

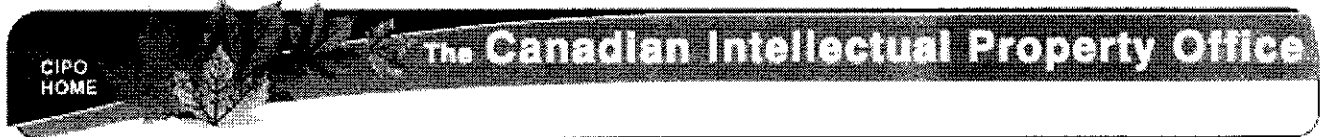


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(54) METHOD OF PRODUCING HYDROCARBONS AND OTHER VALUABLE PRODUCTS FROM CARBONACEOUS MATERIAL

(54) METHODE DE PRODUCTION D'HYDROCARBURES ET AUTRES PRODUITS DE QUALITE DE MATIERE CHARBONNEUSE

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This invention relates to the production of hydrocarbons and other valuable products from carbonaceous material capable of being hydrogenated, and more particularly to a low temperature hydrogenating, isomerizing and cracking process.

5 One object of this invention consists in providing a cracking process which produces a surprisingly high yield of valuable hydrogenated and isomerized cracked products.

Another object of this invention consists in providing a hydrogenating and isomerizing cracking process which operates
10 at comparatively low temperature and more particularly at a temperature below 200° C. and by the reaction conditions of which the danger of corrosion of the apparatus used, is greatly reduced.

Still another object of this invention consists in
15 providing a hydrogenating and isomerizing process which requires much less energy than any of the known hydrogenation, isomerisation, and cracking processes, thus allowing a more economical recovery of valuable reaction products from low carbonaceous material.

20 A further object of this invention is to provide, in a simple manner, very effective hydrogenation, isomerisation, and cracking catalysts which enable to subject various kinds of starting material to the hydrogenating, isomerizing, and cracking process according to this invention.

25 Other objects of this invention will become apparent hereinafter in the specification and in the claims annexes hereto.

The process of this invention consists in subjecting carbonaceous material capable of being hydrogenated, to the action of hydrogen containing gases in the presence of metals, of elements which, by loss of an electron, attain metallic character, or of organo-metal complex compounds of such metals or elements on the one hand, and of non-metallic elements of groups VI and VII of the periodic system, or of their compounds which are capable of splitting off protons either directly or from their reaction mixture on the other hand. The hydrogen partial pressure during such reaction is at least 1 atmosphere and is preferably between 20 and 200 atmospheres. It may even be higher. The reaction is advantageously carried out at increased temperature, preferably at a temperature between 45° C. and 280° C. The organo-metal complex compounds may be separately synthesized and, after formation, are then added to the carbonaceous material to be treated. Suitable intermediate compounds and waste materials which are capable to form said complex organo-metal compounds, may also be used. Furthermore, one may proceed in such a manner that said organo-metal complex compounds are formed in the cracking chamber, for instance, by adding the corresponding metals or alloys of such metals to the reaction mixture and by adjusting the reaction conditions so that the required amount of said extremely labile complex organo-metal compounds is always present in the reaction chamber and the reaction mixture. By these means, it is possible to adjust the process to any given requirement and to any commercial and/or technical need which may arise.

Complex organo-metal compounds, intermediate and waste products which may be used in the process according to this

invention are, for instance, the following:

Residues of the catalytic cracking process with aluminum chloride according to McAfee.

Organo-metal compounds according to Grignard.

5 Residues of the catalytic isomerisation process by means of aluminum chloride.

Residues of Friedel-Craft processes, for instance, of alkylating aromatic compounds by means of aluminum chloride.

10 Residues of the catalytic reduction of aldehydes and ketones according to Meerwein and Ponnendorf.

Residues of the reduction process according to Bonvault-Blanc.

15 Organo-metal compounds, such as lead alkyl, lead phenyl, zinc alkyl, aluminum alkyl compounds, metal carbonyl compounds and others more.

Mixtures and alloys of such metals and elements of metallic nature with themselves or with organo-metal compounds or mixtures of said organo-metal compounds may also be used as catalysts.

20 Most probably so-called ansolve acid residues are formed which contain, combined therewith by means of secondary valences, organic residues, said residues adhering to the external sphere of the anion or the cation respectively. Said residues are arranged according to Rosenheim's heteropoly acids or around a
25 metallic central atom in said ansolve complexes according to Meerwein's theory. Hydrogen is added to said complex by replacing one or several bonds whereby an organo-metal hydrogen complex compound is formed.

30 When adding metals or metallic elements to the organic starting material, it is of advantage and a preferred embodi-

ment of the invention to provide chemical compounds in the reaction mixture which cause formation of complex organo-metal compounds. Such chemical compounds are, for instance, the following:

5 Halogen,
 halogen compounds,
 alkyl halogenides,
 carbonyl compounds,
 carbon oxides,
10 carbon oxyhalogenides,
 carbon sulfides,
 carbon oxysulfides,
 mercaptanes,
 thioethers, halogenated ethers,
15 ketones,
 aldehydes and others more.

It is contrary to expectations that hydrogenation according to this invention does not take place in definite stoichiometric proportions. On the contrary, when maintaining
20 a suitable hydrogen partial pressure in the reaction mixture of
 at least 1 atmosphere above atmospheric pressure, an amount of
 hydrogen is consumed which exceeds many times the amount of
 metal used, calculated upon the average molecular weight of said
 metal. In some instances the hydrogen consumption reached the extra-
25 ordinarily high amount of about 15 % of the charged starting
 material. Thereby, in all cases, only a fraction of the amount
 of metal expected according to Law of constant and multiple
 proportions is required and consumed.

