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E. BERL
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FROM PLANT MATERIAL

2,551,579

Filed June 30, 1944

2 Sheets-Sheet 1

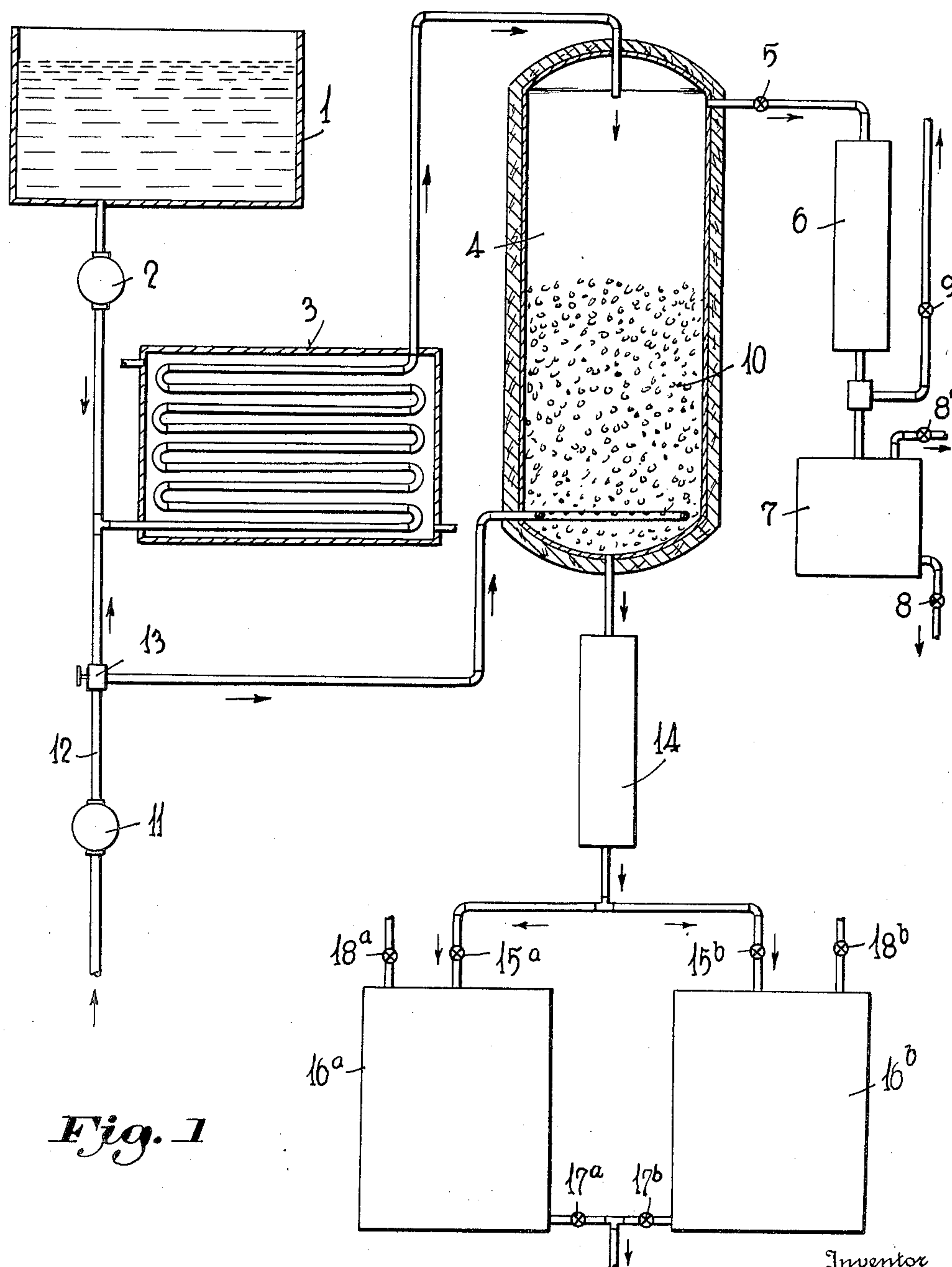


Fig. 1

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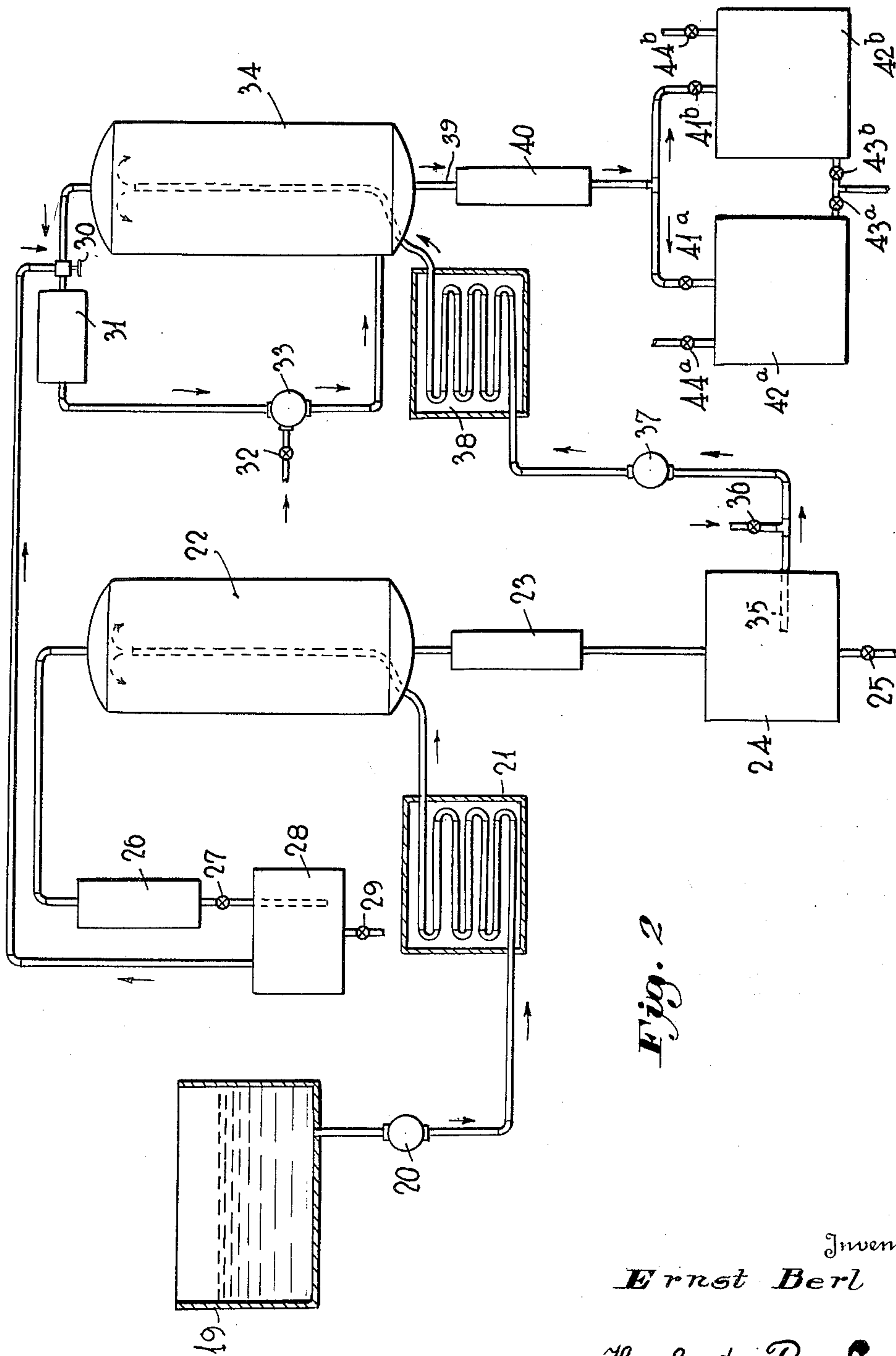


Fig. 2

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UNITED STATES PATENT OFFICE

2,551,579

PRODUCTION OF VALUABLE ORGANIC COMPOUNDS FROM PLANT MATERIAL

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Application June 30, 1944, Serial No. 542,916

7 Claims. (Cl. 260—125)

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This invention relates to the production of hydrocarbons from plant material. This is in part a continuation of my application Serial No. 376,906, filed January 31, 1941, now abandoned.

