into CaO_2.

This observation has acquired no industrial significance, but it greatly
assisted in the development of our high-pressure method: our problem was
to keep apparatus, consisting of a decomposition vessel and a precision ma-
nometer, oxygen supply pipes and valves, completely leak-proof for several
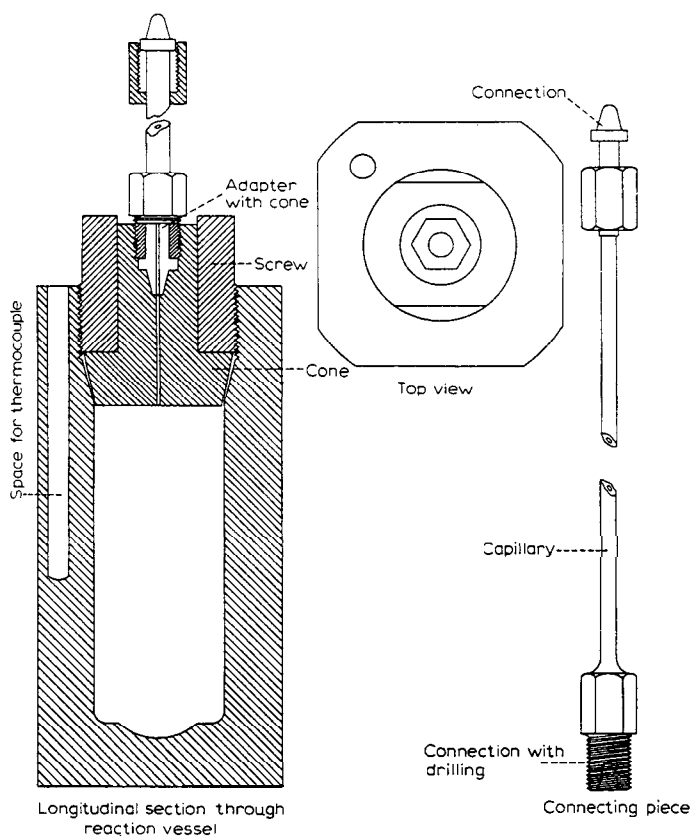weeks at temperatures up to 400°. Since the capacity of the reaction bomb had

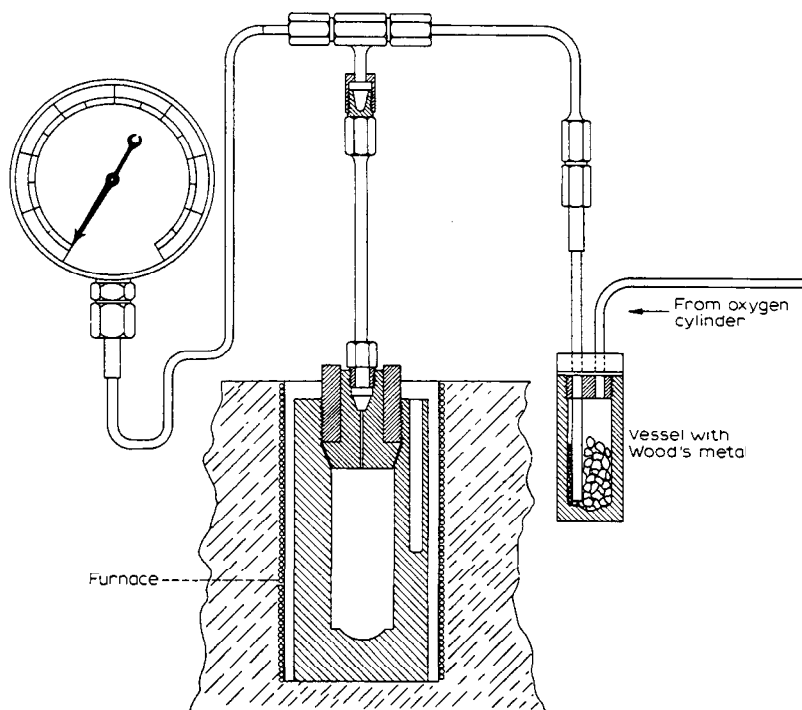Fig.1. High-pressure experimental vessel, 1910.

Fig.2. Experimental vessel for peroxide equilibria, 1910.

to be restricted to a few hundred cubic centimetres, infinitesimal gas losses would have resulted in considerable errors of measurement during the weeks required for establishing equilibrium. Figs. 1 and 2 show the apparatus used. Pressure vessels of similar design and various sizes were used by us for years and may well still be suitable for small laboratory tests.

Even in the investigations into direct production of calcium peroxide in an alkali melt with highly compressed oxygen it was found to be necessary to bring the high-pressure gas into contact with the suspension of lime in caustic alkali melt by agitation or some other means of mixing. At that time, in 1911, experience was still lacking in the manufacture of pressure-resistant stuffing boxes suitable for sealing a relatively rapidly rotating agitator shaft. We built a pressure vessel having a small electromotor in its upper, cooled part, agitation taking place in the lower, heated part. To avoid the danger of highly compressed oxygen acting on organic substances, the small electromotor was to be fitted with windings of enamelled wire. The mechanic concerned however failed to carry out this instruction, and we had a very un-
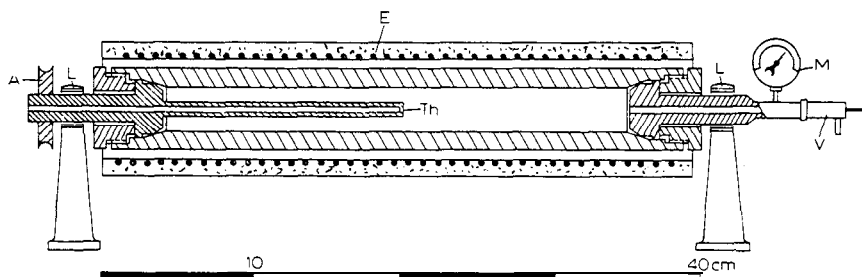
Fig. 3. Rotary vessel, 1912.

pleasant explosion. The quantity of insulating material in the tiny motor was infinitesimal, which did not prevent the part of the pressure vessel containing the motor from exploding on starting up, and the vessel with a wall thickness of about 30-40 mm was shattered which could have done considerable damage.

This experience spoilt our taste for working with highly compressed oxygen, but it furthered our cause in that we realized that such agitators are far too complicated and dangerous. In 1912 we therefore designed the extremely simple so-called rotary bomb shown in Fig. 3. A length of Mannesmann tube was closed at the ends with a high-pressure cone each, to which an extended shaft was attached. The shaft was supported in bearings and was driven by a chain wheel drive or a belt pulley. The pressure vessel rotated in an electrical oven. For temperature measurement, one of the cones had a central drilling, and a tube terminating in the reaction chamber accommodated a fixed thermocouple introduced from outside. Pressure was read on a manometer which rotated together with the apparatus. The design of this convenient apparatus acquired great significance for the further development of our
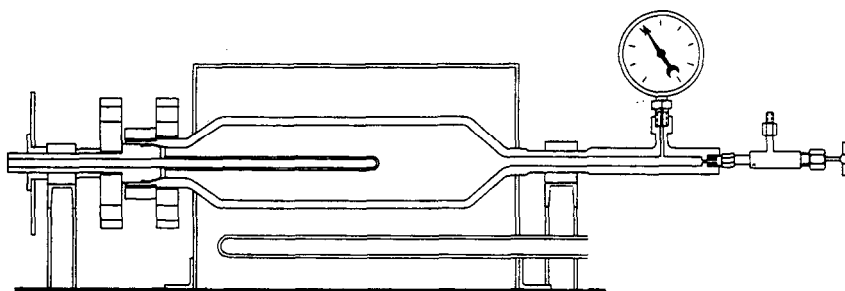

Fig. 4. 5-litre rotary vessel.

work, and we not only used it in our own studies, but made similar apparatus available to other research laboratories. It underwent numerous changes later; we ourselves used it in sizes from 250 cm³ to 40 litres. Fig. 4 shows the 5 l vessel, which was mainly used at a later date.

Production of hydrogen

Work on catalytic hydrogenation and the development of technical hydrogenation reactions of hardening of fats and of the ammonia synthesis directed the attention of expert circles at that time to methods for the production of pure and cheap *hydrogen*. At that time, the process of the Badische Anilin- & Soda-Fabrik for the catalytic conversion of carbon monoxide of water gas into hydrogen and carbon dioxide was still unknown. The best available method for producing hydrogen seemed to be that according to Linde in which the carbon monoxide of the water gas was separated from the hydrogen by liquefaction at low temperatures.

