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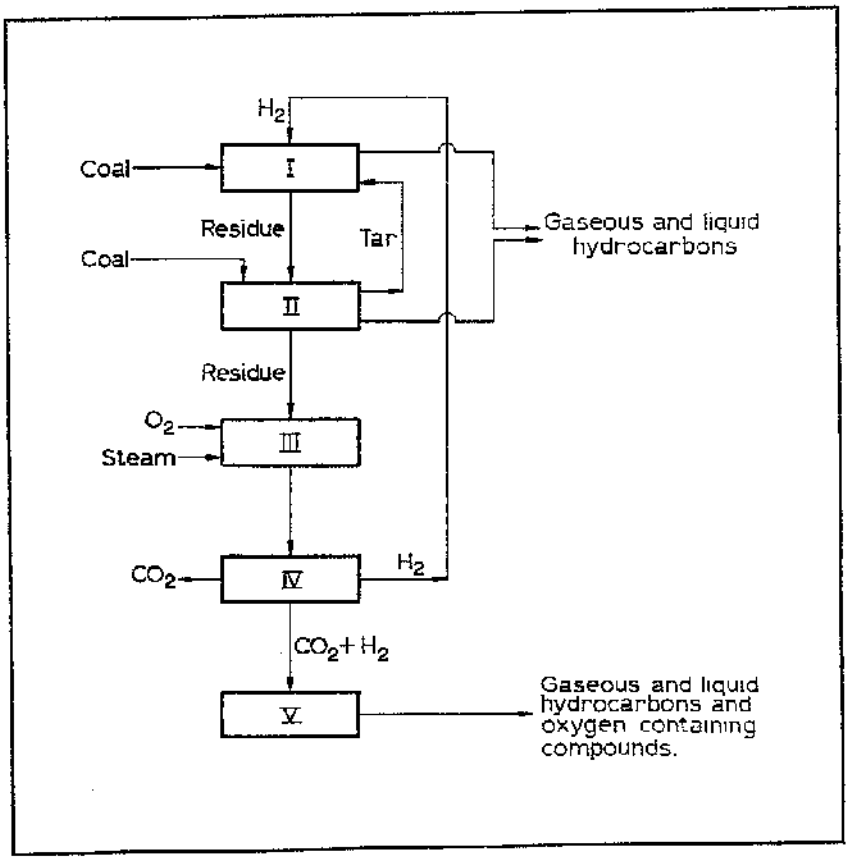
(54) Production of Liquid Hydrocarbons from Coal

(57) Liquid fuels including motor fuels, are produced by hydrogenating coal, subjecting the ash and oil-containing residue to carbonisation at 300—700°C gasifying the carbonisation residue under pressure with oxygen and carbon dioxide and/or steam, and working up the resulting gas mixture into hydrogen which is recycled to the hydrogenation step and a synthesis gas containing hydrogen and carbon monoxide from which liquid fuels are produced by the Fischer-Tropsch process.



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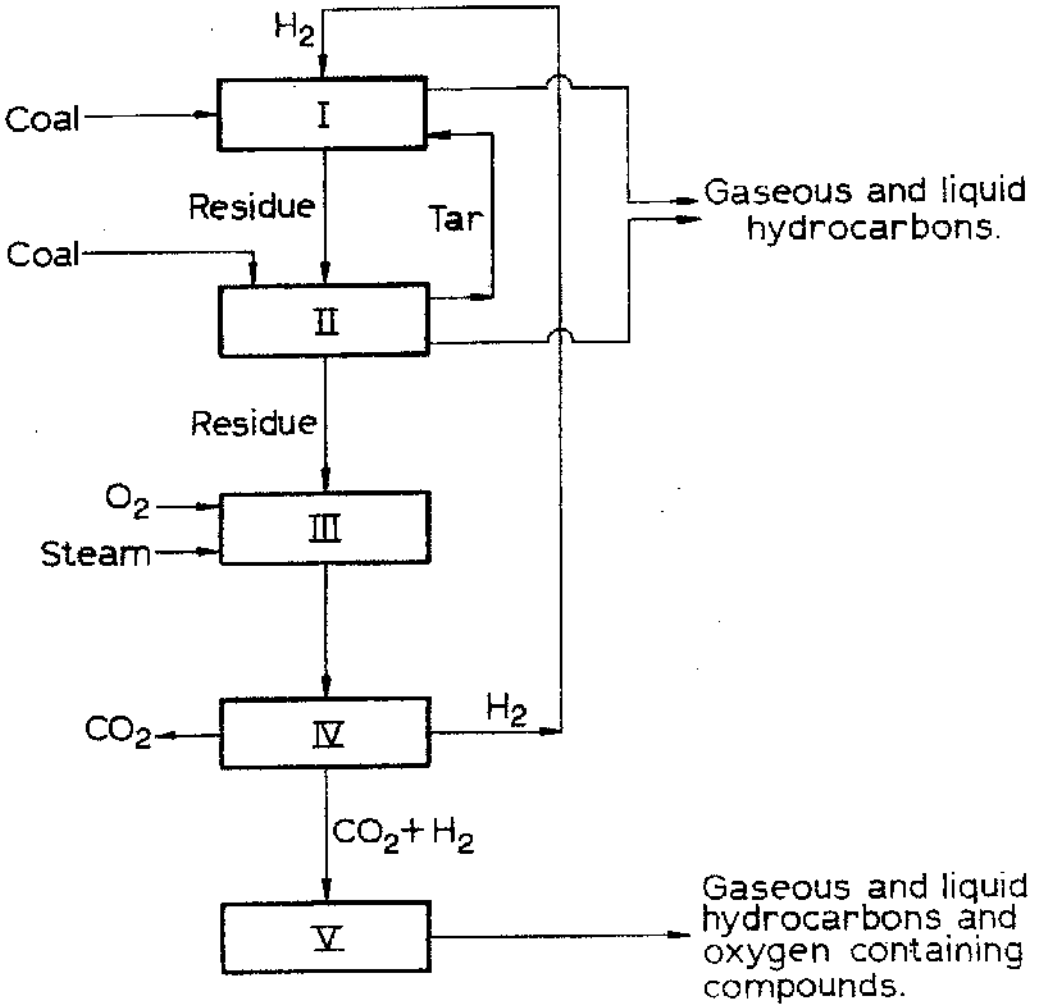
H2
Coal
I
Residue
Tar
Coal
II
Gaseous and liquid hydrocarbons.
Residue
O2
Steam
III
CO2
IV
H2
CO2+ H2
V
Gaseous and liquid hydrocarbons and oxygen containing compounds.