The production of liquid hydrocarbons is now carried out on a large scale with lignites and younger bituminous coal as the starting materials. In one known process, hydrogenation of the older lignites or the younger bituminous coal proceeds directly, with or without the addition of appropriate catalytic material, whereby through a combination of cracking and hydrogenation liquid hydrocarbons result, which contain aliphatic, hydroaromatic and aromatic hydrocarbons and which, therefore, have a rather high anti-knock value. Another known process converts fuels directly or indirectly from a mixture or carbon monoxide and hydrogen. This water-gas mixture can be converted by means of appropriate catalysts into aliphatic hydrocarbons, mostly of the straight chain character. This process can be carried out like the aforementioned process under pressure or without pressure. The liquid hydrocarbons obtained exhibit a rather low anti-knock value and have to be modified by the formation of branched aliphatic hydrocarbons possessed of a higher anti-knock value. The same process makes possible the production of solid paraffins of very high molecular weight.

Both processes use raw materials prepared by nature at former geological periods. In view of the fact that, for the production of one part by weight of liquid or solid hydrocarbons, about four or five parts in weight of coal are necessary, the consumption of those valuable raw materials is rather high.

In a previous publication (Annalen der Chemie, vol. 504, p. 38-71) I disclosed the conversion of pure cellulose—in the form of cotton linters—first into a protoproduct and then by hydrogenation or by cracking into a liquid oil. Prior to the invention to be disclosed herebelow it was impossible to convert plant lignin by simple means into liquid or semi-liquid materials. Conversion was possible only by very expensive processes requiring the use of costly apparatus. The process of the publication aforesaid was relatively simple insofar as process steps are concerned, but was expensive insofar as raw material is concerned. Prior to the present invention, I believed, in common with the rest of the scientific world, that the only suitable raw material for such a process was pure or substantially pure cellulose. All scientific experience with the treatment of plant

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lignin indicated that it could not be converted into useful products in such a process, because such work as had been done on plant lignin had been done after isolation of the lignin by the saccharification or other conversion of the carbohydrates, and when so treated it had been found, as above stated, that the processing gave no practical results.

It is an object of this invention to provide an economical process whereby liquid or semi-liquid fuel and other valuable hydrocarbon products can be produced from inexpensive plant material.

Another object of the invention is a process whereby hydrocarbon fuel display high anti-knock properties can be produced from plant material.

Still another object of the invention is the conversion of inexpensive plant material into artificial bituminous asphalt as an intermediary product in the production of valuable end products.

Other objects of the invention will become readily apparent from the following description.

In accordance with the present invention, liquid hydrocarbons and asphalts, also phenols, can be formed easily from carbohydrates and carbohydrate and lignin containing materials such as plants, algae, seaweed, grasses, leaves, wood, peat, corn stalks, straw, bagasse, molasses or the like. The conversion of such material, produced continuously by nature on a large scale, can be effected discontinuously or continuously by heating the aforementioned raw materials with aqueous solutions or suspensions of alkaline reacting substances, such as lime, magnesia, sodium-, potassium, calcium-, magnesium carbonate, sodium hydroxide, ammonium hydroxide, sodium-, potassium-, ammonium sulphide, zeolites, iron hydroxide, iron carbonate, iron sulphide, or mixtures thereof, etc., at an elevated temperature. Under these conditions the carbohydrate and lignin content of the plant matter are attacked and both constituents contribute to the final product. Under the influence of these alkaline reacting materials on the plant material at the elevated temperatures of between 150° C. and 370° C. (377° C. is the approximate critical temperature of water) in presence of water a bitumen-like material is produced, which is composed of aliphatic, hydroaromatic and aromatic compounds together with large amounts of phenol compounds and phenol carbonic acids which latter can be separated easily from the neutral substances by formation of phenolates, which when

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acidified form free phenols and phenol carbonic acids. The bitumen-like material acts easily with oxygen. It can be converted by hydrogenation or cracking into liquid hydrocarbons, containing aliphatic, hydroaromatic and aromatic hydrocarbons. They possess a rather high anti-knock value. The carbon content of the original carbohydrate material is about 40 to 44%, that of the lignin is 62 to 65%. Carbohydrates and lignin are converted by the process of my invention into bitumen-like material with about 75 to 80% of carbon and 19 to 14% of oxygen. When the said bitumen-like material is subjected to complete hydrogenation or cracking, it loses its oxygen and yields a crude oil, containing between 86 and 91% of carbon. Incomplete hydrogenation or cracking results in an asphalt-like intermediate material with about 82 to 86% of carbon and about 10 to 12% of oxygen. The liquid hydrocarbons referred to are found to possess boiling points of between 40 and above 250° C. at normal pressure and are practically free from oxygen.