In 1911 I conceived the notion that it should be possible to carry out the *water gas reaction,* which occurs at a technically satisfactory velocity and then according to the formula $C + H_2O = CO + H_2$ only at temperatures of the order of 900°, at considerably lower temperatures, at which the position of the equilibrium is practically such that the reaction corresponds to the formula $C + 2H_2O = CO_2 + 2H_2$.

The object therefore was to inhibit the troublesome formation of carbon monoxide completely. To achieve this aim, it would have been necessary to work at temperatures below 600°, at which steam practically ceases to act on coal. The aim was to discover whether, as it were by increasing the steam concentration, i.e. by using liquid water, the reaction velocity might not be increased sufficiently to adjust the equilibrium. In following this train of thought, the attempt had to be made to make liquid water react with coal in the vicinity of the critical point, i.e. at pressures of about 200 atm. This reaction was studied for a period of time with the apparatus according to Fig. 5, and we succeeded on a modest scale in oxidizing coal under these conditions into carbon dioxide and hydrogen, in particular when we dissolved metal compounds as catalysts in the water, the chlorides of thallium in particular proving successful. We failed however to achieve oxidation velocities which would have rendered technical exploitation of this reaction promising. Observations were however made in these experiments which were of importance
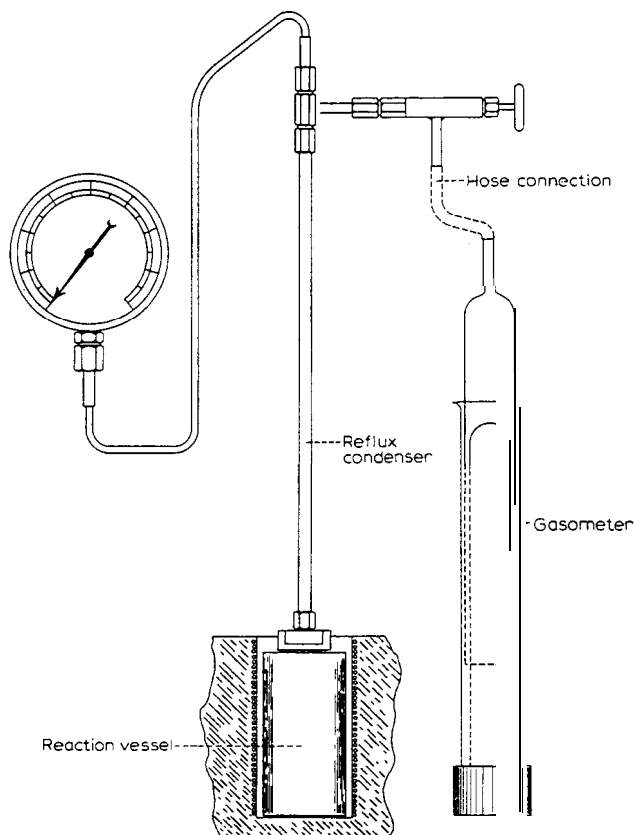
Fig. 5. Experimental vessel for high-pressure hydrogen from iron, 1911.

for our later high pressure work. When peat was used as coal material be-
cause of its finely distributed form on one occasion, it was observed that excep-
tionally large amounts of carbon dioxide formed, and that carbonaceous resi-
due remained in the vessel whose elementary analysis approximated ex-
traordinarily to the composition of natural flame coals. A closer study of this
phenomenon revealed that what was involved was the coalification reaction,
the reaction of the conversion of plant substance into coal, which became
soon after the subject of prolonged investigations of importance for later
developments, to which I shall revert below.

On the other hand it was discovered that under certain conditions the water
containing metal salts greatly attacked the iron walls of the vessels with evolu-
tion of hydrogen. The latter phenomenon was investigated and it was dis-
covered that it is possible to convert iron, treated in a suitable form with

liquid water at temperatures between 300 and 350°, almost quantitatively into Fe_3O_4 with formation of large amounts of hydrogen, and that this reaction progresses extremely rapidly. In these circumstances, the water acts as it were as an acid and is decomposed by the metallic iron. It was remarkable that this reaction by contrast with the effect of steam on iron at high temperatures is not a pure surface reaction, but that fairly finely distributed iron, e.g. filings, produces hydrogen with practically quantitative yield. The Fe_3O_4 could be reduced with coal or carbon monoxide gas and used for hydrogen

Fig. 6. Apparatus for producing high-pressure hydrogen.
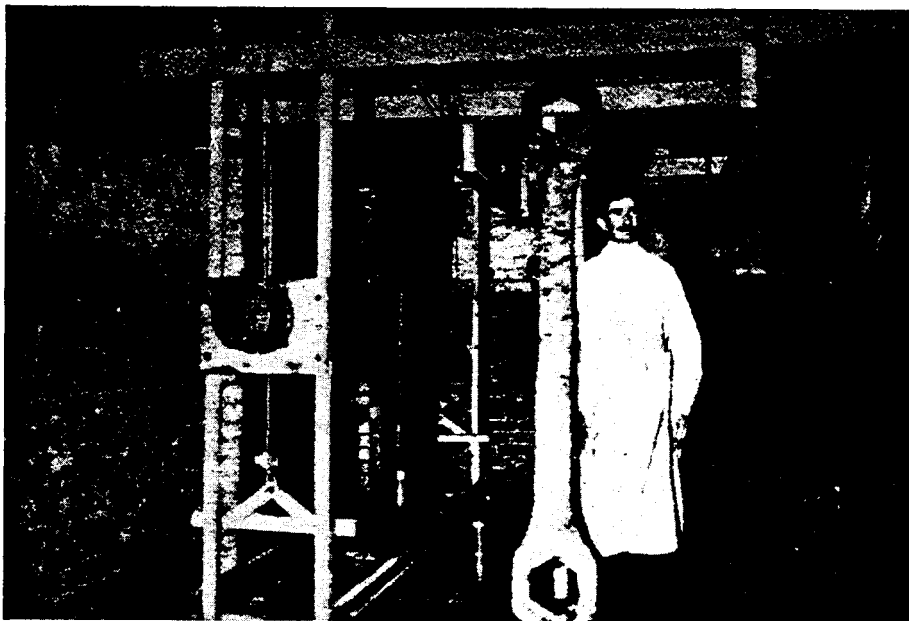
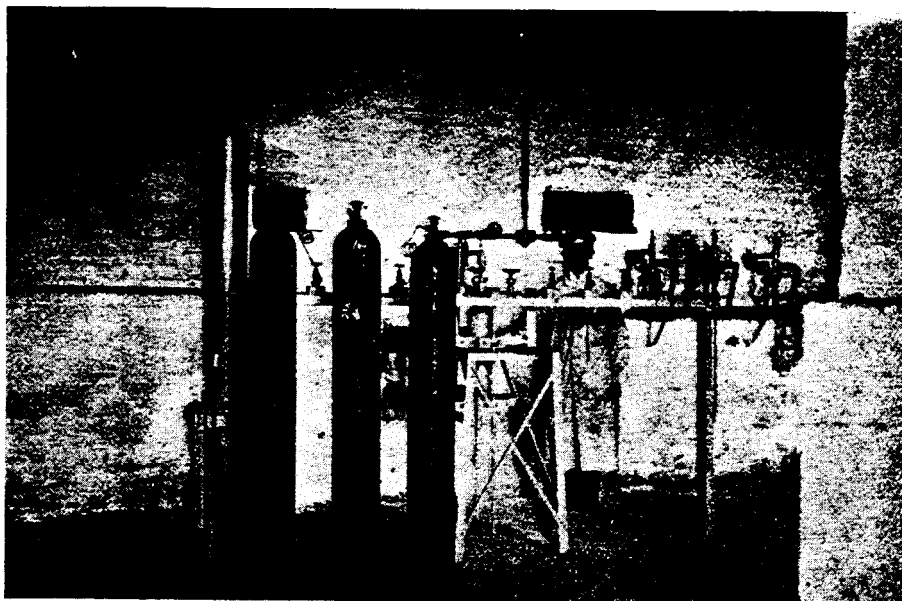Fig. 7. Apparatus for producing high-pressure hydrogen.

Fig. 8. Apparatus for producing high-pressure hydrogen.

production again, but as a result of the formation of iron carbide its effectiveness gradually declined. The hydrogen produced was exceptionally pure (the impurities amounted to no more than hundredths of 1%) and it could be drawn off from the reaction vessel at pressures of 200-300 atm. In further work on this reaction we first directed our attention to the development of apparatuses considerably exceeding the scope of laboratory facilities. In a small factory in a Hanover suburb we erected a battery of three vessels of 40 l capacity each and produced hydrogen continuously, which we drew off into pressure cylinders at the production pressure of 200 atm. The illustrations that follow (Figs. 6, 7, 8) give some details of this installation which looks extremely primitive today, but could only be put together with difficulty at that time.