SPECIFICATION

Production of Fuels

This invention relates to a process for producing liquid fuels, including motor fuels, from coal by hydrogenating coal under elevated pressure and recovering relatively low-boiling hydrocarbon mixtures from the high-boiling hydrogenation residues.

In view of the expected shortage of petroleum which, hitherto, has been the main basis for the production of liquid fuels, including motor fuels, increased efforts are now being made to use coal instead of petroleum as the starting material for the production of fuels. For example, it is known that coal suspended in a heavy oil can be hydrogenated by the Bergius process in which hydrogen is added onto the coal under high pressure to form liquid hydrocarbon mixtures. Another known process is based on the reaction of the synthesis gas containing carbon monoxide and hydrogen, obtained by gasifying coal, by the Fischer-Tropsch process. In addition to hydrocarbon mixtures, relatively large quantities of oxygen-containing compounds are also generally formed in this known process. On account of the present market situation, neither of these two known processes represents a viable proposition. Accordingly, efforts are being made to find ways of improving the economy of the process. Thus, the hydrogenation of coal may be combined with the Fischer-Tropsch synthesis. In this process, coal is reacted with hydrogen under elevated pressure. After the oil fractions have been removed as far as possible, e.g. by vacuum distillation, the oil-containing hydrogenation residues are subjected to gasification with partial oxidation to form a gas which is worked up partly into hydrogen for the hydrogenation step and partly into the synthesis gas required for the Fischer-Tropsch synthesis. Although the economy of producing fuels, including motor fuels, from coal can be increased by the proposed process, considerable technical problems arise which again reduce the value of the process. These problems lie, in particular, in the working up of the coal hydrogenation residues by distillation and in the conversion of the distillation residue into the required gases.

We have now found that these difficulties can be avoided and the economy of the process increased even further by carrying out the process for producing liquid fuels, including motor fuels, from coal by hydrogenating coal under elevated pressure, working up the hydrogenation residue with inclusion of a gasification step carried out in the presence of oxygen to form hydrogen and a synthesis gas containing hydrogen and carbon monoxide and producing hydrocarbon mixtures and oxygen-containing compounds from the synthesis gas by the Fischer-Tropsch process in such a way that the ash- and oil-containing hydrogenation residue left after the removal of gaseous and liquid hydrocarbons is subjected to low-temperature carbonisation at a temperature of from 300°C to 700°C, the low-temperature carbonisation residue accumulating is gasified under elevated pressure in the presence of oxygen and steam and/or carbon dioxide as gasifying agents, the gas mixture thus obtained is worked up partly into hydrogen and partly into a synthesis gas containing hydrogen and carbon monoxide, the hydrogen thus obtained is used for the hydrogenation step and the synthesis gas for the Fischer-Tropsch process and the gaseous and liquid hydrocarbons accumulating in the process steps are worked up in known manner into fuels, including motor fuels.

Both brown coal and mineral coal may be used as starting materials in the process.