From my previous publication, dealing with the conversion of pure cellulose or carbohydrate, it appears that 55.2% of their original carbon content is contained in the protoproduct. In contrast with this, repeated experiments according to the process of my present application reveal that 64.5% of the original carbon in sugar cane appears in the protoproduct. Water-free sugar cane contains approximately 16.65% lignin with 28.2% of the sugar cane carbon and 83.35% carbohydrates with 71.8% of the sugar cane carbon. Applying to the carbohydrate constituent the yield figure of 55.2% of my previous publication, there should be obtained in the protoproduct $71.8 \times .552 = 39.6\%$ of sugar cane carbon. The following table, based upon more than 50 experiments covering a period of years, shows the average yields in carbon from sugar cane, the carbon content of the sugar cane being 100:

	Per cent of original carbon
In the protoproduct.....	64.5
In hydrogenated bitumen containing gasoline, kerosene, asphalt and residue.....	61
In gasoline, kerosene, lubrication oil and residue	59.9
In gasoline, kerosene and lubrication oil---	44.7

It is obvious from the foregoing that the lignin constituent has furnished a material amount of the liquid and semi-liquid material. Otherwise, the increased yield above the figure of 35.9% postulated on my previous publication would not be possible.

It is also important to note that a very large part of the carbon recovered in the protoproduct appears ultimately in the commercially desirable fractions, gasoline, kerosene and lubrication oil. This further serves to show the importance of the invention and the valuable part which the lignin constituent contributes to the final result.

Further proof of the fact that the lignin constituent contributes to the valuable end products is found in the fact that a substantial percentage of CH_3O (methoxyl) is present in the conversion products of lignin-containing plant material but is not found in the conversion products of carbohydrates alone.

The discovery that lignin-containing plant materials may be used has great commercial significance. This is best shown by a cost comparison. From the Statistical Abstract of the United States for the year 1941, p. 755, it appears that

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the average yield of cotton per acre for the years 1936-1940 was 239 pounds and that the average price per ton was \$191.20. Production figures for sugar cane in the same period show an average annual production of 18.55 tons per acre in continental United States and 36.5 tons in Hawaii. The figure for Cuba, Puerto Rico and the Philippines compare closely with the figures for Hawaii. The average price of the sugar cane (wet weight) in the continental United States for these years was \$2.97. In the other countries mentioned the price is undoubtedly much lower. In comparison, therefore, it is seen that the production per acre per year in cotton is 0.12 tons and in green sugar cane is 18 to 36 tons, and that the price for sugar cane (dry weight) is \$15.85 (or \$11.88 based on 80% or 75% water content in green sugar cane) per ton as against \$191.20 for cotton. These vast differences in yield and cost open up, at a price which is well within commercial possibilities, sources of raw material which were not available according to my old publications.

In the foregoing comparison of raw material costs, I have referred to green sugar cane on a dry weight basis, however, bagasse, which is sugar cane from which about 10 to 15% of its weight has been extracted, may be used. Bagasse finds no use at the present time except for burning under boilers and, to a very limited extent, for use in wall-board. Consequently, my invention makes it possible to utilize a material that has been, to all intents and purposes, a waste material, and thereby to conserve a product, mineral oil, which is rapidly becoming exhausted. As pointed out above, other waste materials available in very large quantities, e. g., seaweed, sawdust, corn stalks or straw may also be used.

By the process disclosed herein, I start with plant material where in the cellulose and the lignin are both present. I have made the surprising discovery that in these circumstances the lignin behaves differently from plant lignin which has been separated from the carbohydrates, so that it is susceptible to processing at relatively low cost and with a yield of solid, semi-liquid and liquid material from the lignin constituent of the plant material. Prior to the making of the present invention it was my belief that substantially pure carbohydrates are the only suitable source materials for such a process and that lignin, far from contributing advantageously to the process, would probably interfere with its function.

A fundamental part of my present invention, therefore is that the plant lignin, if connected with carbohydrates in the original plant material, behaves differently from lignin which has been isolated by the saccharification or other conversion of the carbohydrates. Isolated lignin can hardly be converted into semi-liquid or liquid material, whereas, by the present process, using as starting substances plant material containing both cellulose and lignin, the lignin constituent responds to the treatment and contributes to the final result.