The pressure vessels which were heated from the outside and in which several charges were processed every day, were sealed at the base by a conical closure held in position by a heavy screw. A man-sized spanner was used to disengage this contraption to place a new iron charge in position.

In this plant, as in our laboratory, the high pressure installation was on principle operated in a room separate from the control room. Regulating of heating, observation of pressures, drawing off of gases, etc., occurred in a control room separated from the reaction vessels by a stout wall.

In 1913 we had arrived at a method of working which permitted high pressure reactions to be conducted in apparatuses of 40-50 l capacity.

Saponification of organic chlorine compounds

At about the same time I started, together with Kurt H. Meyer, experiments on the hydrolysis of difficultly saponifiable organic chlorine compounds, in particular the *conversion of chlorobenzene into phenols* with caustic soda solution. This reaction, which cannot be carried out under normal conditions, is successful, as we were able to show, if chlorobenzene is heated with caustic soda solution at temperatures of about 300°; apart from phenol, phenyl ether forms in the first reaction phase, which can be converted into phenol after prolonged treatment, so that the chlorobenzene can be converted into phenol practically completely. The process can be carried out in a few hours and provides a cheap method for producing phenol from benzene in conjunction with alkali electrolysis. It has been carried out on a large scale in the USA under exploitation of our patents which were confiscated during the war, and continues to be used successfully there.

This reaction of course requires the use of the rotatable autoclave, to achieve thorough mixing.

Mention should be made in discussing this work of the conversion of ethylene chloride into ethylene glycol by treatment of ethylene chloride with bicarbonate solutions; these investigations were also made in 1913 and 1914. As was discovered at a later date, this reaction proceeded at a temperature which corresponded to a pressure of about 15 atm, so that high pressure methods were not strictly necessary in the later technical operation of glycol production.

Hardening of fats

As early as 1912 we worked on the problem of the hydrogenation of organic substances with the aid of highly compressed hydrogen. By virtue of the increased concentration of hydrogen at high pressure we hoped to achieve effects similar to those made possible at normal pressure by the action of catalysts. Special interest attached at that time to the hydrogenation of unsaturated vegetable and animal oils and fats. It was an obvious idea to study the hardening of fats with high pressure hydrogen, in particular with strongly unsaturated fats, such as the train oils. The results of treating such substances with high pressure hydrogen at about 300°, a temperature at which these oils in a reducing atmosphere can still be treated undecomposed, was, as the iodine numbers showed, a considerable decrease of the unsaturated character. It was however discovered that this phenomenon also occurred if treatment was carried out under the same conditions not with compressed hydrogen, but with compressed nitrogen. What was involved was, as could be established, a polymerization process. No addition of hydrogen at high pressure without catalysts to the unsaturated fractions of the fatty substances could be observed.

Oil hydrogenation

The action of highly compressed hydrogen in the treatment of heavy mineral oils was very different.

As early as 1910, Ludwig Landsberg had suggested that I should examine the problem of splitting heavy oils and oil residues into benzines. Experts were able to predict that the development of motor cars would lead to a

considerable increase in petrol consumption, although no one at that time had an accurate idea of the extent of this development. The cracking processes known at the time were extraordinarily imperfect. The losses that occurred in the cracking of oils in the form of coke, methane, and unsaturated hydrocarbons, were very high, and the formation of hard petroleum coke which separated on the walls of the cracking apparatus rendered the technical operation of the process difficult and expensive. After spending some time on this problem, I became convinced that the defects of the cracking processes and the poor quality of the unsaturated benzines produced could only be finally remedied *by ensuring that the hydrogen discharged during cracking in the form of methane was replaced by fresh supplies of hydrogen* with the object of inhibiting the separation of hydrogen-deficient products leading to coking. It was to be expected that the benzines formed under such circumstances would have fairly saturated character.

Having obtained some data on the progress of the cracking reaction, we investigated the effect of highly compressed hydrogen on petroleum hydrocarbons under the temperature conditions at which the cracking reaction occurred. We attempted as it were to embed *the highly-compressed hydrogen in the molecular structure, loosened by high temperature, of the high-boiling petroleum fraction.* These experiments which were at first done in a vertical autoclave, clearly showed absorption of hydrogen by the cracking oils, non-occurrence of coke separation, and less unsaturated character of the lighter oils formed.

The application for the first patent on the *high pressure hydrogenation of oils* was filed in May 1913, some time after we had obtained experimental evidence of the practicability of the reaction. The delay in filing the application caused a lot of trouble later.

It was soon discovered that the temperature range in which the hydrogen had to be brought to react was narrowly restricted. It was important to work in a temperature range in which the velocity of the hydrogenation reaction was not excelled by that of the cracking reaction, and to keep the partial pressure of the hydrogen sufficiently high to ensure rapid progress of the hydrogenation reaction. At the same time care had to be taken to ensure that sufficient hydrogen was available to each splitting oil particle at all times. Naturally, this latter requirement could only be satisfied if sufficient mixing of oil and hydrogen was assured. It therefore represented a great step forward in the practicability of the oil hydrogenation reaction when we carried out this experiment in the rotary bomb mentioned above which permitted intimate mixing of gas and liquid.
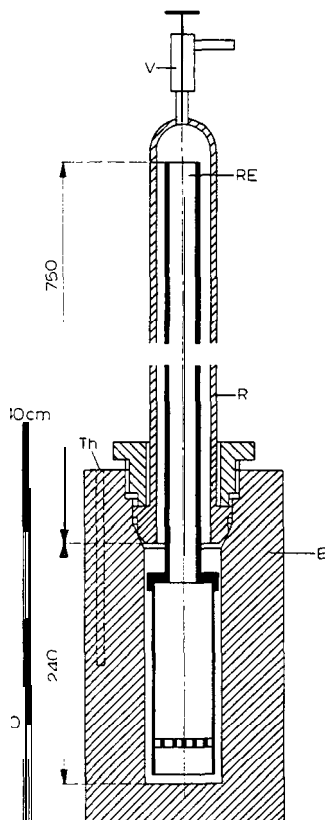
Fig. 9. Hydrogenation work. Vessel with insert, 1914.

Special experiments in which contact between the iron wall of the pressure bomb and the oil to be hydrogenated was prevented, proved that with oils the hydrogenation effect also occurs if any influence of the iron vessel walls is excluded, i.e. when metallic contact substances are prevented from participating (Fig. 9). The fact was however even then discovered and patented that addition of metals or metal oxides has a special effect in high pressure hydrogenation of oils, if the hydrogenation of sulphur-containing raw materials is involved.

It was soon discovered that the removal of the light products formed, and the supply of fresh hydrogen, had a very favourable effect on the process of the hydrogenation reaction. To put such operating conditions into effect, we had to use a fixed apparatus with agitator, because the rotary vessel did not permit continuous discharge of the substance (Fig. 10).

