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54 **Process for the hydrogenation of carbonaceous material.**

57 In the hydrogenation of coal and substances derived therefrom, the catalyst is provided by adding nickel carbonate to the reaction mixture.

Process for the hydrogenation of  
carbonaceous material

The present invention relates to the hydrogenation of coal and substances derived therefrom, and particularly to the hydrogenation of these materials in the presence of a catalyst.

5                   Slurries of coal with oil can be hydrogenated at high temperatures and high hydrogen pressures to yield methane and light petroleum liquids and gases. It is known to hydrogenate coal slurries in the presence of a heterogeneous catalyst, e.g. Co-Mo supported on an  
10 alumina or silica base. The use of such supported catalysts increases the take-up of hydrogen and improves the yield and quality of the desirable "distillate" fraction, that is to say light oils and liquid fuel, but this is economically prohibitive. Also, the alumina or  
15 silica base tends to promote coke formation which blinds and deactivates the catalyst. Coke should also be avoided because it clogs the hydrogenation reaction and reduces the yield of the desirable distillate. Furthermore, the presence in the carbonaceous feedstock of  
20 impurities, e.g. sulphur, titanium dioxide, vanadium, clays and silica, fouls the catalyst and renders it inactive.

A great deal of research has gone into developing supported catalysts that can reduce coking and resist being fouled by impurities, but the limited  
25 stability of these supported catalysts has made their use uneconomic.

Unsupported heterogeneous catalysts have been proposed for the hydrogenation of coal, but they suffer from one or more of the disadvantages that:

- 30                   (1) they are not as effective as supported catalysts;  
                  (2) they are unstable under hydrogenation conditions;  
                  (3) they are difficult to separate from

the solid residue obtained after  
hydrogenation in order to be recycled.

The present invention is based on the discovery that in the catalytic hydrogenation of coal the  
5 use of nickel carbonate to provide the catalyst reduces  
coke formation and improves the conversion of the coal  
to hydrogenated products, including the desired  
distillate fraction.

Accordingly the present invention consists  
10 in a process for the hydrogenation of coal and  
substances derived therefrom in the presence of a  
catalyst, in which the catalyst is provided by the  
addition of nickel carbonate to the reaction mixture.

The coal is preferably ground and hydrogenated  
15 in the form of slurry with a heavy oil (pasting oil) and  
the nickel carbonate is preferably added to the coal  
in the form of a slurry of nickel carbonate in oil,  
either before or during hydrogenation.

The temperature at which the hydrogenation  
20 is carried out depends on the products desired, more  
light-weight products being produced at higher  
temperatures. While the use of high temperatures  
tends to cause increased coke formation, we have found  
that the amount of coke is reduced by the addition  
25 of nickel carbonate. Also the nickel carbonate  
addition increases the amount of the desired distillate  
that is obtained by hydrogenation.

The hydrogenation process of the present  
invention is preferably carried out at a temperature  
30 in the range of from 400 to 500°C since at temperatures  
above 500°C coke formation is excessive and at tempera-  
tures below 400°C insufficient hydrogenation is achieved.  
The hydrogen partial pressure used is preferably  
from 3,500 to 35,000 kN/m<sup>2</sup>. Higher pressures

are impracticable and lower pressures result in insufficient hydrogenation.

5 After hydrogenation, a typical procedure is to cool the reaction mixture, vent the gases through a condenser and distil the hydrogenation products to recover the liquid products (the distillate). The distillation residue or bottoms, which contains the catalyst, can then be mixed with further coal and the hydrogenation stage repeated. Advantageously some of the distillation bottoms is bled off to avoid an excessive build-up of coke and viscous heavy oil. The material bled off will of course contain some catalyst, and it is preferably coked to recover further distillate and the coke residue then treated to recover the nickel content of the catalyst.