Hydrogenation is carried out in known manner under elevated pressure, for example under a pressure of from 200 to 1000 bars, and at elevated temperature, preferably at a temperature of from 300°C to 600°C and advantageously in the presence of a catalyst, for example iron oxide. After suitable preparation by drying and grinding, the coal-containing starting material is preferably suspended in a heavy oil obtained during the hydrogenation step and is introduced in this form into the hydrogenation reactors. The ash- and oil-containing hydrogenation residue largely freed from liquid hydrocarbons is subjected to low-temperature carbonisation to obtain the highest possible quantity of oil fractions from the hydrogenation residue. For example, short-time low-temperature carbonisation with a circulating heat carrier, which may optionally be under elevated pressure, is particularly suitable for this purpose. If desired, coal may be additionally introduced into the low-temperature carbonisation process. The low-temperature carbonisation residue is gasified at 750°C to 1400°C in the presence of oxygen and steam and/or carbon dioxide as gasifying agents using, for example, conventional pressure gasification processes with partial oxidation at the starting material. Depending on the required ratio of hydrogen to synthesis gas, the gas mixture obtained in the gasification unit is worked up in known manner, for example by the conversion, e.g. on an iron oxide catalyst, of carbon monoxide with steam to form hydrogen and carbon dioxide, for example at 400°C to 500°C, and corresponding gas washes. The hydrogen thus obtained is used for hydrogenating the coal. After corresponding adjustment of the ratio of carbon monoxide to hydrogen, hydrocarbons and oxygen-containing compounds are synthesised in known manner from the synthesis gas by the Fischer-Tropsch process. Liquid hydrocarbon mixtures boiling in the same temperature range as petrol and middle oils are predominantly obtained. In this way, it is possible to increase the yield of required products in relation to the known process and to improve economy.

It is, of course, possible to obtain further quantities of hydrogen or synthesis gas from coal by standard gasification and gas treatment. In this case, too, the process is carried out in the

presence of oxygen, i.e. with partial oxidation of the coal to generate heat required for gasification. The coal may optionally be gasified together with the coke from the low-temperature carbonisation unit. The coal to be gasified may even be initially subjected to low-temperature carbonisation in known manner at a temperature of from 300°C to 700°C and the low temperature carbonisation residue obtained subjected to gasification. It can be advantageous to introduce the high-boiling low-temperature tar fractions into the hydrogenation step.

Working up of the gaseous and liquid products obtained, from methane to the heavy oil or tar, into the required products may be carried out by standard techniques of the type available in the refining sector.

One possibility of carrying out the process according to the invention is illustrated by way of example in the accompanying drawing where secondary installations have not been included in the interest of simplicity.

In the hydrogenation unit I, brown coal is hydrogenated at a temperature of about 450°C and a pressure of 350 bars. After separation of the gaseous and liquid hydrocarbons formed, the ash- and oil-containing residue left is delivered together with coal to a low-temperature carbonisation unit II in which further gaseous and liquid hydrocarbons accumulate. The low-temperature carbonisation residue enters the gasification unit III in which it is gasified at 1300°C to 1400°C in the presence of oxygen and steam as gasifying agents. In the gas treatment unit IV, the gas mixture is worked up in known manner with inclusion of gas washes and, where necessary, a catalytic conversion of carbon monoxide with steam to form hydrogen and carbon dioxide, partly into hydrogen and partly into a gas mixture consisting mainly of carbon monoxide and hydrogen. The carbon dioxide accumulating is removed from the process. The hydrogen enters the hydrogenation unit I. The gas mixture of carbon monoxide and hydrogen is introduced into the Fischer-Tropsch synthesis unit V in which hydrocarbons and oxygen-containing compounds are obtained in known manner. Coal is additionally introduced into the low-temperature carbonsation unit II. The high-boiling tar obtained in the low-temperature carbonsation unit II is introduced into the hydrogenation unit I.

Claims

1. A process for the production of a liquid fuel which comprises hydrogenating coal under an elevated pressure whereby gaseous and liquid hydrocarbons are removed, subjecting the remaining ash and oil-containing hydrogenation residue to carbonisation at a temperature of from 300°C to 700°C, gasifying the resulting carbonisation residue under an elevated pressure in the presence of oxygen and steam and/or carbon dioxide as gasifying agents, working up the gas mixture thus obtained partly into hydrogen and partly into a synthesis gas containing hydrogen and carbon monoxide, recycling the hydrogen thus obtained for use in the hydrogenation step, subjecting the synthesis gas obtained in the Fischer-Tropsch process and, recovering a hydrocarbon mixture from the synthesis gas and working up the gaseous and liquid hydrocarbons accumulating into fuels.

2. A process as claimed in Claim 1, wherein the tar obtained as carbonisation residue in the carbonisation step is used either completely or in part for the high-pressure hydrogenation step.

3. A process as claimed in Claim 1 or 2, wherein the hydrogenation residue is subjected to the carbonisation reaction together with coal.

4. A process as claimed in any of Claims 1 to 3, wherein hydrogenation is carried out under a pressure of from 200 to 1000 bars.

5. A process as claimed in any of Claims 1 to 4, wherein hydrogenation is carried out in the presence of iron oxide catalyst.

6. A process as claimed in any of Claims 1 to 5, wherein hydrogenation is carried out at a temperature of 300°C to 600°C.

7. A process as claimed in any of Claims 1 to 6, wherein gasification is carried out at a temperature of 750°C to 1400°C.

8. A process for the production of liquid fuel substantially as herein described with reference to the accompanying flow sheet.

9. A liquid fuel obtained by a process as claimed in any of Claims 1 to 8.

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