It is known to convert unsaturated compounds by means of hydrogen in statu nascendi in the presence of metals into saturated compounds. However, it could not be expected and is entirely unobvious that it is possible to add much larger amounts of hydrogen as corresponds to the stoichiometric proportion, to such metallic catalysts when maintaining suitable conditions of temperature and pressure which may be varied according to the requirements. The general rule may be postulated that the organo-metal hydride complex compounds at a molecular weight, which increases with increasing partial pressure of hydrogen in the reaction mixture, Temperature increase above 200° C., in general, is of no marked influence. When using aluminum complex compounds, a temperature of about 160-170° C, is usually sufficient.

As starting materials for the hydrogenation, cracking, and isomerisation process according to this invention there may be used all those carbonaceous materials which are also used in the known Bergius process, such as natural and/or synthetic hydrocarbons and/or their derivatives, such as, for instance, fats, oils, waxes, coal extracts, bituminous materials, pitches, gondron (mixture of hard asphalt with high boiling mineral oils), stearin pitch, masut, low temperature distillation and carbonisation products of coal, lignite, peat and other organic materials (light oils, medium oils, heavy oils, tars, low temperature tar), distillation products from oil bearing shales, mineral oils, and their distillation residues, residues from cracking processes, acid sludges and tars, residues of the oil and fat consuming and working up industry, peat, wood, lignin, cellulose containing materials, any other liquid oily material rich in carbon, such as asphalt, asphalt base oils, fuel oils, and in general organic materials, such as phenols, alcohols, ethers,

esters, acetals, aldehydes, ketones, either separately or in mixture with each other.

The reaction is carried out in suitable shaking, stirring, rotating and the like apparatus in continuous operation
5 and/or in batch processes in one and/or in several stages.

The steel used for the reactor should contain as little carbon as possible since the carbon will be removed in the course of time by hydrogenation. It is very surprising, for instance, that the aluminum dust and the aluminum turnings used are not
10 substantially attacked during the process although free hydrochloric acid is present in the reaction mixture. Due to the fact that hydrogenation may be carried out below 200° C. the critical temperature range of 280-380° C. within which halogen attacks the apparatus, is avoided.

15 The reaction products may be subjected to a fractionating treatment either before the reaction or immediately thereafter or during intermediate stages of operation. The material to be hydrogenated may be passed through the corresponding metal compound under increased hydrogen pressure in the liquid
20 or in the slurry phase. It may be conducted in gas or vapor form over the metal compounds which may be deposited on suitable carriers. The metal may also be added to the starting slurry. Or the metals may serve as fillers in the reaction chambers and towers. It is of great importance to intimately mix the reaction
25 mixture with and to very thoroughly distribute the hydrogenating gas therein. This is accomplished by spraying or injecting or atomizing the starting material in the reaction chamber, for instance, through suitable nozzles or other feed devices. Filler bodies, distributing baffle plates and other suitable means
30 should be provided to cause such intimate mixing and contacting

of the starting material, the hydrogenating gas, and the catalyst. As soon as the reaction is partly or fully completed, the reaction products are withdrawn from the reaction chamber and are worked up and separated from each other in suitable separating, fract-
5 ionating and the like devices. They may then be used for further reactions or worked up to useful and valuable products. Catalyst material which might be entrained in and carried along by the reaction products may be recycled into the process according to this invention.

10 As source of hydrogen there may be used electrolytically produced hydrogen, fuel gas, illuminating gas, natural gas, oil still gas, coke oven or coal gas, or any other gas containing sufficient amounts of hydrogen, i.e. the hydrogen gas need not be very pure.

15 The usual auxiliary plant installations, such as plants for producing hydrogen containing gases, compressors, circulating, distilling, refining apparatus, installations for removing phenolic components in the starting oil and the reaction products, for conditioning of coal, for converting waste gases
20 in hydrogen containing gases, for producing high pressure steam for heating purposes and others more should be provided. Combination of the new hydrogenation cracking process with a low temperature distillation plant, with sources of natural gases, with alkali electrolysis plants, aluminum or other light metal factories
25 etc. may furthermore reduce the costs of the process.

In contrast to the synthetic process according to Fischer-Tropsch, the process of destructive hydrogenation as developed by Bergius and later, by I.G. Farbenindustrie A.G., is based on the decomposition of carbonaceous material and hydro-
30 carbons by the addition of hydrogen under high pressure.

The temperature and the pressure employed when working according to said process are, in general, as high as 410-460° c. and 200-700 atmospheres. Such high temperatures require not only large amounts of energy in order to initially heat the starting material, but the necessary equipment, apparatus, and devices must be highly resistant to corrosion and hydrogen diffusion. Furthermore, said process approaches the limits whereby spontaneous methane formation takes place to such an extent that it is difficult to operate fully automatically and continuously. As construction material, a highly resistant and expensive chromium molybdenum stainless steel must be used. This construction material and the equipment for heating the reaction mixture under high pressure render the process very expensive and raise the costs of the finished products considerably. Furthermore, the waste catalyst sludge is useless and must be especially worked up which operation, again, increases the costs of the process. Another disadvantage of the process is the dangerous and obnoxious coke formation in the reaction vessels and the pipe lines when operation has to be interrupted or stopped.

The present invention endeavors to overcome the disadvantages of said known process. It allows to reduce the hydrogenation temperature to below 200° C. This means that the corrosion problems are not as difficult to overcome as in the high temperature process. Very valuable products are obtained according to the new process, especially heavy oils, such as Diesel oils, lubricating oils, gasoline, fuel gases and others more.

Yields and properties of the reaction products vary in accordance with the starting material used. The following table may illustrate the composition of the various products

which may be obtained by the new process:

5 A. Gaseous products: 3-6 % of the charge. They consist chiefly of iso-butane. Methane, ethane, propane, n-butane pentanes may also be present, besides carbon monoxide, carbon dioxide, and hydrogen sulfide.

10 B. Liquid reaction products: About 95 % of the charge. The crude oil has a density, at 20° C., of 0.775-0.850. The boiling range of said crude oil is between 40° C. and over 500° C. (calculated from values determined by vacuum distillation).

