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Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

**0 264 743
A2**

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EUROPEAN PATENT APPLICATION

21 Application number: **87114786.4**

51 Int. Cl.4: **C10G 1/00**

22 Date of filing: **09.10.87**

30 Priority: **22.10.86 IT 2207286**

43 Date of publication of application:
27.04.88 Bulletin 88/17

64 Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

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54 **Process for the preparation of a synthetic fuel from coal.**

57 The description concerns a process for the preparation of a synthetic fuel derived from coal, consisting of mixtures of asphaltenic hydrocarbons and oils, the said process comprising pretreatment of the coal whereby the coal is caused to react in an aqueous suspension with carbon monoxide in the presence of a hydroxide or alkali metal carbonates (preferably sodium or potassium) at a temperature of between 350 and 430°C, preferably between 370 and 400°C, the reaction time being between 5 and 60 minutes, preferably between 5 and 30 minutes, with as necessary separation out of any derivatives obtained in this manner from coal that has not reacted and of the minerals contained in the coal itself, and with catalytic hydrogenation with hydrogen and if necessary with a solvent that is a donor of hydrogen, in the presence of a catalyst that is in itself already known.

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"PROCESS FOR THE PREPARATION OF A SYNTHETIC FUEL FROM COAL"

The present invention concerns a process for the preparation of a synthetic fuel derived from coal, and more precisely of a synthetic fuel consisting of mixtures of asphaltenic hydrocarbons and oils.

There are well-known processes in existence for the liquefaction of coal using carbon monoxide, water and a suitable catalyst for the production of hydrogen "in situ" for liquefying coal.

5 These processes produce a mixture of hydrocarbons of a high molecular weight, comprised of preasphaltene, asphaltenes and oils, with the ratios between them differing in accordance with the operating conditions applied.

The mixture obtained from processes of this kind is not in itself capable of being used as a fuel in that it is only partially soluble in the usual mixtures of hydrocarbon solvents (such as, for example, gas oils, petroleum naphthas, etc.)

10 It has, surprisingly, been discovered that by pretreating coal in a reducing system with carbon monoxide, water and a basic catalyst in suitable operating conditions, and submitting and derivatives derived from this pretreatment to a further process of catalytic hydrogenation, quantities are obtained of a mixture of hydrocarbon products that are completely soluble in the usual aromatic solvents and partially

15 soluble (around 30 - 40%) in paraffinic solvents.

The process that is the subject of the present invention, for the preparation of a synthetic fuel, derived from coal, consisting of mixtures of asphaltenic hydrocarbons and oils, comprising pretreatment of coal by causing the coal to react in an aqueous suspension with carbon monoxide in the presence of a hydroxide or an alkali metal carbonates (preferably sodium or potassium) at a temperature of between 350 and 430°C,

20 preferably between 370 and 400°C, the reaction time being between 5 and 60 minutes, preferably between 5 and 30 minutes, with as necessary separation out of any derivatives obtained in this manner from coal that has not reacted and of the minerals contained in the coal itself, and with catalytic hydrogenation with hydrogen and, if necessary, with a solvent that is a donor of hydrogen, in the presence of a catalyst that is in itself already well-known.

25 The term "mixture of asphaltenic hydrocarbons" relates to such hydrocarbon mixtures as are soluble in organic aromatic solvents (benzene, toluene, etc.) and non-soluble in paraffinic solvents (such as hexane, heptane, etc.).

The term "mixture of oils" is in reference to such hydrocarbon mixtures as are completely soluble in paraffinic solvents.

30 Donor solvents, which may possibly be used, are those that are used in traditional liquefaction processes (as, for instance, hydrogenated anthracene oil, tetralin, etc.).

The catalysts used for the hydrogenation process, which are in themselves well-known, are for example those with a base of Ni and Mo or of Co and Mo, variously supported.

35 The pressure in which pretreatment of the coal takes place depends both on the amount of water that is fed in with the coal, that is to say in the aqueous coal solution, which should preferably have a ratio by weight of between 2:1 and 5:1 in respect of the initial quantity of coal, and on partial pressure of the carbon monoxide that is used, which should for preference be between 40 and 80 atmospheres; this pressure should preferably be selected from a range of between 150 and 300 atmospheres.

