

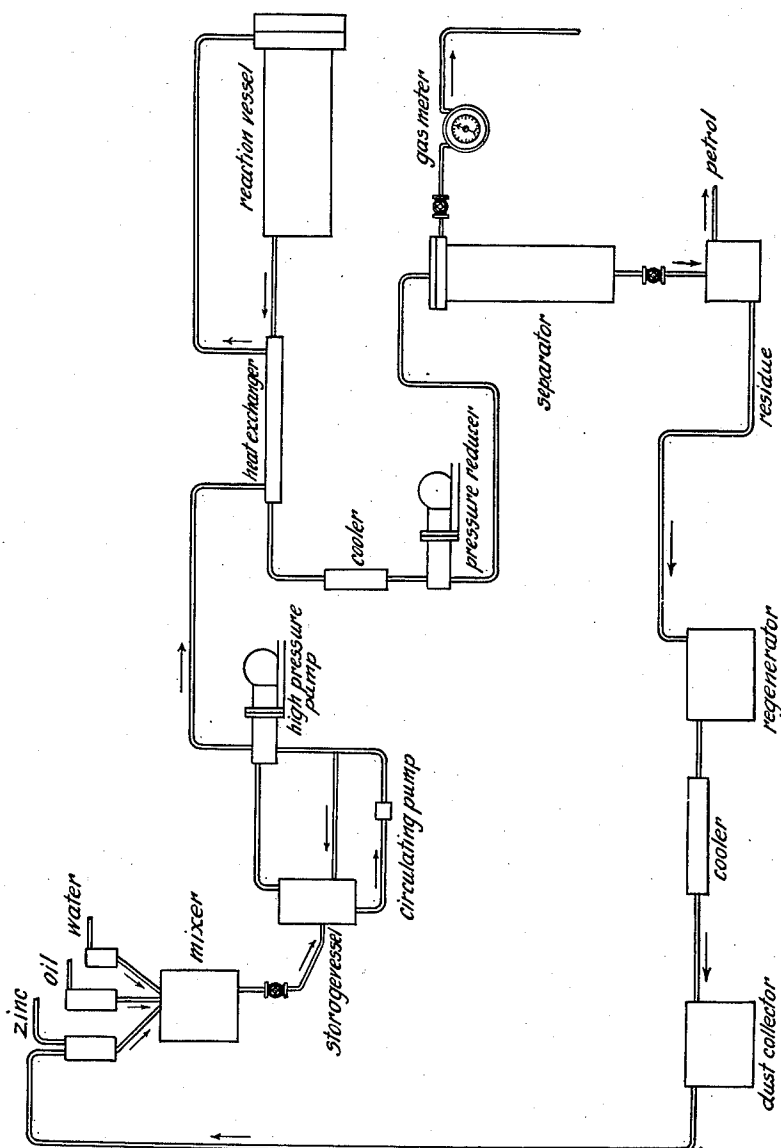
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PROCESS OF HYDROGENATING CARBONACEOUS MATERIALS

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PROCESS OF HYDROGENATING
CARBONACEOUS MATERIALSTheodor Wilhelm Pfirrmann, Castrop-Rauxel,
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My invention refers to the treatment of carbonaceous materials and more especially to a treatment whereby solid or liquid materials of the kind referred to which boil at higher temperatures are converted into products of higher value.

My invention is a modification of the process disclosed in a copending application for patent of the United States filed by Richard Bayer on September 21, 1929, Serial No. 394,393, according to which liquid products are produced from solid or liquid carbonaceous materials by subjecting same at high temperatures and high pressure in an autoclave to the action of nascent hydrogen developed by the interaction of water and finely subdivided (spongy) iron admixed to the materials under treatment. In this process the ferric oxide resulting in the reaction, after having been removed from the reaction vessel, is reduced again to metallic iron with the aid of reducing gases, the metallic iron being reintroduced into the reaction.