Flash point: 129° C.

Burning point: 216° C.

Fractions: 31 % of the crude oil distill between 110-320° C.,

25 25 % between 200-360° C.,

45 % between 320-500° C.

On fractional distillation the following fractions are obtained:

a. Gasoline and light oils:

20 4.5-16 % of the charge.

Density, at 20° C.: 0.735-0.759.

Flash distillation of a mixture of several charges:

Initial boiling point: 43° C.

25 5 % 69° C.

10 % 79° C.

20 % 98° C.

30 % 113° C.

40 % 126° C.

30 50 % 139° C.

60 % 153° C.

70 % 171° C.

80 % 195° C.

90 % 223° C.

95 % 295° C.

5

End point: 295° C.

Color: White, clear, like water.

Odor: Agreeable, aromatic, "sweet".

Octane number: About 80 (without lead tetraethyl).

10

Limits of boiling point:

Up to 75° C.: 6 %

75-100° C.: 17 %

100-145° C.: 30 %

145-200° C.: 30 %

15

110-320° C.: 60 %

b. Heavy oils:

About 80 % of the charge.

Density, at 20° C.: 0.80 - 0.85.

Boiling point at 760 mm: Between about 185° C. and
over 500° C.

20

Color: Light yellow to amber yellow, with green
fluorescence.

Appearance: Very oily liquid.

Stagnates at a temperature between 2 - 5° C.

25

Paraffin content: About 20 %

Sulfur content: 0.2 - 0.4 %

Conradson test: 0.5 - 1.0 %

Viscosities after removal of paraffins:

OE/50° C.: From 6 to about 25.

30

VP : 2.

c. Sludge:

Density: About 1.2 - 1.8.

Liquid to solid mass.

Color: Black.

5 Odor: Aromatic, but biting.

Carbon content: 30 - 66 %

Hydrogen content: 3.8 - 7.5 %

Mol ratio of C : H : Between 1:1.69 and 1:0.99.

Molecular weight: About 750.

10 Content of inorganic material: 25.6 - 44.9 %.

Surprisingly little or no corrosion was observed when carrying out the process according to this invention.

The process according to this invention is especially useful for the manufacture of lubricating oils. It is, of course, 15 not limited thereto but may find extensive application also for the production of gasoline and fuel oils. It is especially suitable for working up residues derived from various manufacturing processes and may even be applied for the economic disposal of acid sludges from the petroleum and the like refinery.

20 One of the most important factors of the process according to this invention is to recognize the right moment of completed catalyst formation, because at that moment hydrogenation in the advantageous manner as described above, sets in and can be readily continued until the best possible yields of 25 valuable reaction products are obtained.

The following examples serve to illustrate the invention without, however, limiting the same to them.

Example 1:

100 parts by weight of a low temperature distillation oil boiling between about 100° C. and about 400° C., are intimately mixed with 5 parts by weight of aluminum dust. Said mixture is intimately mixed with hydrogen under a partial pressure of about 50 atmospheres and is continuously injected, by means of a nozzle, into a reaction tube which is loosely filled with aluminum turnings. The oil-aluminum dust-hydrogen mixture passes thereby through a liquid Gustavson's compound, thus, is distributed over a large area. The temperature, during the reaction, is maintained at about 185° C. Gustavson's compound is produced, for instance, according to "Journal of the Chemical Society (London)" volume 42, page 27 (1882). After about 10 hours, formation of the catalyst is completed and very effective hydrogenation sets in. The reaction mixture of oil, aluminum dust, and hydrogen is then continuously passed through the reaction chamber. At the same time small amounts of chlorine are also introduced into the chamber.

A saturated reaction product of dark color together with excess hydrogenating gas and gaseous reaction products is continuously withdrawn from said chamber. It is freed, in a manner known per se, from any sludge entrained therein. The gaseous reaction products amount to about 6 % of the charged oil. They are chiefly composed to about 60 % of isobutane. The liquid reaction product consists of saturated hydrocarbons boiling between about 35° C. and about 350° C. The yield is about 92 % calculated with respect to the amount of oil subjected to hydrogenation. About 8 % of hydrogen, calculated with respect to the charged oil, are consumed. Space velocity: 1.0 kg. per kg. of catalyst per hour.

About 90 % of the excess hydrogenation gas are re-cycled while about 10 % of fresh hydrogenating gas, for instance, containing 95 % of hydrogen and 5 % of carbon monoxide, carbon dioxide, methane and other low-molecular hydrocarbons, oxygen, and nitrogen are added thereto. The sludge separated from the
5 reaction product is passed through a sludge pump and is also returned to the reaction chamber. The liquid reaction product, after washing with water or with aqueous acid and lye, is subjected to fractional distillation.

10 Example 2.

The same low temperature distillation oil as used in example 1, is introduced by injection into the reaction chamber. At the same time hydrogen is pumped into said chamber under a pressure of about 300 atmospheres. The oil which is there-
15 by saturated with hydrogen, is then passed at about 200° C. through liquefied sodium contained in said chamber. The withdrawn reaction product is separated from accompanying solid particles and sludge. Said solid particles and sludge are returned to the reaction chamber. The reaction product itself is
20 subjected to fractional distillation.

100 parts by weight of the starting oil yield 90 parts by weight of an oil boiling between about 30° C. and about 330° C. Furthermore about 10 parts of gaseous products are obtained. The liquid as well as the gaseous reaction
25 products are saturated and are free of phenols, alcohols and also of sulfur. The sulfur may be recovered from the waste gases wherein it is present in the form of hydrogen sulfide.

Example 3.

Aluminum dust is activated by treating with an alcoholic mercurichloride solution. Such activated aluminum dust is then intimately mixed with a liquefied soft bituminous coal having a softening point of about 25° according to Kraemer-Sarnow's method (in the following examples designated by "KS"). The mixture is injected into a reaction chamber at 170° C. and under a hydrogen pressure of about 40 atmospheres. From a mixture of 6 parts by weight of activated aluminum dust and 100 parts by weight of said bituminous material there are obtained, by continuous recirculation, about 96 parts by weight of withdrawn reaction product, about 6 parts of sludge, and about 5 parts of gaseous products. Said gaseous products consist chiefly of iso-butane, they contain a little propane and some butane but almost no methane and ethane; pentanes are also not detectable in said gas.