Work on the high-pressure hydrogenation of oils, in which Herr Paul Kal-nin assisted me in a valuable way, had progressed sufficiently at the beginning of 1914 to enable us to work on a slightly larger scale, i.e. with the 40-litre reaction vessel which I have already shown you.
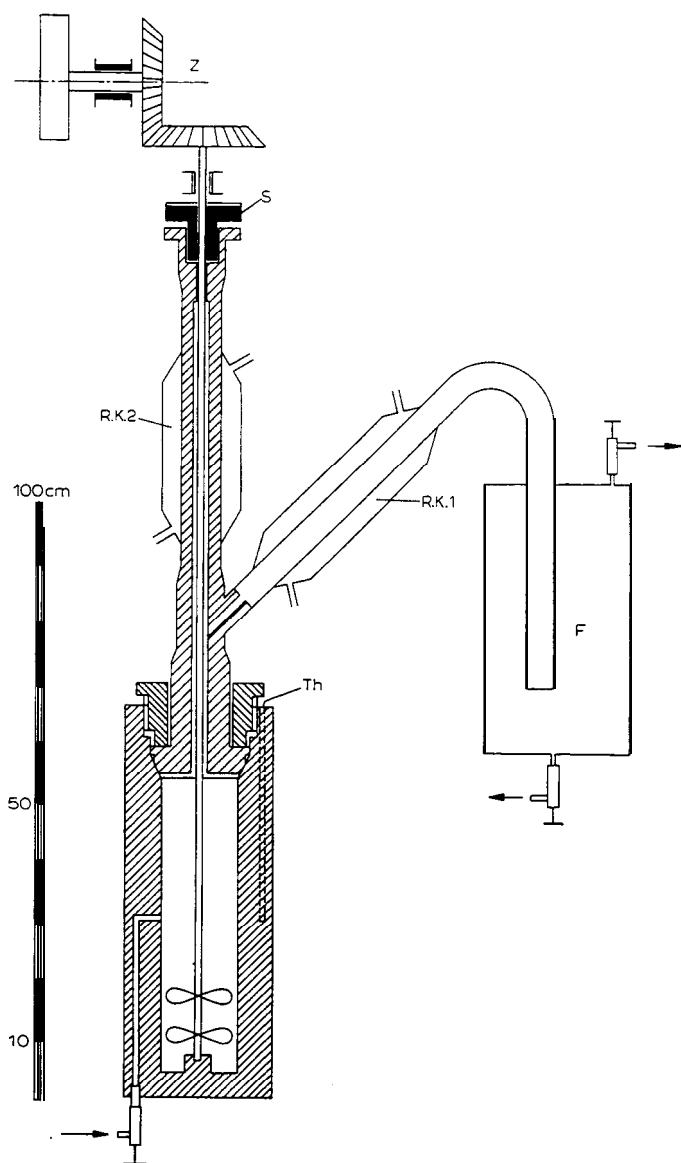
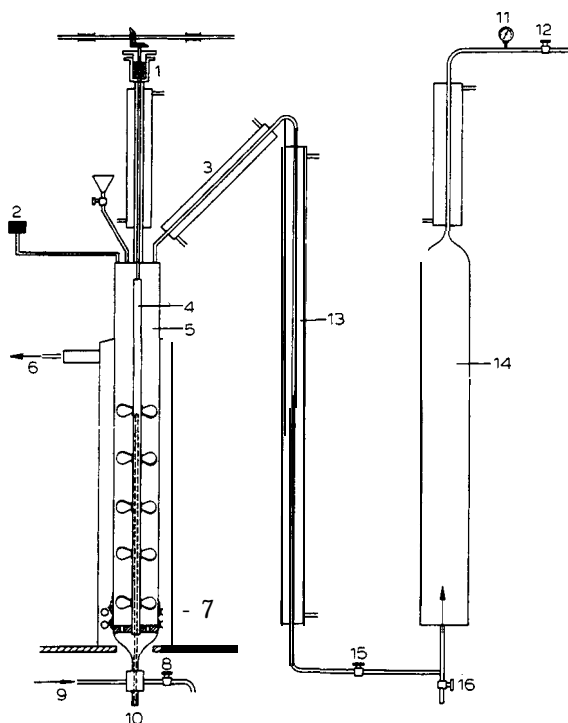Fig. 10. Hydrogenation work. Vessel with agitator, 1914.

Fig. 11. 40-litre vessel with (vertical) agitator, 1914.

1 = stuffing box	9 = hydrogen supply pipe
2 = manometer	10 = thermocouple
3 = reflux condenser	11 =manometer
4 = agitator shaft	12 =drain valve for unconsumed hydrogen
5 = decomposition vessel	I3 = cooler
6 = discharge	14 = distillate cylinder
7 = heater	15 = throttle valve
8 = discharge valve	16 = drain valve for distillate

Fig. 11 shows this somewhat more technical experimental apparatus. By contrast with later work, we used a vertical, externally heated, vessel into which hydrogen entered from below and bubbled through the liquid which was at the same time kept in motion by an agitator. The oil vapours flowed through a reflux condenser, in order to retain the heavy products which were then condensed under pressure in a conventional cooling system and collected in a distillation flask; excess hydrogen was discharged through a valve with small quantities of split gases. This step ensured discharge of the decomposed light products from the reaction space and renewal of hydrogen. A heavy

gas oil was processed at that time which was hydrogenated at a temperature of 430° and a pressure of 120 atm. About half the gas oil was converted into benzine without any formation of coke.

The investigations of the years 1913 and 1914 extended to the splitting of gas oils and distillation residues of crude oils from Galicia and Rumania. It was found that coke formation was avoided even when processing heavy residues by proper distribution of hydrogen, that the benzines formed had practically saturated character, that the sulphur in the oils was substantially separated as hydrogen sulphide, and that a further fraction of the sulphur was absorbed by added iron oxide, whereas the distillation products contained only slight amounts of sulphur.

The objects of our research were somewhat modified by the war in that the development of an industrial large-scale plant for the practical operation of hydrogenation came to the fore. This industrial work included hydrogenation of oil and coal; it will be discussed in more detail below.

Investigations into the origin of coal

I have already mentioned that we observed as early as 1911 in the treatment of peat in the presence of liquid water at temperatures above 300° that considerable quantities of carbon dioxide formed in this process, and that the composition of the powdery residue was close to that of natural fat coals. This observation prompted us to study this decomposition process of plant substances more closely because it might be similar to the process of metamorphism which these substances undergo in Nature in the course of millions of years during the gradual transition of vegetable substance into bituminous coal. Considerations of energy show that the principal constituent of plant substance, i.e. cellulose, which is formed by the influence of solar energy in the assimilation process and the subsequent reaction processes in the plant, is, thermodynamically speaking,   an unstable substance whose rate of decay is however so slow at normal temperatures that the process escapes observation. Very large quantities of energy are liberated by cellulose decomposition, which is generally known from the processes of strongly exothermal carbonization of wood.

Very many researchers have attempted over the years to convert the plant substance, i.e. cellulose or wood, which contains apart from cellulose mainly the thermochemically similar lignin, into coal, by heating, i.e. by increasing

the rate of decomposition of cellulose, and when we began to examine the problem recent, elegant studies had been reported by Klason, Heidenstam, and Norlin, who had attempted to prevent the superheating of the carbonizing substance due to the heat of decomposition of cellulose, by introducing steam. In composition the carbonization products obtained by them approximate to natural coal, but their hydrogen content is still too low, because it was still impossible by the methods used to exclude overheating completely which leads to decomposition of the coal substance as it forms.

In our experiments, the carbonizing peat was in intimate contact with liquid water which was unable at the working temperature in the high pressure vessel to change to steam but absorbed and distributed the heat generated by the decomposition of the molecules, because it is a good conductor of heat. In the case under discussion, the water under high pressure served not as a reactant, but only as a heat-distributing medium, as it were a thermostat liquid.

With the same apparatus we carried out extensive and systematic experiments on the decomposition of the cellulose in wood and other plant substances at temperatures between 290 and 350°, in the presence of liquid water, i.e. at pressures of up to about 200 atm. The quantities of carbon dioxide and water formed were measured quantitatively. Per 2 parts cellulose, there were formed 2 parts carbon dioxide and 5 parts water, and a powdery substance which corresponded approximately to $C_{10}H_8O$. The hydrogen content fluctuated within narrow limits. If the hydrogen content of the solid substance was small, the gases contained slightly larger amounts of it. It would be devious to give details here about this reaction on which I worked for many years, at first with Hugo Specht and John Billwiller, and later with Paul Erasmus. In recent times, the reaction has reawakened the interest of chemists and has been studied in particular by Berl. I would like to mention that both cellulose and lignin, treated in this manner, lead to practically the same carbonaceous end products.
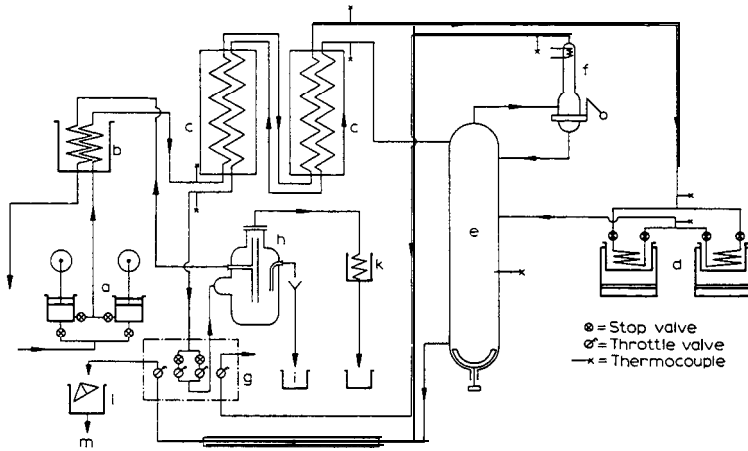
Coalification of cellulose effluents