Iron appeared to be the only metal allowing the process to be carried out in a commercial manner, since iron is readily reduceable and on such reduction is obtained in pulverulent, spongy condition requiring no further comminution and allowing the reaction mixture to be conveyed by pumping, while other metals capable of reacting with water under formation of nascent hydrogen at a sufficiently high reaction velocity are either not reduceable at all or only with difficulty, or, if reduced, form compact masses which require comminution by mechanical means. Experience moreover showed that metals comminuted in such manner showed a tendency to clogging the pipes, the pumps being moreover worn down by them in a short time.

Contrary to these assumptions I have now found that the process of hydrogenating carbonaceous matter in the manner above described can also be carried out in a simple and very efficient manner with zinc metal instead of the iron hitherto used, provided only that the zinc oxide forming in the reaction is reduced in such manner that the metallic zinc formed by reduction is obtained in very fine subdivision.

While it is well known to reduce zinc oxide and zinc ores by means of solid carbon, such reduction with gases containing oxygen, even in combined form, such as water-gas, which contains carbon monoxide or hydrogen, is not feasible since in this reaction carbon dioxide or water are formed which react at once with the finely subdivided zinc under formation of zinc oxide.

I have now found that zinc oxide can be reduced with great advantage, besides with solid carbon, also with hydrocarbons, such as methane or its higher homologues or with liquid hydrocarbons in the vapour phase, if a temperature of about 1000° is maintained.

If the zinc oxide is reduced with the aid of such vapours, more especially if these vapours are present in excess of the stoichiometric quantity, the resulting metallic zinc is obtained not in solid form, but in the form of finely subdivided zinc powder, which can be employed directly in the hydrogenation process described above, since it can readily be forced by pumping into the reaction vessel together with the oil and water.

It is, however, also possible to reduce the zinc oxide with the aid of solid carbon, provided that some gaseous hydrocarbon or hydrocarbon vapour is present to carry away the distilling zinc in the form of a fine powder.

The hydrogenation reaction employing zinc as reagent with water to develop hydrogen occurs according to the equation



This reaction occurs under a greater development of heat than the reaction with iron, so that the reaction mixture need be preheated to a lower temperature only. Apart therefrom zinc reacts far more quickly with the water than iron so that as compared with iron it allows the conversion of a greater volume of the oil in the same reaction vessels.

As a rule no additions to accelerate the reaction between the zinc and the water are required, the reaction occurring almost instantaneously, but such accelerators may be added in the case where less than the molecular quantity of zinc is employed. I have found that in some cases the reaction between the zinc and the water must even be retarded, and in these cases I prefer using only the molecular quantity, or even less, of water, adding the water (successively) at different points of the reaction system.

A further advantage offered by the use of zinc as compared with iron consists therein that zinc does not favour the formation of methane. In other words less of the oil under treatment is converted into gases so that the yield of hydrocarbons is higher than if iron is used in the reaction.

Equally as with the iron also zinc allows operating with sulphur containing materials and in this case the products obtained are almost free from sulphur, part of the sulphur being in this

case combined in the form of zinc sulphide, which on being regenerated does not become volatile and may be converted by oxidation into zinc oxide and is returned into the process.

The hydrogenation with zinc is particularly suitable in the case where solid carbonaceous materials such as pitcoal, lignite and the like shall be combined with hydrogen. If the reaction is carried through with iron, the iron must be separated from the ashes contained in the raw material by subsequent treatment. When zinc is used, however, the oxide which remains in the residue or ash after the hydrogenation reaction may be reduced under high temperature conditions so that metallic zinc is volatilized. Such zinc is carried away by the gases in metallic form as a vapour and is recovered by condensation in pure condition as a powder, while the residues are substantially freed from zinc.

When using the equivalent quantity of water, up to 99% of the zinc are converted into zinc oxide. In certain cases it may prove useful to employ water in excess of the calculated quantity, since the water in excess replaces a certain percentage of the oil in the solid material so that the excess of water is present in the zinc oxide, while the oil is easily available in liquid form. Instead of providing an excess of water in the reaction vessel from the beginning, it may also be subsequently added to the hydrogenation mixture and in this case the oil is also displaced from the zinc oxide.

The drawing is a flow sheet illustrating the process.