40 The yields obtainable as a result of the pretreatment have been found to be equal to or even higher than 90% in reference to the organic part of the coal (dmmf = dry mineral matter free).

It if is found necessary to separate out the intermediate product from any coal that has not reacted and from the minerals, this can preferably be effected by applying solution heat treatment in polar solvents (including, for example, tetrahydrofuran (THF))

45 So far as hydrogenation of the derivatives is concerned, it is preferable for the hydrogen to be supplied at a pressure of between 60 and 100 atmospheres.

The derivatives obtained from the pretreatment process can after being separated out, as necessary, be submitted in toto to hydrogenation or only a part of them can be so treated, with the oils obtained from them being separated out and then mixed in with the product of hydrogenation.

50 The product obtained through the process with which the present invention is concerned as an atomic hydrogen/carbon ratio of 0.9 to 1.2, and a mean molecular weight of between 250 and 350

The product obtained can if required be treated further with a second hydrogenation process in order to raise the level of hydrogenation and reduce the molecular weight and the ether atoms content (sulphur, nitrogen, oxygen).

The example we give below is intended to illustrate the significance of the present invention, and is in no way to be taken as exhausting the invention's applications.

Example

A test experiment was conducted on some Illinois No. 6 coal; its elementary analysis data are shown in Table 1 below.

5 For the pretreatment phase, 15 g of coal and 90 ml of an aqueous solution of 2 M of KOH were placed in a 1.1 autoclave.

The autoclave was then pressurized with 40 atmospheres of CO and brought up to a temperature of 400°C for 30 minutes.

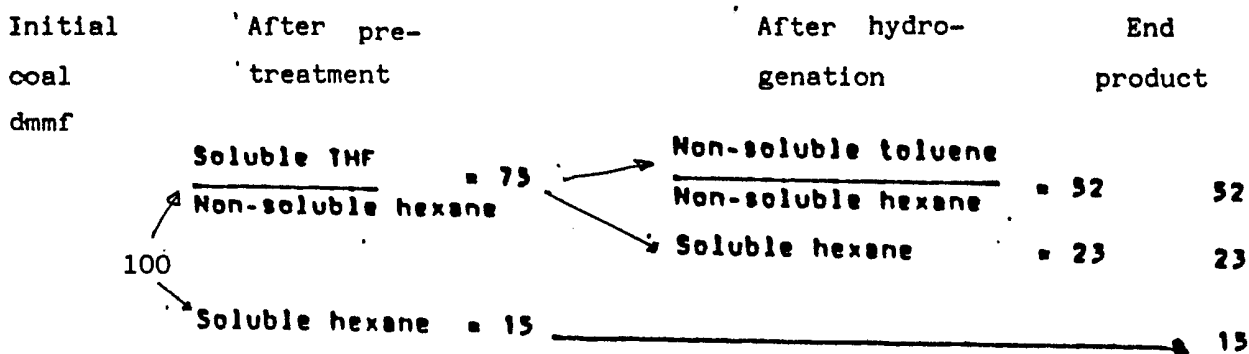
10 On the completion of the reaction the product was recovered by means of tetrahydrofuran (THF) and then filtered to separate the mineral matter and the non-reacting coal from the soluble products (90% of dmmf).

The soluble fraction in the THF was then evaporated and treated with an excess of hexane for the purpose of recovering the oil products (15% of the dmmf).