The liquid portion of said reaction product boils between about 20° C. and a temperature somewhat higher than 450° C. The latter boiling point is calculated from the boiling point determined on vacuum distillation. 55% of said oil are gasoline boiling below about 200° C., 20 % are of the medium oil type, 15 % of the heavy oil type while the remainder (about 10 %) are paraffins of excellent power of crystallisation.

25

Example 4.

Turnings of electron metal AZ 91 (an alloy of 89.5-89.8 % of magnesium, 9 % of aluminum, 1 % of zinc, and 0.2-0.5 % of manganese are reacted, according to the method of Krause and Wendt, Berichte der deutschen chemischen Gesellschaft" volume 56, page 466 (1923), with ethylbromide

30

in ether. A mixture consisting chiefly of aluminum, zinc, and magnesium organo-metal compounds is obtained thereby. 20 parts by weight of said compounds, without isolating the same, are reacted gradually with altogether 160 parts
5 by weight of a naphthenic residual oil, the benzine and Diesel oil fractions of which were topped off, in a shaking autoclave at a temperature of 170° C. and a hydrogen pressure of about 50 atmospheres. About 8 % by weight of hydrogen are absorbed. The liquid saturated reaction product is sub-
10 jected to fractional distillation whereby a crude oil is obtained in a yield of about 98 % of the starting oil, said crude oil having a boiling range between about 20° C. and about 450° C. (calculated from the boiling point determined by vacuum distillation.)

15 Example 5.

5 parts by weight of commercial tetraethyl lead (so-called Q-fluid) are dissolved in 100 parts by weight of paraffin oil. The mixture is forced at 200° C. under a pressure of about 100 atmospheres of hydrogen through a
20 reaction chamber filled with pieces of earthenware or the like. Yield: About 100 % of an oil boiling between about 20° C. and about 360° C.

Example 6.

A naphthenic residual oil as used in example 4
25 is subjected to distillation with aluminum chloride at 170° C. whereby decomposition takes place and "Gustavson's compound" is formed, said compound being present in the form of a dark tar. 50 parts by weight of said "Gustavson's compound" are mixed with 5 parts of aluminum powder and the
30 mixture is introduced under a pressure of about 50 atmo-

spheres by means of a sludge pressure pump into the reaction chamber. At the same time 50 parts of liquefied soft bituminous coal having a softening point of 25° C. KS, are injected into said reaction chamber at a temperature of about 170° C. and under a hydrogen pressure of about 60 atmospheres. The reaction takes place under generation of heat. The bituminous material is cracked and hydrogenated whereby the space velocity is about 0.5 liters per liter of catalyst per hour. An oil is formed which boils between about 20° C. and about 450° C. (calculated). Said oil contains 53 % of a benzine fraction boiling up to 200° C., 21 % of middle oil, 16 % of heavy oil, and 10 % of paraffin. The yield, calculated with respect to the soft bituminous coal charged, amounts to 95 %. 4 % of gaseous products are formed containing about 60 % of iso-butane. The liquid sludge separating in the separating device, has a density of about 1.3 and is recycled into the reaction chamber. The gaseous products may also be recycled. The completely saturated oil obtained is subjected to fractional distillation and is worked up to various valuable products, in a manner known per se.

Example 7.

Illuminating gas and a low temperature distillation oil are forced at 168° C. and under a pressure of about 180 atmospheres through a reaction chamber. Said reaction chamber is loosely filled with turnings of electron metal AZ 91. A liquid residue, obtained on alkylating hydrocarbons according to Friedel-Kraft's method, is at the same time introduced under pressure into the reaction chamber. After

passing through the reaction chamber, the saturated fractions of the reaction mixture are separated from the liquid sludge in a separating device. The sludge is returned into the reaction chamber. The pressure of the gaseous fractions is reduced and the gases are also partly recycled into the reaction chamber. The liquid oil fraction is filtered through coal, washed neutral, and subjected to fractional distillation. Yield: 95-98 % calculated with respect to charged low temperature distillation oil. Boiling range of said oil: Between about 20° C. and about 450° C. (calculated).

Example 8.

Sludge obtained in a hydrogenation cracking process according to one of the preceding examples is allowed to stand for several weeks in contact with air. The sludge is then liquefied by heating while covered with bituminous coal of 25° C. KS. After intimately mixing said liquefied sludge and said bituminous coal, the mixture is fed under a hydrogen pressure of about 150 atmospheres into a reaction chamber filled with aluminum wool. 97 % of the charged bituminous coal are converted into oil while at the same time 5 % of gaseous products are formed. The oil boils between about 20° C. and about 450° C. (calculated). The heavy sludge separating out of the thin liquid reaction oil has a density, at 20° C., of 1.2 It is recycled into the reaction chamber. The oil is further worked up and refined in a manner known per se.

Example 9.

5 parts by weight of iron pentacarbonyl are intimately mixed with 100 parts by weight of a residual oil from which benzine and Diesel oil fractions were stripped off.

The mixture is fed together with illuminating gas containing 5 parts by volume of ethyl chloride, through a reaction chamber at a temperature of about 250° C. and under a total pressure of about 150 atmospheres. Said reaction chamber is packed with filler bodies of aluminum silicate. A saturated crude oil is obtained which boils within a range of about 20° C to 400° C. (calculated). It is worked up to various products in a manner known per se. Yield on one passage through the reaction chamber: 30 %.