The results of studies on the processes that occur during the decomposition of plant substance on heating in the presence of liquid water prompted Erik Hägglund and me to study the recovery of the effluents of the sodium and sulphate cellulose industry from the point of view of the coalification reaction. Nowadays, these effluents which contain lignin and other constituents

of wood that are soluble in alkaline media, are evaporated with expenditure of considerable quantities of coal, and the inorganic salts are liberated from the organic substances by combustion. It is known that highly offensive odours occur whenever the sulphate process is employed. We attempted to coalify the lignin dissolved in the effluents, i.e. to conduct separation of the organic substance from the aqueous solution under avoidance of evaporation by
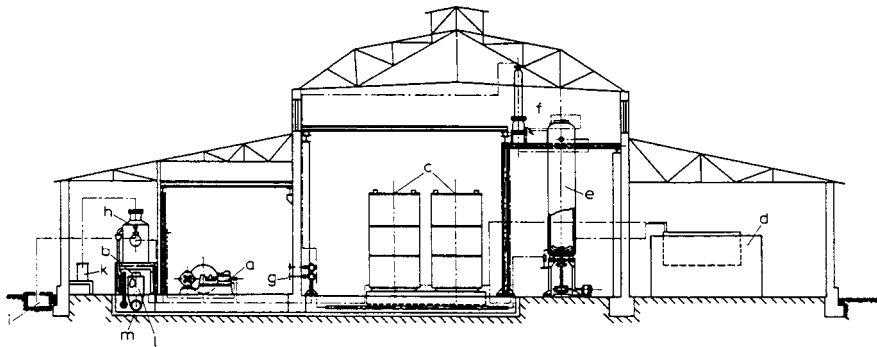
(a)

(b)

Fig. 12. Diagram of cellulose effluent decarbonization.

a pump	g control post
b pre-heater	h tar separator
c heat exchanger	tar receiver
d lead bath furnace	k cooler for alcohol vapour
e reaction vessel	l scales for coal slurry y
f column	m screw conveyor

heating the effluents under pressure to about 300°. At this temperature the organic substance decomposes substantially into carbon dioxide and a readily separable coal-tar mixture. A little methyl alcohol also formed, and considerable quantities of acetic acid are found in the solution. Application of this process therefore avoids evaporation of very considerable quantities of water from the effluents. There is no need to burn the organic substance: it is largely recovered as coal and tar and there is moreover a fairly considerable yield of acetic acid.

The acetic acid obtained need not be isolated after each boiling process, because storing of acetic acid in the effluents is by no means disadvantageous for the cellulose boiling process. It is sufficient if after each boiling process about 5 of the solution is concentrated to produce the acetic acid which is obtained in the form of sodium acetate. This process is likely to gain importance for the cellulose industry. Fig. 12 shows the experimental apparatus for the operation of effluent carbonization.

Hydrogenation of coal

The investigations into the conversion of cellulose into coal by coalification in conjunction with our studies on the hydrogenation of heavy oils opened the way to the discovery of the process for *liquefying coal.* We had observed that a product forms from cellulose with splitting of certain quantities of carbon dioxide and water which we considered to be similar to natural coal, and we had further observed that the hydrogen in this so-called synthetic coal is unstable. The attempt to formulate this process of cellulose decomposition led me to a hypothetical concept of the constitution of this coal-like substance formed from cellulose. I assumed that our artificial coal is a compound of carbon, hydrogen, and oxygen - that coal is not carbon, was not obvious at the time - whose structure must resemble that of certain unsaturated compounds of terpene-like character, and that this compound should be capable of absorbing not inconsiderable quantities ofhydrogen. By hydrogen absorption, such a compound would approach the class of heavy petroleum hydrocarbons. As a consequence of these trains of thought of whose hypothetical character I have always been aware, it was an obvious step to attempt hydrogen addition to coal and to endeavour at the same time to discover whether the hydrogen-charged coal can be split into medium and light hydrocarbons. This experiment was done analogously with the oil hydrogenation tests at

my suggestion by my assistant Hugo Specht in the summer of 1913, and *even the first test showed that* **80**% *of a coal obtained by cellulose coalification passed on treatment with hydrogen at about 150 atm pressure and at temperatures between 400 and 450°, into gaseous, liquid and benzene-soluble substances.*

On being repeated with natural coal these experiments gave practically the same results. They became the basis of the process for the production of liquid and soluble compounds from coal, i.e. of the process which we soon called "*coal liquefaction*" and for which I filed a patent applicationin the autumn of 1913.

It was soon discovered in the course of the experiments that the addition of hydrogen to the coal substance resulted in not inconsiderable evolution of heat. We prevented the noxious, decomposing effect of this heat by hydro-genating the coal in suspension with a suitable oil which was liquid at the operating temperature. The added oil had practically the same effect as the water added during coal&cation. It absorbs the heat occurring at the site of the reaction, distributes it, and by this means avoids local overheating. Once again it is mainly a heat distributing liquid, although at the same time it undergoes splitting at high temperature under the effect of the hydrogen.

The first experiments with coal hydrogenation were carried out, similarly as the experiments with oil, in our small vertical experimental pressure vessel; further development was carried out in the rotary vessels which made for good penetration of the reacting material by hydrogen. Soon after the dis-covery of this reaction it was found that all so-called younger coals are more or less suitable for the process, both brown coals and bituminous coals, and that wood and lignin could of course also be liquefied, particularly after previous coalification. Not amenable to the hydrogenation reaction were the hydrogen-deficient and anthracite coals, whose carbon content in the ash-free substance exceeds 85%. This observation was in agreement with the view we had formed from certain results of earlier coalification experiments. It was found that the addition of metal oxides, in particular iron oxides, has a favour-able effect on the hydrogenation of coal also. We attributed this effect to the prevention of polymerization of the heavy fractions, brought about by the sulphur present.

During hydrogenation, a certain amount of gas forms; a considerable amount of carbon dioxide in young brown coals: little of this is formed in bituminous coals. Methane and some ethane always form, and about half the oxygen present in the bituminous coal is found as water in the reaction product. The nitrogen is found in the distillation product in the form of

ammonia and nitrogen bases, most of the sulphur escapes as hydrogen sulphide. Most of the carbon is present as light, medium, and heavy oil, a carbon residue goes to waste as hydrogen- and oxygen-deficient compound with the ash as non-liquefied substance. This fraction ofnon-liquefied carbon depends on the nature of the coal used. In brown coals it is extraordinarily small, in the best case no more than 1%, in coals with a high fusain content it rises to 20% and more.

Circumstances did not permit us to carry out systematic investigations, either in oil or coal hydrogenation, into the effect of catalysts on increased absorption of hydrogen by the cleavage products of the basic substance. Scattered observations had shown as early as 1920 and 1921 that detailed investigations into this subject would be promising, but we lacked experience, experimental apparatus, and staff for carrying out such investigations effectively. We had to content ourselves with developing the hydrogenation processes in the manner in which they can be operated in the direct process without subsequent catalytic treatment.

Industrial high-pressure apparatus

Sufficient light had been thrown in 1914 on the hydrogenation reaction of heavy oils and coal with the assistance of Messrs. Specht, Kalnin, Billwiller, to permit deliberation as to whether and how industrial apparatus for the operation of these reactions on a large-scale could be erected. Industrial high-pressure apparatuses had at that time only been built for gas reactions in the homogeneous system. It was our task to construct apparatuses in which liquids, solids, and gases could be introduced, heated, mixed, and made to react, and from which the reaction products could be continuously discharged. Industrial apparatus for the hydrogenation of coal and oil was developed during the years 1915-1925 in our Mannheim-Rheinau factory particularly with the assistance of Messrs. Tillmann, Debo, Prof. Riedler and Löffler.

Since temperature and pressure conditions are practically the same for the hydrogenation of heavy oils and coal, and considering that intimate contact between the hydrogen and the liquid or suspension to be hydrogenated is essential in both reactions, it could be assumed from the beginning that an apparatus suitable for oil hydrogenation could, suitably supplemented, be applied to the liquefaction of coal. In both processes it was necessary to introduce *solid substances* into the reaction apparatus - relatively small quantities

of iron oxide for desulphurization in oil hydrogenation, the entire raw material in coal hydrogenation. It was obvious from the start that the introduction of solids into a high-pressure reaction chamber and the discharge of solid residues would present special difficulties, and it took several years before a suitable solution of this technical problem was discovered.