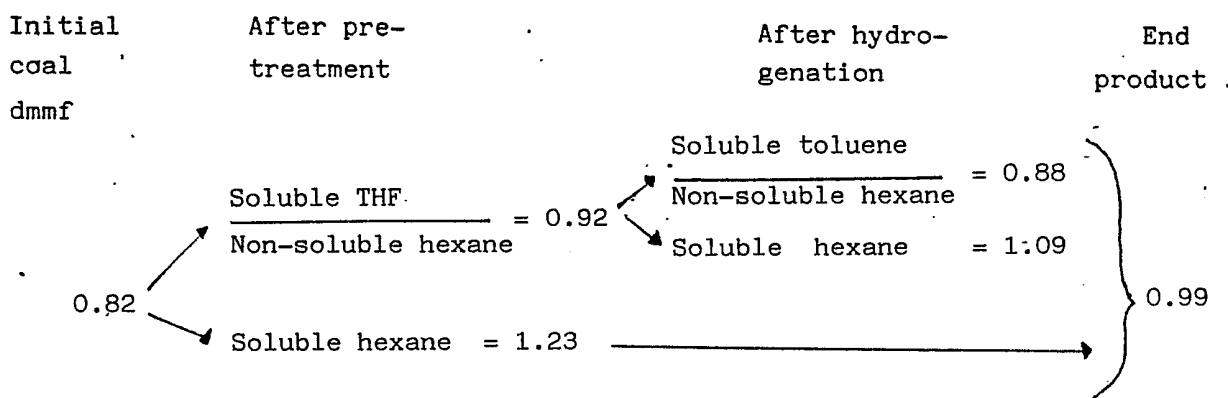
15 2 g of the product of the fraction soluble THF/non-soluble hexane were next hydrogenated in 30 ml minireactors with the addition of 5 mlf of tetralin , 0.2 g of Shell 324 Ni-Mo catalyst and 80 atmospheres of H₂ at a temperature of 400°C for 300 minutes.

On the completion of the reaction, quantities were recovered of a product that was completely soluble in toluene and 23% soluble in hexane.

20 In all, with an initial quantity of 100 g of coal dmmf, on the termination of the process 90 g were recovered of a mixture of hydrocarbons that was completely soluble in organic solvents and 38% soluble in paraffinic solvents, as shown in the following table :



35 The hydrogenation level of the end product mixture was raised by 17%, bringing the H/C ratio up from 0.82 to 0.99, as is shown in the following table :



5

TABLE 1

Direct definitive analysis of Illinois No. 6 coal

	dried in air	dry	dmf*
10	% moisture	4.57	
	% ash	11.43	11.98
15	% volatile substances	35.74	37.45
	% fixed carbon	48.26	50.57
20	% carbon	66.42	69.60
	% hydrogen	5.06	4.77
	% nitrogen	1.50	1.57
25	% sulphur	3.43	3.59
	% oxygen (diff.)	12.16	8.49
			10.76

30 * mineral matter = 14.91% calculated by the Parr method

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Claims

1) A process for the preparation of a synthetic fuel consisting of mixtures of asphaltenic hydrocarbons and oils, having an atomic hydrogen/carbon ratio of between 0.9 and 1.2 and a mean molecular weight of
40 between 230 and 350, which comprises pretreatment of coal whereby the coal is caused to react in an aqueous suspension with carbon monoxide in the presence of a hydroxide of an alkali metal carbonates preferably sodium or potassium, characterized in that the temperature is between 350 and 430°C and the reaction time between 5 and 60 minutes, and that the derivatives thereby obtained are submitted to catalytic hydrogenation and, if required, with a solvent that is a donor of hydrogen, in the presence of a
45 catalyst that is in itself that is in itself already well-known.

2) A process in accordance with Claim 1, wherein the pretreatment process is conducted at a temperature between 370 and 400°C.

3) A process in accordance with Claim 1, wherein the reaction time for the pretreatment process is between 5 and 30 minutes.

50 4) A process in accordance with Claim 1, wherein hydrogenation is conducted with the hydrogen being supplied at a pressure of between 60 and 1000 atmospheres.

5) A process in accordance with Claim 1, wherein the derivatives obtained from the pretreatment process are submitted only in part to hydrogenation, with separation of the oils obtained therefrom.

6) A process in accordance with Claim 1, wherein the derivatives are given further treatment following
55 hydrogenation by a second hydrogenation process.

7) A process in accordance with Claim 1, wherein the derivatives obtained from the pretreatment process are, before being submitted to hydrogenation, separated out from any coal that has not reacted and from the minerals in the coal itself.