10 Example 10.

Altogether 200 parts by weight of a benzine having a boiling point between 60° C. and 180° C. and obtained by high pressure synthesis according to Bergius, are mixed with 0.4 parts by weight of sulfur chloride. The mixture is gradually passed through a reaction tube at a temperature of about 75° C. and a hydrogen pressure of about 150 atmospheres. The reaction tube is filled with pieces of earthenware which are impregnated with a liquid molecular compound of aluminum chloride and sulfur chloride. As soon as the catalyst is formed and vigorous reaction sets in, the pressure is reduced to about 50 atmospheres. The reaction yields about 60% of a liquid fraction which starts to boil at about room temperature and distills up to about 190° C. About 40% of gaseous products are formed. Said gaseous fraction contains about 60% of iso-butane, indicating that about 24% of the starting material are converted into iso-butane. The liquid fraction is isomerized to a large extent and contains, in contrast to the starting material, 150% more compounds with tertiary carbon atoms. The tertiary carbon atoms were determined according to the method of

Lifschitz and Moldawski "Journal of General Chemistry U.S.S.R." volume 67 (5), pages 422-431 (1935). Said fraction is free of chlorine and of sulfur (the sulfur content is below 0.05 %).

5

Example 11.

A mixture of hydrocarbons (synthetic benzine obtained by high pressure hydrogenation), free of aromatic components and chiefly consisting of naphthenic and paraffinic hydrocarbons, is saturated with about 2 % by weight of chlorine. The hydrocarbon mixture boils between about 40° C. and 200° C. and has a density, at 20° C., of about 0.764. The hydrocarbon-chlorine mixture is passed under pressure through a reaction tube which is filled with magnesium scrap. At the same time a crude hydrogen gas containing 96.7 % of hydrogen, 0.4 % of carbon dioxide, 0.3 % of carbon monoxide, 2.3 % of air, and 0.3 % of hydrocarbons, is fed into said reaction tube under a pressure of about 100 atmospheres. Within 11 hours the catalyst is formed and hydrogenation sets in. Thereupon, the above mentioned mixture of hydrocarbons is continuously passed through the reaction chamber. 300 liters of hydrogen are consumed by 1 kg. of the hydrocarbon mixture. Space velocity: About 1 kg. of hydrocarbon mixture per 1 kg. of catalyst per hour. The products obtained boil between about -40° C. and about 250° C.. 42 % by volume of said fraction consists of benzines with an octane number of 83 and boiling between 70° C. and 180° C. The products are saturated and practically free of chlorine. Furthermore, about 10 % of gaseous products are formed containing about 60 % of iso-butane.

Example 12.

Ferric chloride is dissolved in sulfur chloride. The solution is passed through a reaction tower containing montmorillonite granules of 5 mm edge length. Said montmorillonite granules are thoroughly impregnated with an aluminum chloride-potassium chloride double compound by treating said granules with a melt of molecular amounts of aluminum chloride and potassium chloride and decanting excess of the molten mass from the granules. The granules are then spread out in a dry, cool atmosphere to cool the same, and are introduced into the reaction tower as soon as possible. A residual oil of a density, at 20° C., of 0.889, obtained from German naphthenic petroleum, said residual oil boiling above 360° C., is injected by means of an atomizing nozzle into the reaction tower. Simultaneously, the abovementioned ferric chloride solution is injected into said reaction tower whereby the amounts of ferric chloride solution and residual oil are supplied in the proportion of 1 : 50. At the same time a hydrogen containing gas with 96 % of hydrogen, is introduced into the tower under a pressure of about 120 atmospheres. As soon as the catalyst has formed upon the carrier material, spontaneous hydrogen absorption takes place at a temperature of about 185° C. The reacted oil-ferric chloride mixture is continuously discharged and replaced by corresponding amounts of non-reacted mixture. The discharged material is separated in a separating device. The gaseous products are removed and hydrocarbons are separated therefrom by washing and fractional condensation whereby excess hydrogen and the waste gases are driven off. The residual gas is

added to fresh hydrogen containing gas in an amount of about 30 % by volume and is returned into the reaction tower. The hydrocarbons obtained thereby are converted and the hydrogen recovered therefrom is also returned and added to fresh hydrogen gas introduced into the reaction tower. The liquid fraction withdrawn from the separating device, is washed neutral and is subjected to fractional distillation under pressure. Several fractions are obtained. 40% of the liquid reaction product consist of a benzine fraction having a boiling point between 70° C. and 180° C. The fractions with a boiling point above 180° C. are either worked up directly to paraffin and lubricating oils, or they are returned into the reaction tower for further hydrogenation and cracking.

Example.13.

15 Solid natural paraffin of a melting point of 45° C. is molten. 1 part of a solution of equal amounts of aluminum chloride and thionyl chloride, is added to 100 parts of said molten paraffin. The molten mixture is passed under pressure through a reaction chamber filled with aluminum 20 turnings, in the presence of hydrogen gas containing 4 % of hydrogen chloride. Thereby the temperature is maintained at about 170° C. and the total pressure is about 100 atmospheres. The catalyst is formed within about 9 hours. Thereafter about 400 liters of hydrogen are absorbed by 1 kg. of 25 paraffin. For each kg. of catalyst (consisting of aluminum turnings and molecular compound adhering thereto), 0.9 kg. of paraffin are reacted per hour. The yield is about 45 % of a benzine boiling between 70° C. and 185° C., 6 % of gaseous products containing about 60 % of iso-butane, and about 49 %

of high boiling oils and waxes having a boiling point between 185° C. and 460° C. The iodine number of the benzine is 0.0, the octane number higher than 80.

Example 14.