Suitable reaction apparatuses were cylindrical, forged or pressed steel vessels which could at that time, in 1915, be fabricated with a diameter of about 80 cm. Because of this restriction on the diameter, cylinders of considerable lengths had to be used to get a reaction chamber of significant size. We decided to use a vessel 8 m long. The fundamental question was if these cylinders should be arranged vertically or horizontally. With the vertical arrangement, the reaction had to be conducted in a relatively high column of liquid, through which the reaction gas flowed and to which it imparted turbulence. Provided the quantity of flowing gas was sufficient, it appeared feasible to work without an agitator and to leave the hydrogen to perform the task of mixing or agitation. In this arrangement it had to be accepted that during agitation the newly supplied reaction material constantly mixed with the as yet unprocessed material, and that the residue drawn off always contained still unprocessed or only partly hydrogenated material. We therefore decided to use a horizontal vessel with agitation, which the raw material entered at one end, while the hydrogenated products were drawn off at the opposite end. Hydrogen and oil were heated before entering the vessel approximately to the reaction temperature, to make maximum use of the expensive reaction space. Since, at the operating temperatures, the strength of iron is considerably
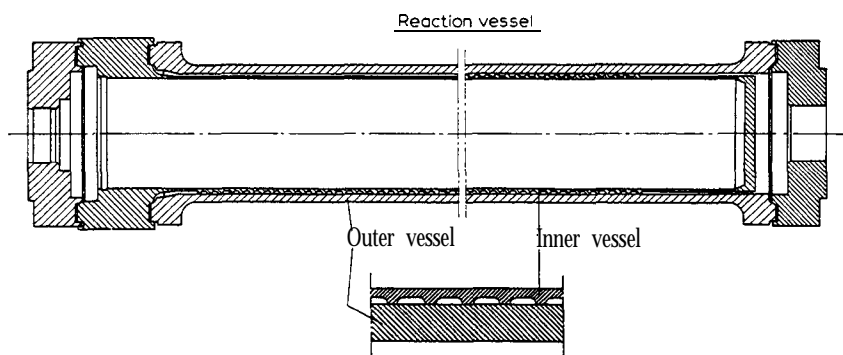

Fig. 13. Bergin plant Rheinau of the Deutsche Bergin AG für Kohle und Erdölchemie, Mannheim-Rheinau.

below the maximum strength attained at 300°, we decided from the start to dispense with heating of the pressure vessel from outside, because any external heating would have meant that the iron was brought to temperatures higher than the maximum temperatures necessarily required for the reaction. Heating was effected inside the pressure vessel in that into the pressure vessel there was built a second relatively thin-walled pipe (Fig. 13). Heating medium practically at the same pressure as that prevailing in the reaction space was pumped through the narrow space between the two pipes.

Originally, the heating medium selected was naphthalene, the only liquid substance which withstood the temperature required for any length of time. Difficulties in operation arose because of the position of the melting point of naphthalene, and we therefore later used a compressed gas (nitrogen or combustion gases) as heat carrier, which method of heating proved highly successful.

The heating gas was pumped by a high-pressure circulating pump in the manner (Fig. 14) such that it passed from the pump in the cold state first through a double-coil system in which the vapours issuing from the vessel
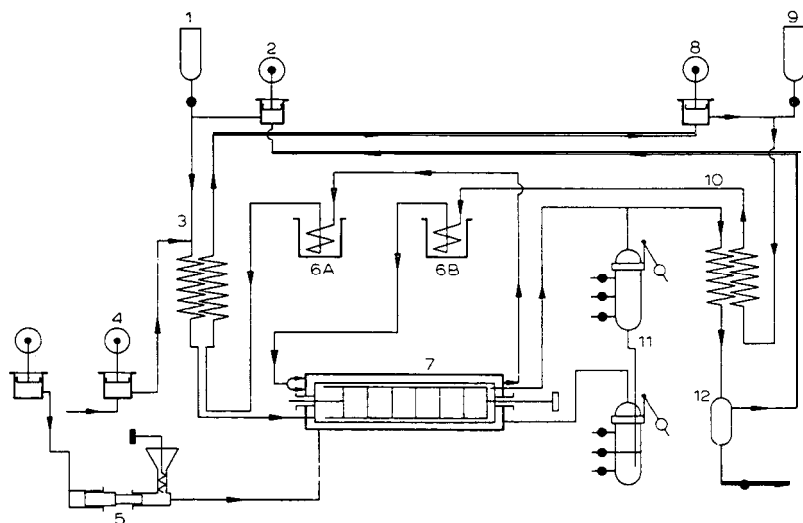
Fig. 14. Diagram of high-pressure apparatus.

1= hydrogen cylinder	7 = reaction vessel
2 = hydrogen pump	8 = heating medium pump
3 = heating system	9 = heating medium container
4 =pump	10 = condenser
5 = paste press	11 = equalizers
6 =heating furnaces (A and B)	12 = collectors

condensed. In this manner, it was heated to above 300°. It was then heated in a furnace, passed through the jacket space of the vessel into a second heating furnace and then to a further double-coil system where it generated the heat for heating the hydrogen and the oil. The cooled heating gas returned to the pump. In this way good thermal economy and readily controllable heating was ensured. The temperature in the reaction chamber could be held constant within a few degrees for weeks at a time. The products discharged from the condensers were collected in high-pressure vessels.

The more rapidly the products formed are removed from the reaction system, the better the cleavage reaction progresses. Hydrogen was therefore used in excess. It had to be kept in circulation. It left the reaction vessel together with the vaporous and liquid products, was cooled and separated in the product-collecting vessels from the condensable oils and from most of
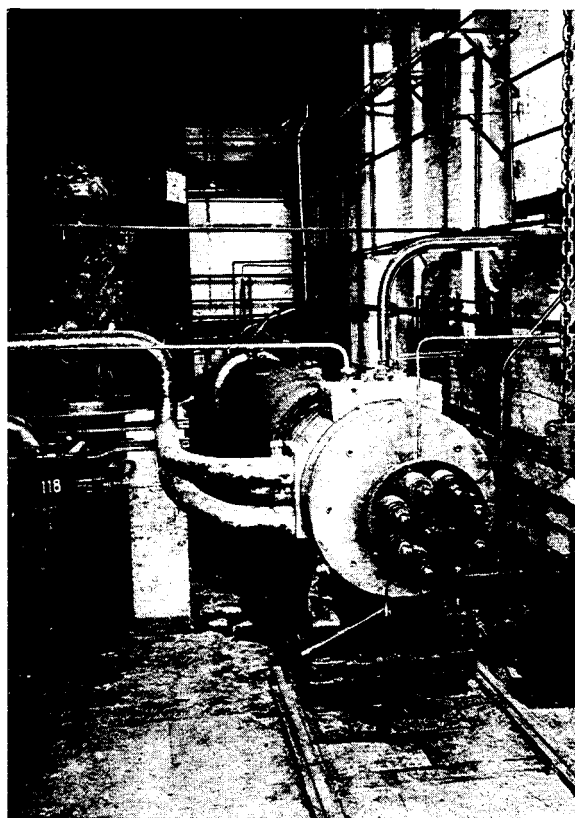
Fig. 15. High-pressure vessel.
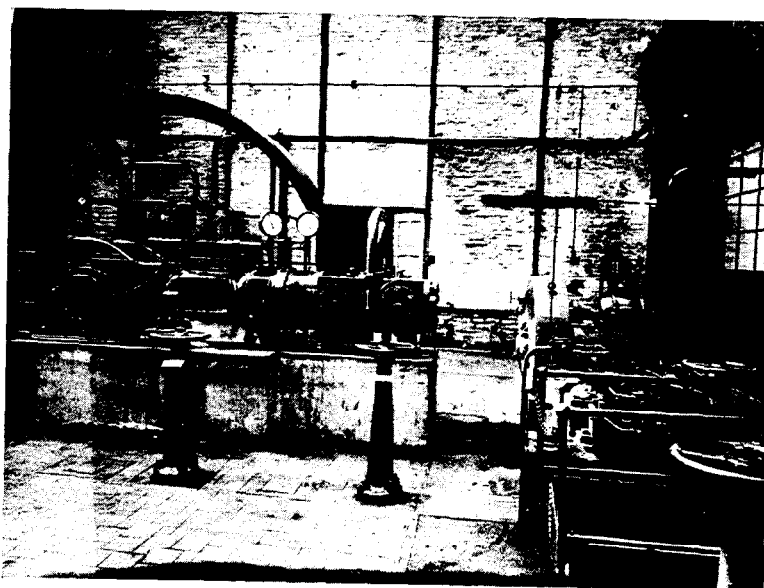
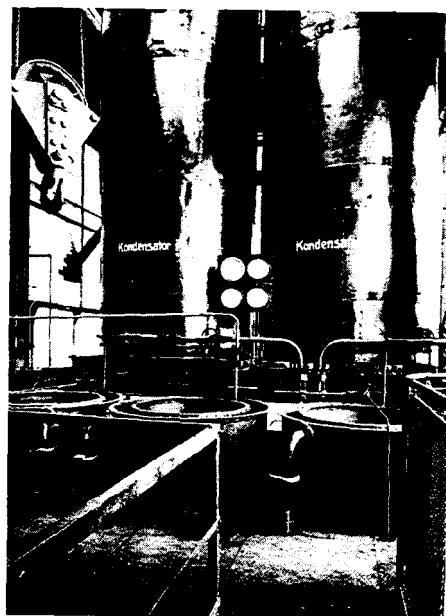Fig. 16. Circulating pump for compressed nitrogen.
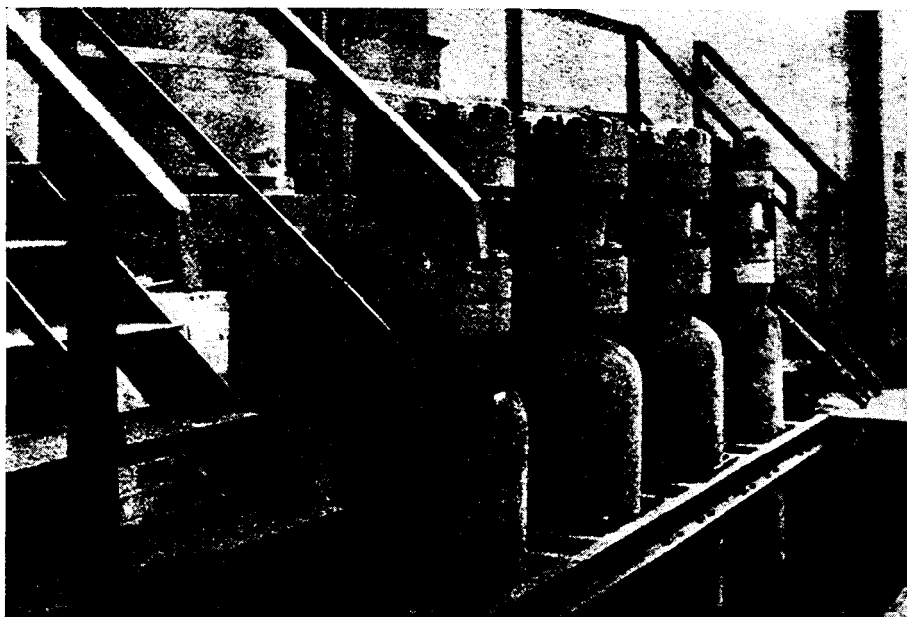