As already stated, the processes of the present invention can be carried out discontinuously or continuously. Then working discontinuously, the plant material containing carbohydrates and lignin, water and alkaline reacting material, e. g., limestone, are heated to temperatures of between 150° C. and 370° C. Instead of limestone, I may use dolomite, magnesite, or the corresponding hydroxides, or alkali-, or ammonium hydroxides or carbonates or iron hydroxide or iron carbonate,

or sulph-hydrates, or sulphides. Under these conditions, the carbohydrates and lignin are converted into a bitumen-like material, containing from between 14% to 19% of oxygen. At the same time, gases are produced which contain, besides carbon dioxide, aliphatic hydrocarbons, mostly methane. In the aqueous solution are found a great number of compounds, from which can be isolated phenols and phenol carbonic acids and esters, like formic acid methyl ester, and other substances, like acetone and lower fatty acids. In order to recover these rather valuable substances from the aqueous liquid, well known chemical and physical methods should be resorted to. The resulting watery liquid after addition of new amounts of alkaline reacting material may serve for the next operation.

The bitumen-like material has a rather low viscosity and a brownish-black color. In contact with air, polymerisation takes place with the formation of substances which are more viscous and ultimately become more or less solidified. Known methods permit the extraction from this bitumen-like material of any acid-reacting substances, such as phenols and phenol carbonic acids. The bitumen, called "protoproduct," contains oxygen bound in different forms, for instance in form of ketones and complex phenols or phenol carbonic acids with aliphatic side chains. The protoproduct has a thermal content of about 140,000 B. t. u. per gallon as compared to 105,000 for gasoline.

This bitumen-like material can be used as a source for phenols by treating it with alkali or with liquid water at high temperatures and pressure. Phenols then are more soluble than in cold water. Furthermore, phenol anhydrides are hydrated under formation of phenols. One can, furthermore, get increased yields of these phenols by carrying out an incomplete hydrogenation which splits off aliphatic side chains without eliminating the phenol group oxygen. In this way phenols are obtained which can be used for those purposes where phenols find normal use, for instance for explosives, plastics, disinfectants, etc.

In order to get oxygen-free hydrocarbons, this bitumen-like material, the protoproduct, has to be hydrogenated under conditions whereby practically all oxygen present is removed. This can be done with hydrogen or hydrogen containing gases, e. g., water gas under pressure (50-500 atmospheres) at elevated temperature (325-475° C.) and the use of appropriate hydrogenation catalysts, for instance molybdenum, tungsten or tin compounds. If the hydrogenation is practically complete, then hydrocarbons free of or with small amounts of oxygen with boiling ranges from 30° C. up to 250° C. (at pressures of 3-4 mm. mercury) are obtained. Analysis shows that the resulting hydrocarbons are of aliphatic, hydroaromatic and aromatic nature. The higher boiling fractions which give an excellent lubrication oil contain OCH₃-methoxyl groups. This is proof that they derive from the lignin content, because carbohydrates alone give compounds free of methoxyl.

The production of those hydrocarbons can be accomplished in different ways. One can treat the plant material containing carbohydrate and lignin, preferably in the presence of alkali and moisture, first at temperatures up to 370° C. in order to produce the protoproduct. Hydrogenation catalysts have to be added to the plant material. The conversion and hydrogenation proc-

esses are carried out in a one-step process during and after the bitumen-forming process with hydrogen or hydrogen containing gases, e. g., water gas under pressure. In order to carry out the hydrogenation the temperature has to be kept at between 325 and 450° C. Then oxygen-free hydrocarbons result besides compounds which contain OCH₃ groups. About 45% of the carbon of the plant material used can be converted into these liquid hydrocarbons.

One can carry out the conversion separately from the hydrogenation. The production of the protoproduct takes place at temperatures up to 370° C. Then to the resulting protoproduct hydrogenation catalysts are added and the hydrogenation is carried out at elevated temperatures (350-475° C.) and initial hydrogen pressures (at room temperatures) up to 500 atmospheres. The processes can be carried out continuously or discontinuously.