5 Aluminum chloride containing 10 parts by weight of zinc chloride, 10 parts by weight of ferric chloride, and 1 part by weight of chromium chloride per 100 parts by weight of aluminum chloride, is mixed to form a paste with twice
10 its amount of soft bituminous material having a flow point of 35° C. All the halogenides should be in the anhydrous state although a small content of hydrate does not cause disturbances and, therefore, is without danger. Said paste, together with a cracking gas containing 45 % of hydrogen, about 50 % of hydrocarbons, and 5 % of air to which 3 % of chlor-
15 ine gas are admixed, and together with three times its amount of the soft bituminous material used for pasting, are passed under pressure through a reaction chamber filled with small pieces of montmorillonite whereby a temperature of 168° C. and a total pressure of about 120 atmospheres is maintained.
20 After 9 hours the catalyst is formed and hydrogen is briskly absorbed. Hydrogen absorption amounts to about 500 liters per 1 kg. of bituminous material. About 0.8 kg. of said bituminous material are continuously passed through the reaction chamber for each kg. of catalyst per hour. The reaction
25 mixture, before working up, is passed through a second chamber which is also filled with pieces of montmorillonite. Any solid particles present in the reaction product precipitate therein and adhere to the montmorillonite. As soon as the first reaction chamber does not operate properly, hydrogenation and cracking

is continued in the second reaction chamber. The catalyst in the first chamber is regenerated by treating with hydrogen and hydrogen chloride (1 : 1) at a temperature of about 150° C.

5

Example 15.

A reaction chamber is used as it is described by Kroenig "Die katalytische Druckhydrierung von Kohlen, Teeren und Mineraloelen" Berlin-Goettingen-Heidelberg 1950, page 240. About one quarter of the volume of said chamber is filled
10 with a mixture of 1 part by weight of finely ground montmorillonite and 1 part by weight of a low temperature distillation oil from brown coal or lignite or from oil bearing shale, said oil boiling above 140° C. and containing about 17 % of creosote, 76 % of paraffins, 6 % of water,
15 and 10 % of coke and ash. Hydrogen containing about 95 % of hydrogen, is then introduced into the reaction chamber under a pressure of about 100 atmospheres and at a temperature of about 190° C. The hydrogen enters the chamber from the bottom, and, therefore, causes the mixture of mont-
20 merillonite and oil to whirl and to be thoroughly mixed and contacted with said hydrogen. At the same time, an amount of about 5 % of the chamber volume of hydrogen halogenide gas is added to the hydrogen gas. Into said thoroughly stirred and whirled mass, there is injected the liquefied
25 catalyst residue of a previous hydrogenation charge containing, as an average, about 30-35 % of aluminum, 10-12 % of chlorine or another halogen, and residual organic matter, and, 5 % of fresh, technical grade, anhydrous aluminum chloride. The temperature, during reaction, is maintained

at about 150° C. A hydrogen pressure of about 100 atmospheres is kept for about 8-10 hours. By continuous recycling the reaction mass by means of pumping, it is thoroughly mixed and brought in contact with the hydrogen. Formation of catalyst and setting in of the reaction can be readily recognized by closing the feed valves whereby the pressure decreases. As soon as the catalyst is formed, the reaction products are continuously withdrawn from the chamber and fresh low temperature distillation oil is continuously charged into the chamber. Said fresh oil is mixed, before admission to the chamber, with 30 % by volume of finely ground brown coal or lignite dust. Fresh hydrogen and about 60 % of the waste gases, if necessary, after conversion into hydrogen, are also introduced continuously into the chamber, in order to replace the consumed hydrogen. It is also necessary to continuously add about 1 % of aluminum chloride dissolved in sulfur chloride in order to replace the loss of aluminum chloride entrained in the withdrawn reaction products and, thus, removed from the chamber. The withdrawn liquid, which is under a pressure of about 100 atmospheres, is introduced into a second high pressure reaction chamber filled with fresh montmorillonite dust. In said second chamber the organo-metal portions of the liquid are precipitated on the surface of said mineral dust. The liquid withdrawn from said second chamber is worked up as described in the preceding examples, after gaseous reaction products have been separated therefrom. 40-45 % of a highgrade benzine boiling between 70° C. and 190° C., Diesel oils, lubricating oils, and paraffins are obtained. About 6 % of gaseous products are formed, said gas

containing about 65 % of iso-butane. When the mineral dust in the second chamber is saturated with the catalyst compound, said chamber is switched and becomes the first reaction chamber while a third chamber which is also filled with
5 montmorillonite dust is used as second chamber. The first chamber containing the spent catalyst is subjected to a regenerating treatment, for instance, by treating the spent catalyst with halogenated hydrocarbons, such as ethylene chloride, or with hydrogen chloride and/or hydrogen sulfide
10 whereby the pressure is maintained at about 100 atmospheres.

Example 16.

Fuel oil boiling above 250° C. is mixed with about the same amount by volume of waste aluminum chloride sludge derived from a Friedel-Kraft synthesis. The mixture is heated
15 at 180-225° C. until all the constituents of low boiling point are distilled off. During said heating process, synthetic montmorillonite powder is added to the mixture while stirring vigorously by means of a strong stirring device. The mass, while still hot, is discharged from the reaction
20 container whereby humid atmospheric air is to be excluded and, after cooling and solidifying, is crushed to pea-sized granules. The granules are filled into a reaction chamber as described by Kroenig (l.c.) until about 1 % of its space volume are taken up by the same. They are treated therein
25 for 12 hours, under vigorous whirling, with recirculated hydrogen containing gas, such as cracking gas, illuminating gas, gas from low temperature distillation, hydrogen gas obtained by electrolysis and the like. The temperature is thereby maintained between about 100 ° C. and about

about 150° C. and the pressure at about 50 atmospheres. Thereafter shale oil of any composition containing admixed thereto about 3 % by volume of a mixture of equal parts of aluminum chloride and zinc chloride is introduced into the reaction chamber. The pressure is increased to about 150 atmospheres and the temperature to about 185° C. Hydrogen which is not consumed during reaction is returned into the reaction chamber and the consumed hydrogen is replaced by fresh, hydrogen containing gas. At the same time the reaction products are continuously withdrawn at such a rate that 1.5 tons of oil per 1 ton of catalyst per hour are reacted whereby about 300-500 m³ of hydrogen are absorbed by each ton of shale oil. These ratios must, of course, be maintained only if a fully saturated reaction product is desired. The reaction product corresponds in general in its composition to that of the preceding examples.