Fig. 17. Condensers.

Fig. 18. Collecting tanks for finished products.

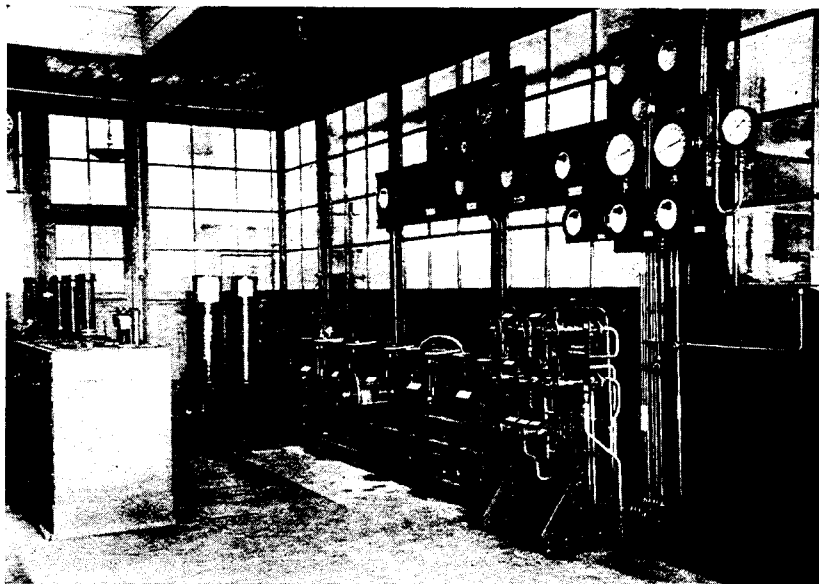Fig. 19. Control post and measuring instruments.
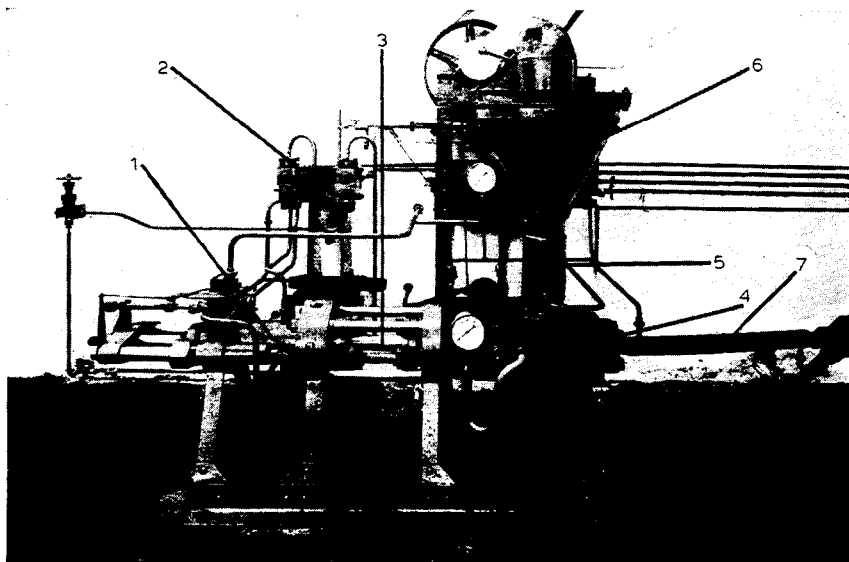
Fig. 20. Control post and measuring instruments.

Fig. 21. Paste press for coal feed.

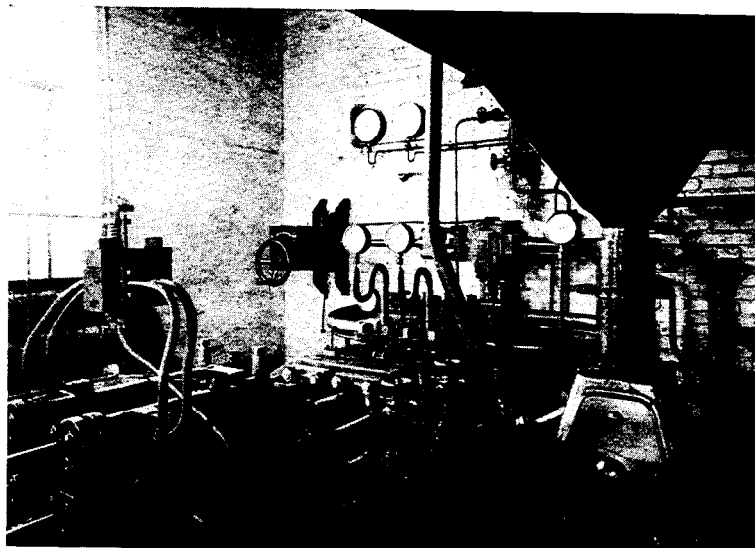|	
I = hydraulic cylinder	5 = screw conveyor
2 = reversing valve for 1	6 = filling funnel
3 = piston rod	7 = transport pipe
4 = cylinder for the paste	

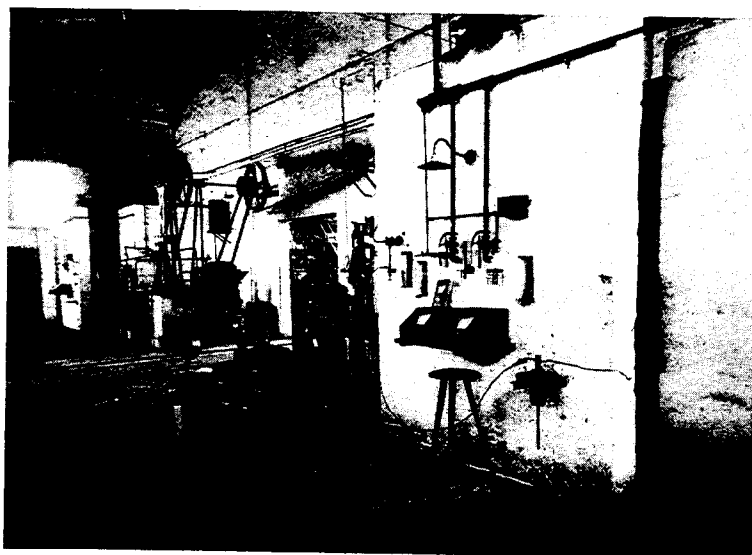Fig. 22. Paste press for coal feed.