In those cases where the hydrogenation of the protoproduct is not intended, the elimination of the bound oxygen can be carried out by a cracking process. The oxygen-containing protoproduct has to be heated to temperatures between 250 and 600° C. without catalysts or in presence of substances with highly developed internal surfaces, i. e. activated carbon, silica gel, aluminum silicates, zeolites, permutites, copper compounds and asbestos, or colloidal silicic acid, etc. under pressure. Then an intramolecular combustion takes place. The oxygen present is removed, mostly in form of carbon dioxide and water, alcohols, ketones and fatty acids. Oxygen-free hydrocarbons result, containing besides aliphatic and hydroaromatic hydrocarbons a rather large amount of aromatic hydrocarbons and consequently these hydrocarbons produced from plant material containing carbohydrates and lignin in accordance with the process of my invention exhibit a high anti-knock value. Coke is produced besides low-boiling hydrocarbons and higher-boiling or melting residues. In all cases they contain aliphatics, aromatics and hydroaromatics. If this cracking process is carried out at temperatures above 500° C., the amount of aromatic hydrocarbons is greatly increased. When the hydrogenation or cracking is not carried out completely, then the higher-boiling fractions show the presence of asphalt-like material, which can be used for the same purposes as natural asphalt.

In order to carry out the aforementioned conversion processes, the plant material containing carbohydrate and lignin is preferably disintegrated and then mixed with the alkaline reacting substances in solution or in suspension. The resulting mass is conducted through heated tubes with the help of pumps. The heating of the tubes is effected from the outside to the desired temperature, at which the conversion of the plant material proceeds. After having converted the carbohydrate and lignin of the plant material into a bitumen-like material, the reaction product is removed from the heating zone by passing either through a reduction valve or into reservoirs, which after having been filled alternately, press the converted material through a cooling device so that a separation of the reaction products can be effected into gas, aqueous liquid and bitumen. The gas, liquid and semi-liquid reaction products can then be utilized.

The bitumen separated from the gas and the aqueous liquid can be converted with small loss of carbon-containing material into liquid hydrocarbons by hydrogenation, whereby appropriate

catalysts, like molybdenum, tungsten, or tin compounds, not subject to being poisoned by sulphur compounds, can be employed.

Nitrogen-containing substances can be produced by reacting the plant material or the bitumen with a source of reactive nitrogen, such as NH_4OH .

Sulphur-containing compounds can be formed by reacting the plant material or bitumen with a source of reactive sulphur, such as sulphides like Na_2S or FeS or sulph-hydrates by reacting it with substances containing the SH group such as NaHS .

Valuable products containing bound sulphur and nitrogen in the molecule are obtained from plant material containing carbohydrates and lignin by reaction with a source of reactive sulphur and nitrogen, e. g. $(\text{NH}_4)_2\text{S}$ or NH_4HS .

In the accompanying drawings I illustrate two arrangements for carrying out the process described above. They are merely by way of example and are not intended to limit the scope of the present invention in any way.

Figure 1 diagrammatically shows an arrangement whereby the formation of the protoproduct and its hydrogenation are carried out at the same time in the same apparatus.

Figure 2 shows an arrangement in which the conversion into protoproduct is carried out before its hydrogenation.

In the arrangement shown in Figure 1 a mixture of plant material containing carbohydrates and lignin with water and alkali in container 1 is fed by pressure pump 2 into the pipe still 3. In pipe still 3 the mixture is subjected to an elevated temperature in accordance with the above disclosure. From there it goes to the reaction tower 4 (preferably insulated). Such gaseous products as are already formed at this stage, as well as unused hydrogen or hydrogen containing gas (see later), are drawn off through valve 5 and sent through a condenser 6. The liquids formed in that condenser are collected in tank 7, and may be drawn therefrom through valves 8, 8¹. Those gases that were not condensed in condenser 6 are drawn off by reduction valve 9.

The liquid part of the mixture emerging from pipe still 3 is allowed to flow downwardly in reaction tower 4 which may be filled with packing material 10 (preferably the packing material described in my U. S. Patent No. 1,796,501). Baffle plates (not shown) or other conventional means to slow down the descent of the mixture may be utilized in addition to or instead of the packing material 10.

Hydrogen or hydrogen containing gases, e. g. water gas are fed into the system by compressor 11 through pipe 12. A valve or other suitable connection at 13, which divides the hydrogen stream, permits part of the hydrogen stream to mix with the disintegrated plant material prior to its entry into the pipe still 3, while the other part of the hydrogen stream proceeds to the bottom of reaction tower 4.

By the time the mixture reaches the bottom of reaction tower 4 it has been converted into practically completely hydrogenated material. It moves through condenser 14. The end product goes through valve or valves 15a and 15b into tank or tanks 16a, 16b, from where it may be drawn off by valves 17a, 17b. Valves 18a and 18b allow the release of pressure in the tanks 16a and 16b.