In practising my invention I may for instance proceed as follows:—

Example 1

100 parts by weight of a finely ground bituminous coal are forced by pumping together with 120 parts zinc powder, 40 parts water and 100 parts brown coal tar, serving as a carrier, into a pressure-resistive reaction vessel equipped with an agitator and heated to a temperature of about 450° C., the pressure within the vessel being maintained at about 250 atms. The reacted mixture travels through the reaction vessel and after leaving it is passed through a heat exchanging device. 85% of the bituminous matter are thus converted into liquid oils, about 25% of which may be used as liquid fuel, while the rest boiling between 220 and 360° C. can be used either as a fuel for Diesel engines, or for heating purposes or may be employed as starting material for the manufacture of lubricating oils, or it may be returned into the process together with fresh coal.

In a similar manner comminuted wood can be hydrogenated, the wood substance being converted completely into oil. From 100 parts air-dried wood about 50 parts of an oil were obtained.

The gases leaving the reaction vessel contain only from 5-10% hydrogen, the rest being methane, to which some ethane is admixed. The zinc oxide contained in the residue together with carbon and ashes is heated to about 1000° C. in a vertical step-grate furnace together with a corresponding quantity of untreated coal, methane being at the same time introduced into the furnace. The zinc leaving the furnace together with the gases is recovered in condensers in the form of powder, while the gases may be utilized to heat the furnace.

Example 2

A mixture of 10 parts by weight brown coal tar

oil boiling above 250° C. and containing up to 5% sulphur with 10 parts zinc powder and 3.5 parts water, which may contain a few per cent soda or potash, is heated in a reaction vessel to about 455° C., the pressure rising to about 350 atms. About 102% by volume of a comparatively low boiling oil are obtained, which contains less than 0.1% sulphur, 42% boiling up to 180° C., further 30% between 180 and 220° C. The rest may be once more subjected to hydrogenation or utilized as liquid fuel or as a starting material for the manufacture of a lubricating oil. The zinc oxide resulting in the reaction is reduced to zinc powder with the equivalent quantity, or more of methane.

Similar results are obtained with a tar produced from lignite. The phenols of the tar are converted to the greater part into aromatic hydrocarbons. Thus for instance a brown coal tar containing 85% phenols, after having been subjected to hydrogenation at 475° C. only contained about 9% phenols. The fraction still containing phenols may be re-introduced into the process so that practically a complete reduction of the phenols may be obtained.

If raw materials are treated which do not readily lend themselves to hydrogenation, a specific hydrogenation catalyst may be added and in this case, instead of alkalis, chromium, chromium salts, molybdenum compounds or the like may be added in watery solution.

For example, 15 parts of molybdic acid are dissolved in the water required for performance of the reaction by adding and heating with about 15 parts of caustic soda solution of 20% strength. 10 parts of ammonium sulphide are added and the solution is diluted to such an extent as to contain 5% molybdenum. This solution may be used in the process as described and in place of the soda solution, referred to in Example 2. In this form of the process the known hydrogenation catalysts are enabled to act in molecular solution, i. e. in an extreme grade of subdivision.

Zinc has proved to be particularly useful in the hydrogenation of crude oils (petroleum) since in the oil districts the methane and other hydrocarbons required for its reduction are available in great quantities; the natural gas available in these districts can be used directly for regenerating the zinc oxide.

Natural emulsions of crude oils, which on account of the water content are difficult or impossible to treat, may be hydrogenated according to the present process with zinc and water to great advantage.

The residues from the cracking processes may also be reacted in this manner, for instance 100 parts by weight of cracking residues of crude oil of 300° C. initial boiling point, being subjected to treatment for hydrogenation with 100 parts zinc and 28 parts water at about 450° C. and a pressure of about 400 atms. The resulting product, of which about 102% by volume are obtained, consists of about 38 parts by volume gasoline and 25 parts by volume petroleum, the rest boiling above 300° C., which may, either be subjected to further hydrogenation, or may be used as starting materials for the manufacture of lubricating oils.