Example 17.

Lignite dust is mixed with low temperature distillation oil to a paste containing about 35 % of coal. Such paste is passed, together with a mixture of 80 % of a gas containing about 95 % of hydrogen (so-called O-gas), 10 % of cracking gas, and 10 % of hydrogen sulfide, through molten sodium metal. The reaction chamber is provided with zinc baffle plates which are arranged in such a manner that the gases bubbling through the molten metal, distribute said metal over a large area. The temperature is about 190-220° C., the total pressure about 200 atmospheres. After several hours, the catalyst is formed and hydrogen absorption sets in spontaneously. Hydrogen is absorbed with an hourly speed of 0.6

parts of paste for each part of metal having absorbed at its surface the catalytic molecular compound. About 500-600 liters of hydrogen are absorbed by each kg. of paste. The withdrawn reaction product is separated into about 10 % of gaseous compounds, 12 % of benzine boiling below 200° C., Diesel oil, lubricating oil, and paraffins. 50 % of said paraffinic reaction products, corresponding to about 39 % of the total yield, consist of high melting paraffin wax.

Example 18.

10 Pit-wet peat containing 6 % of solid substances is first dried, for instance, according to the process of Stadnikoff ("Neuere Torfchemie" Dresden and Leipzig 1920) or according to any other suitable method, to a dry content of about 60-70 %. It is mixed to form a paste in the proportion
15 of about 1:1, with a heavy oil boiling between 250° C. Said slurry, after mixing with 1 % of zinc dust, is fed under pressure into a chamber according to Kroenig (l.c.). A Pressure of about 100 atmospheres is maintained within said reaction chamber by introducing hydrogen gas of any purity containing
20 admixed thereto about 3 % of chlorine gas or about 5 % of hydrogen chloride gas. A temperature of about 250° C. is maintained, while reacting the mixture. Spontaneous reaction sets in. The solid peat substances liquefy and, at the same time, water is released. At the top of the reaction column a slurry
25 of water and calcium hydroxide with about 30 % of calcium oxide is fed to the reaction mixture. The withdrawn reaction products are then separated. The alkaline or neutral aqueous layer is removed. The gaseous compounds are either directly or after conversion recycled into the reaction chamber. The oils obtained

are subjected to fractional distillation. The high boiling fraction is used for forming a paste with peat, and the oils of lower boiling point are worked up to valuable products.

Example 19.

5 In the place of peat, as described in example 18, wood flour is used and subjected to the same hydrogenation cracking process. Saturated oils, alcohols, and tars are obtained.

Example 20.

10 In the place of peat, lignine is used and is subjected, in mixture with a heavy oil, as described in example 18, to hydrogenation. Saturated oils, phenols, and hydrogenated phenols, such as cyclohexanol and methyl cyclohexanols are obtained thereby.

Example 21.

15 Lignine and heavy oil are subjected to a hydrogenating and cracking treatment as described in example 18. Instead of adding zinc dust to the paste, the reaction chamber is loosely packed with duraluminum wool. The hydrogenating gas is mixed with about 15 % of hydrogen sulfide. The catalyst is formed after about 10 hours. The lignine is completely converted to light and heavy oils.

Example 22.

25 A paste of lignine and heavy oil is, as described in example 18, subjected in a rotating pressure resistant container to an intermittent hydrogenating and cracking process. The aluminum alloy (duraluminum) is employed in the form of scrap and the paste is thoroughly mixed there-

with by means of heavy metal balls provided in said rotating reaction chamber, to cause intimate contact with the hydrogenating gas.

Example 23.

5 Tar containing about 35 % of aluminum chloride, as it is obtained as residue from the lubricating oil synthesis is forced by pressure pumps into a high pressure electrolytic apparatus provided with aluminum electrodes. Electrolysis is then carried out at about 150° C. under a
10 hydrogen pressure of about 90 atmospheres and with an alternating voltage of about 20 volts and a current density of about 0.7 amperes per square decimeter. As soon as hydrogen absorption begins, residual oil from cracking processes containing admixed thereto about 30 % of brown coal dust, is
15 inuously introduced into the electrolytic device and the absorbed hydrogen is replaced by freshly produced hydrogen.

The examples given show the effect of the new organo-metallic metal hydride complex compounds according to the present invention. They exhibit a surprisingly high hydrogen-
20 ating activity, allowing hydrogenation at a temperature below 200° C. Said hydride complex, as is evident, must be used in the preformed state or must be formed in the reaction mixture before actual hydrogenation of the carbonaceous material in the presence of hydrogenating gases sets in.

25 In the place of the catalysts used in the foregoing examples, other catalysts may be employed likewise. Especially suitable are those organo-metal complex compounds which are derived from metals, such as lead, and elements which form sulfides, said sulfides being readily decomposed by dilute

mineral acids. Such elements are, for instance, beryllium, calcium, sodium, potassium, boron, titanium, chromium, and those mentioned in the examples. Presence of elements which are capable of forming sulfides stable against aqueous mineral acids, is sometimes of advantage. They should not be present, however, in amounts of more than 1% by weight of the organo-metal complex compound.

It is of greatest importance that the carbonaceous material to be reacted is intimately mixed with the organo-metal complex compound catalyst and the hydrogenation gases. For this purpose the reaction mixture is preferably distributed over a large surface area and hydrogenation gas and carbonaceous material are brought into intimate contact with each other and the catalyst. Ways of effecting said intimate contact are described in the examples. Other methods than those mentioned may also be used for enlarging the catalytically active surface.