A suitable catalyst is added to the mixture in

container 1 when carbohydrate and lignin conversion and hydrogenation are carried out in accordance with the above-described process.

The above-described apparatus may be used without parts 11, 12 and 13 if conversion without hydrogenation is desired. Protoproduct and artificial bituminous asphalt are then obtained as intermediary products which may be used as source material for phenol compounds or may be converted into valuable end products by hydrogenation or cracking separately carried out.

An apparatus for carrying out the hydrogenation separately is shown in Figure 2.

The mixture of the plant material, water and alkaline reacting material is led from container 19 by pressure pump 20 into pipe still 21. From pipe still 21 the mixture goes to the top of the reaction tower 22 and flows therein downwards. It is kept there at the conversion temperature. The converted material flows through a condenser 23 into a receiver 24, which can be emptied through valve 25.

The gasified part of the mixture composed mostly of CO_2 , H_2O and CH_4 is drawn off through condensers 26 and 27 and into tank 28. From this tank 28 condensed material may be drawn off to the outside through valve 29. The gases CO_2 and CH_4 proceed to the absorption and conversion tower 31 through valve 30. CO_2 is absorbed and CH_4 converted into hydrogen. This hydrogen together with unconverted hydrogen from a hydrogenation tower 34 and hydrogen freshly added at 32 are transported by compressor 33 into the bottom of the tower 34 which may be provided with packing material or baffle plates (not shown). The unused hydrogen together with CH_4 produced during hydrogenation leaves 34 at 39 and enters the CH_4 conversion apparatus 31.

The protoproduct collected in 24 leaves at 35. At 35 the hydrogenation catalyst may be added. The mixture with the help of the pump 37 is pumped through the pipe still 38 and enters at the top of the hydrogenation tower 34. There it is hydrogenated. It leaves the tower 34 at 39, goes through a condenser 40 and enters through valves 41a and 41b into the storage vessels 42a and 42b. Those can be emptied through valves 43a and 43b by closing 41a or 41b and opening 44a or 44b.

By subjecting to these discontinuous or continuous processes in accordance with my invention all kinds of plant material containing carbohydrate and lignin, phenols, bitumen, asphalts and finally oxygen-free hydrocarbons of high anti-knock value are obtained. The great advantage of my processes can be seen in the fact that valueless material, like algae, seaweed, peat, grass, leaves, corn stalks, bagasse, wood, molasses, etc. which are produced continuously by nature and which otherwise would be converted by slow combustion into valueless CO_2 and H_2O , can be utilized to good advantage. It follows that it is no longer necessary to resort to lignite and bituminous coal for artificial production of hydrocarbons.

Modification of the process and apparatus described above, all within the scope of the present invention, will readily occur to the expert. The scope of the invention therefore is deemed to be limited by the appended claims only.

I claim:

1. A process for making a semi-liquid bitumen-like partly aliphatic and partly cyclic compound comprising a major portion of carbon and minor

portions of nitrogen, hydrogen and oxygen, said process comprising heating plant material containing both carbohydrates and lignin in a closed system to a temperature between 150° C. and about 370° C. in the presence of water and of an alkaline reacting ammonium compound.

2. A process for making a semi-liquid bitumen-like partly aliphatic and partly cyclic compound comprising a major portion of carbon and minor portions of sulphur, nitrogen, oxygen and hydrogen, said process comprising heating plant material containing both carbohydrates and lignin in a closed system to a temperature between 150° C. and about 370° C. in the presence of water and of a member of the group consisting of ammonium sulphide and ammonium hydrosulphide.

3. A process for making a semi-liquid bitumen-like partly aliphatic and partly cyclic compound comprising a major portion of carbon and minor portions of sulphur, nitrogen, oxygen and hydrogen, said process comprising heating plant material containing both carbohydrates and lignin in a closed system to a temperature between 150° C. and about 370° C. in the presence of water and ammonium sulfide.

4. A process for making a semi-liquid bitumen-like partly aliphatic and partly cyclic compound comprising a major portion of carbon and minor portions of sulphur, nitrogen, oxygen and hydrogen, said process comprising heating plant material containing both carbohydrates and lignin in a closed system to a temperature between 150° C. and about 370° C. in the presence of water and ammonium hydrosulphide.

5. The product made by the process of claim 1.
6. The product made by the process of claim 3.
7. The product made by the process of claim 4.

ERNST BERL.

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