I may apply this process also to the refining of liquid fuels recovered in some other manner, for instance gasoline obtained by cracking, which contains sulphur and non-saturated compounds, or of crude benzene which would other-

wise have to be treated with acid. In the hydrogenation procedure according to the present process the presence of sulphur is not interfering with the reaction, on the contrary it favours the hydrogenation reaction. In the reduction process, however, sulphur is an undesirable substance since zinc sulphide is not being reduced to metallic zinc and does not act as a hydrogen supplier. Therefore, when treating highly sulphurous initial materials the formed zinc sulphide will be reduced to zinc oxide wholly or partly before undergoing the reduction, by means of a roasting process. The extent of removing the sulphur in the roasting process depends on the initial materials.

The hydrogenation by the interaction of metal and water proceeds the better, the higher the pressure. In proportion to the degree of filling of the reaction vessel the pressure in the vessel rises, and the percentage of liquid required for conveying the zinc through the vessel increases correspondingly. Therefore the capacity of a given reaction space rises considerably in proportion to the rising pressure since the time, during which the substances remain in the reaction vessel, rises in proportion to the degree of filling of the vessel. First of all, however, the undesirable formation of hydrocarbon gas, such as methane, is greatly reduced as the pressure rises, and the yield of liquid hydrogenation products is increased. Since the production of the high pressure, as compared with processes operating with hydrogen compressed by mechanical means, can be effected in this process by simple liquid pumps without requiring considerable energy, pressures of 500 atms. and above can be used in actual practice.

The substances to be reacted may be introduced into the reaction vessel either singly or mixed with each other, or the zinc powder may be either admixed to the water or to the oil. An agitator in the reaction vessel will intimately mix the substances.

Since, when forming the hydrogen by interaction of zinc and water, considerable quantities of heat are liberated, it is preferable to introduce the zinc and/or the water into the reaction vessel not at one point but at several distant points to provide for a better distribution of the heat.

The reaction vessel may be arranged vertically or horizontally and the water may be conveyed in equal current or in countercurrent to the zinc and to the materials to be hydrogenated.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

I claim:—

1. In a process of treating solid and liquid carbonaceous materials by heating such materials in a closed container with water and a metal under conditions such that the water is decomposed by the metal to form hydrogen, the

metal is oxidized and the hydrogen reacts with the carbonaceous materials to form liquid products and a residue containing the metal oxide, the improvement which comprises using zinc powder as said metal, separating the zinc oxide-containing residue formed by the reaction from said liquid products, subjecting the oxide-containing residue to the action of reducing gases under conditions such that metallic zinc is vaporized, condensing and recovering metallic zinc from the vapors in the form of fine powder and returning the powder for use as the metal in said process.

2. In a process of treating solid and liquid carbonaceous materials by heating such materials with water and a metal under conditions such that the water is decomposed by the metal to form hydrogen, the metal is oxidized and the hydrogen reacts with the carbonaceous materials to form liquid and gaseous products, the improvements which comprise using zinc powder as said metal, separately recovering said gaseous products, said liquid products and the zinc oxide-containing residue formed during the reaction reducing the zinc oxide in said oxide-containing residue by subjecting it to the action of said gaseous products while heating above the volatilization temperature of metallic zinc whereby the metal is vaporized, condensing and recovering metallic zinc from the vapors in the form of fine powder and returning the powder for subsequent use as the metal in said process.

3. The process of claim 2 wherein said materials are heated with said water and said metal in a closed reaction zone at a temperature between 300° and 500° C. and under autogenous pressure.

4. The process of claim 1 wherein a molybdenum compound is present during heating of said materials with said metal and water, said molybdenum compound acting as a hydrogenation catalyst.

5. In a process of treating solid and liquid carbonaceous materials containing sulphur by heating such materials with water and a metal under conditions such that the water is decomposed by the metal to form hydrogen, the metal forms a sulphide and hydrogen reacts with said carbonaceous materials to form liquid and gaseous products and a metal sulphide-containing residue, the improvement which comprises using zinc powder as said metal, separately recovering the gaseous and liquid products as well as the zinc sulphide-containing residue, roasting the residue to form zinc oxide therein and subsequently reducing the zinc oxide-containing residue by subjecting it to the action of said gaseous products while heating above the vaporization temperature of metallic zinc, condensing metallic zinc vapors and recovering the zinc in the form of a fine powder and returning the powder for subsequent use as the metal in said process.

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