Of course, many other changes and variations in the reaction conditions, the reaction temperature, the pressure under which the reaction is carried out, the starting materials used, the hydrogenation gases employed, the catalysts formed or added, the apparatus used, the methods and devices for increasing the active surface employed, the means of introducing the reaction components into the reaction chamber and of withdrawing the reaction products from said chamber, the methods of working up and recycling the reaction products, and others more may be made by those skilled in the art in accordance with the principles set forth herein and in the claims annexed hereto.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In a method of producing hydrocarbons and other valuable products from carbonaceous material, the steps comprising reacting such carbonaceous material with hydrogen containing gases in the presence of a catalyst selected from the group consisting of metals, elements which, by loss of an electron, attain metallic character, and organo-metal complex compounds of said metals and elements, and a substance selected from the group consisting of non-metallic elements of groups VI and VII of the periodic system at a hydrogen partial pressure of at least 1 atmosphere above atmospheric pressure, and recovering hydrogenated, isomerized, and cracked reaction products from the reaction mixture.

2. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to claim 1, wherein the reaction is carried out under a hydrogen partial pressure of 20-200 atmospheres.

3. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to claim 1, wherein the reaction is carried out at elevated temperatures.

4. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to Claim 1, wherein the reaction is carried out at a temperature of 45-280° C.

5. In a method of producing hydrocarbons and other valuable products from carbonaceous material, the steps comprising first forming an organo-metal complex compound, then reacting said carbonaceous material with hydrogen containing gases, said organo-metal complex compound catalyst, and a substance selected from the group consisting of a non-metallic element of the groups VI and VII of the periodic system, said reaction being carried out at elevated temperature and under a hydrogen pressure of at least 1 atmosphere above atmospheric pressure, and recovering hydrogenated, isomerized, and cracked reaction products from the reaction mixture.

6. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to claim 1, wherein the substance selected from the group consisting of a non-metallic element of the groups VI and VII of the periodic system is admixed to the hydrogenating gas.

7. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to claim 1, wherein the substance selected from the group consisting of a non-metallic element of the groups VI and VII of the periodic system is admixed to the carbonaceous starting material.

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8. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to claim 1, wherein said carbonaceous starting material, said catalyst, said substance, and said hydrogenating gas are distributed over a large surface area and are reacted with each other in a finely divided form and in intimate contact with each other.

9. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to claim 1, wherein the metal of which the organo-metal complex compound catalyst is composed, is arranged in the reaction chamber in conductive connection with the material of the chamber walls, said material being of more noble potential than said catalyst metal.

10. In a method of producing hydrocarbons and other valuable products from carbonaceous material, the steps comprising reacting such carbonaceous material being liquefied at reaction temperature, with hydrogen containing gases in the presence of organo-metal complex compound catalysts of metals selected from the group consisting of lead and metals which form sulfides, said sulfides being decomposed by dilute mineral acids, said reaction being carried out under a hydrogen partial pressure of at least 1 atmosphere above atmospheric pressure and at elevated temperature, and recovering hydrogenated, isomerized, and cracked reaction products from the reaction mixture.

11. In a method of producing hydrocarbons and other valuable products from carbonaceous material, the steps comprising intimately mixing said carbonaceous material with

about 5-6 % of aluminum dust and with a hydrogen containing gas, continuously passing said mixture, at a temperature of about 170-190° C. and under a hydrogen partial pressure of about 40-100 atmospheres through a previously prepared

5 Gustavson's compound catalyst, said catalyst being distributed within the reaction chamber so as to expose a large surface area of catalyst to said mixture, adjusting thereby the space velocity of said mixture to about 0.5-1.0 kg. of carbonaceous material per 1 kg. of catalyst per hour, continuously with-

10 drawing the hydrogenated and completely saturated reaction product from said reaction chamber, separating entrained catalyst sludge from said reaction product and recycling said separated catalyst sludge into the reaction chamber, separating thereafter the gaseous reaction products from the

15 liquid fraction of said reaction product, washing and subjecting said liquid fraction to fractional distillation to recover therefrom gasoline, medium oil, heavy oil, and paraffin.

12. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to

20 claim 11, wherein the carbonaceous material is a low temperature distillation oil of a boiling point above 100° C.

13. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to

claim 11, wherein the carbonaceous material is a mixture of

25 a residual mineral oil and a solid but liquefiable bituminous material.

14. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to

claim 11, wherein the carbonaceous material is a pasty mixture

of a residual mineral oil and a solid carbonaceous material in finely divided form.

15. In a method of producing hydrocarbons and other valuable products from carbonaceous material, the steps comprising intimately mixing a liquefied soft bituminous material with about 5-6 % of finely divided aluminum activated by a treatment with an alcoholic mercuric chloride solution, continuously injecting said mixture under a hydrogen partial pressure of about 40 atmospheres and a temperature of about 170° C. into a reaction chamber, continuously withdrawing the reaction product, separating from said reaction product catalyst sludge carried along by the same and recycling said catalyst sludge into the reaction chamber, separating said liquid reaction product into gaseous reaction products and a liquid fraction, and working up said liquid fraction to gasoline, medium oil, heavy oil, and paraffin.

16. In a method of producing hydrocarbons and other valuable products from carbonaceous material, the steps comprising reacting a residual mineral oil in mixture with a Grignard compound obtained from electron metal, ethylbromide, and ether, with a hydrogenating gas at about 170° C. and under a hydrogen partial pressure of about 50 atmospheres, and recovering from the reaction product a liquid fraction containing substantially saturated hydrocarbons of lower boiling point than that of the starting material.

17. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to claim 1, wherein motmorillonite is employed as carrier material for the organo-metal complex compound catalyst.

18. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to claim 1, wherein the organo-metal complex compound catalyst is formed from aluminum metal, aluminum chloride, and thionyl chloride under addition of hydrochloric acid.

19. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to claim 1, wherein the organo-metal complex compound catalyst is formed from aluminum chloride containing about 10 % of zinc chloride, 10 % of ferric chloride, and 1 % of chromium chloride, under addition of chlorine.

20. In a method of producing hydrocarbons and other valuable products from carbonaceous material according to claim 1, wherein the organo-metal complex compound catalyst is formed from an aluminum-magnesium alloy under addition of hydrogen sulfide.