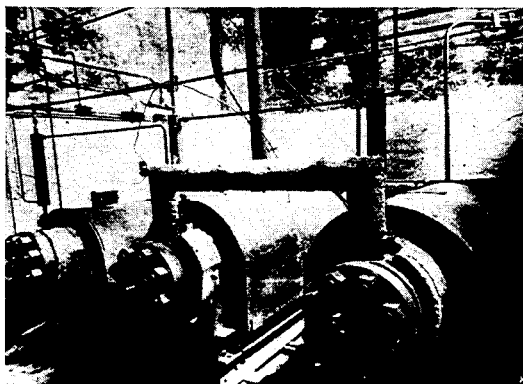Fig. 23. Test rig for small-scale experiments.

Fig. 24. Reaction vessels of continuous experimental plant.

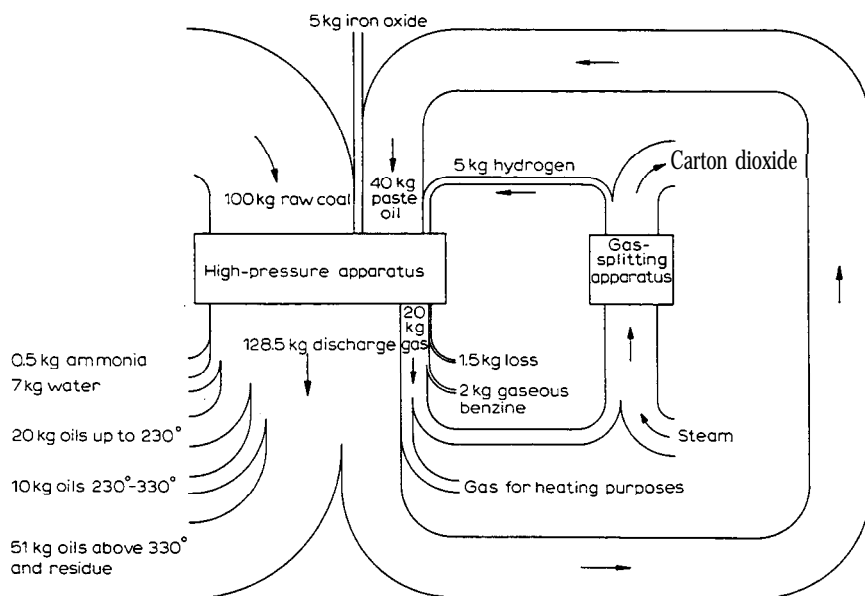Fig.25. Machine-room for continuous experimental plant.

Fig. 26. Flow diagram of continuous method of operation.

the methane which is readily soluble in oil, and was returned to the vessel by a circulating pump. Following various modifications, this arrangement proved very suitable.

Construction work began in 1915, and the apparatus had reached its final form about 1924. Figs. 15-20 show parts of the apparatus.

The design of reliable stuffing boxes for carrying the agitator shaft into the vessel presented great difficulty at first. The construction of an agitator 8 m long was also far from simple. New instruments had to be developed for measuring the flowing high-pressure gases. The design of durable valves which regulated the expansion of the reaction products consisting of liquid, solid, and gaseous substances from 150 atm to 1 atm presented great difficulty, but was accomplished satisfactorily. To feed solid coal as simply as possible continuously to the high-pressure space presented particular difficulty. A suitable method for doing this was found in 1920. The coal was mixed with highly viscous oil, e.g. tar or the heavy fraction of the product formed in coal liquefaction, into paste that was stiff at normal temperatures and which could be circulated by hydraulically-operated pistons with the assistance of a specially designed pump. (Fig. 21 shows the paste press of the small, Fig. 22 that oft he large apparatus.)

In our large experimental apparatus at Mannheim-Pheinau, construction of which commenced in 1916 and which started experimental operation in 1919, we studied mainly the splitting of oil residues on a large scale. Heavy sulphur-containing products, such as the residues of Panuco oils, Persian oil residues, and other products were processed. The maximum daily output was 30 ton. Depending on the starting material, we obtained

25-35% benzine,
40-50% gas oil,

the remainder being heavy products which could be processed to lubricating oils. The waste products were a small percentage asphalt and a few percent methane.

When the large-scale apparatus had been sufficiently tested with oil, it was at the end used for a short period for processing coal.

The study of coal liquefaction was mainly conducted in smaller experimental plants. Preliminary tests, several thousand of them, were carried out in a rotary vessel apparatus (Fig. 23). About 200 different types of coal were investigated in this manner, mainly in the years 1922-1925. For more extensive investigations we used apparatus with a continuous throughput of about 1 ton per day which operated on the same principle as the large-scale apparatus, except that the method of heating it was simpler. Experimental work was successfully conducted at that time by Messrs. Noack, Hofsäss, Schoenemann, Rheinfelder. Figs. 24-25 show the experimental rig.

The diagram, Fig. 26, shows the results of liquefying a normal bituminous coal: 100 parts coal are mixed with 40 parts oil, taken from the process, with addition of a little iron oxide, and are introduced into the high-pressure apparatus in the form of a paste with 5 kg hydrogen. About 128 kg liquid and solid products and 20 kg gas are obtained. About 7 kg water are separated from the discharge; the water contains about ½ kg ammonia.

The following are obtained from the oil:

20 kg products with a boiling point up to 230°
10 kg products boiling between 230 and 330°, and
51 kg heavy oils and asphalt,

in which are contained the inorganic constituents of the coal and the non-liquid or soluble coal substance, amounting, in the case under discussion, to about 10% of the coal used. These products and about 2 kg benzine which are recovered from the gas represent the yield from the coal used.

Corresponding to the 40 kg paste oil supplied, an analogous fraction must be returned to the process. The experimental apparatus permitted operation with a degree of accuracy such that at a daily throughput of 1 ton coal, the products introduced were recovered in the end products except for a loss of about 1%.

As a rule, the processing of brown coals or pitch coals presented less difficulty than did bituminous coal and produced higher yields. I have already mentioned that we were able to open up the ash-free substance of such coals except for a residue of about 1%.

On average, hydrogen consumption amounted to 5%. of the weight of the coal. No difficulty arose in causing considerably larger quantities of hydrogen to be taken up by further pressure treatment of the primary products, which greatly increased the yield oflow-boiling products at the expense of the high-boiling oils. Economical considerations will decide the extent to which hydrogen consumption may be increased in hydrogenation of coal and its liquefaction product.

From the gaseous products, methane and ethane, hydrogen and carbon dioxide can be produced by splitting at high temperature in the presence of steam, employing a process to whose industrial development we successfully applied ourselves for some time. The reaction proceeds in two stages. Methane and steam are converted into carbon monoxide and hydrogen

$$CH_4 + H_2O = CO + 3H_2.$$
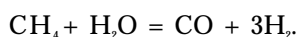
Further hydrogen forms by passing the mixture of carbon monoxide and steam over a catalyst in the presence of excess steam

$$CO + H_2O = CO_2 + H_2$$
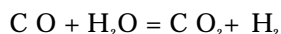
so that, according to the formula

$$CH_4 + 2H_2O = CO_2 + 4H_2$$
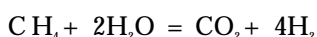
four molecules hydrogen are formed for each molecule CH_4. It is sufficient to split part of the methane-ethane mixture in this way to obtain the quantity of hydrogen required for the process. The carbon dioxide mixed with the hydrogen can easily be separated with water under pressure following the compression of the gases. As far as I know, this principle ofhydrogen production is now being exploited in America for the hydrogenation of oil.

The separation of the heavy oil fractions from the inorganic substances presented major problems. Since this point is of essential importance for the

practical operation of coal liquefaction, we examined it in detail and found separation could satisfactorily be accomplished by filtering the discharges in filter cells at suitable temperatures. We discovered that the more completely the product issuing from the apparatus had been subjected to the action of hydrogen, the more easily separation could be effected. Complete hydrogenation can be achieved in a horizontal vessel if the agitator is so designed as to prevent mixing of unprocessed and semi-finished products with the finished product, which is not possible in vertical hydrogenation apparatus. Oils with good lubricating characteristics were recovered from the heavy fractions of the coal oil.

As already mentioned, we carried out no systematic investigations into the influence of catalysts on the hydrogenation of heavy oils and coal. The elegant investigations into the effect of various catalysts on these hydrogenation processes at the Badische Anilin- & Sodafabrik were carried out when our own researches were nearing conclusion, and these investigations resulted in the hydrogenation processes now being operated at the factories of LG. Farbenindustrie.

My own work on high pressure has now come to an end. Many problems which stimulated the urge to research in the course of work on high-pressure reactions which lasted for almost two decades, must remain uninvestigated, because efforts are now devoted to another field. The need for concentration is an important result of many years of practical research.