10 Advantageously the nickel is leached from the coke by contacting it, in the presence of oxygen, with an aqueous mineral acid solution, e.g. of sulphuric acid, having a pH not greater than 3. The leaching is preferably performed at a temperature of at least 70°C, and most preferably not less than 100°C, and under an oxygen partial pressure of not less than 20 kN/m<sup>2</sup> and most preferably not less than 275 kN/m<sup>2</sup>. The pH is advantageously about 0. The nickel may be recovered from the leach solution in any known way, e.g. by electrowinning. Alternatively the nickel may be recovered from the coke residue by smelting it to a matte, e.g. with pyrrhotite.

15 In any event, when only part of the distillation residue or bottoms is recycled, the remainder being bled off and treated to recover its nickel content, a corresponding amount of nickel carbonate should be added to the reaction mixture to maintain its catalyst content.

20 As will be appreciated from the above discussion, the process of the present invention may be

performed either on a batch basis or continuously, although the latter is preferred.

The reactions that occur in the hydrogenation of coal and coal-derived material are complex. It may be that the nickel carbonate does not itself act as a catalyst but that it is converted under the conditions prevailing during hydrogenation into a different chemical species and it is that different species that acts as a catalyst. Whether or not that is the case, we have found that the addition of nickel carbonate to the hydrogenation reaction is beneficial.

The exact chemical composition of the nickel carbonate is not critical, and for the purpose of this specification and claims the term nickel carbonate includes basic nickel carbonate, which is the form in which it is most cheaply and readily available.

The catalytic hydrogenation of coal according to the invention will now be described in more detail, by way of example only, in the following Example, in which the results obtained with the use of nickel carbonate are compared with those of two other tests, in one of which no catalyst was used and in the other cobalt carbonate was added to the reaction mixture.

#### Example

In each of three tests, 100 g of Cape Breton high-volatile bituminous coal was charged to a low pressure autoclave with 300 g of Domtar aromatic oil, which is a coke oven tar having a boiling point of 260-330°C, which served as pasting oil. In Test No. 1 no catalyst addition was made, and in Tests 2 and 3 0.92 g of  $\text{NiCO}_3$  and  $\text{CoCO}_3$  respectively was added. The compositions of the coal and oil were as follows, in percent by weight:

|             | <u>C</u> | <u>H</u> | <u>N</u> | <u>O</u> | <u>S</u> | <u>Ash</u> | <u>Asphaltene</u> |
|-------------|----------|----------|----------|----------|----------|------------|-------------------|
| Coal        | 71.2     | 4.88     | 1.43     | 7.0      | 1.5      | 12.9       | 0                 |
| Pasting oil | 92.5     | 5.73     | 0.93     | 1.55     | 0.56     | 0          | 2.0               |

5                   The slurry was pressurised and transferred  
to a high pressure autoclave. A mixture of 2 volumes  
hydrogen and one volume carbon monoxide,  
                    was introduced to give a H<sub>2</sub>  
10 partial pressure at room temperature of 13,800 kN/m<sup>2</sup>,  
and the mixture was heated to 450°C. When this  
temperature was attained, the hydrogen partial pressure  
was increased to 18,000 kN/m<sup>2</sup> and held there for 1 hour.  
The autoclave contents were then cooled to 250°C and most  
15 of the gas vented through a cold trap and assayed. The  
slurry was recycled to the low pressure autoclave where  
100 g of coal was again added and the above steps  
repeated. After the 3rd cycle 150-200 g of slurry  
were bled from the system and after the 5th cycle all  
20 the slurry was discharged. This was accomplished by  
collecting the hot slurry (250°C) in a let-down vessel  
while venting vapours through a cold trap. The hot  
slurries were mixed with several volumes of benzene  
to form a low viscosity slurry which was then filtered  
25 through a steam jacketed Buchner filter. The solids  
collected were then washed, dried and assayed for ash  
and organic content. The benzene in the filtrate  
was then flashed off at reduced pressure and the oil  
produced assayed for C, H, N, O, S and asphaltene.  
30 From the data collected a net product yield was  
calculated. The results are set out in the Table  
below.

TABLE

| Test No.                                      | 1                      | 2                      | 3                      |
|---|------------------------|------------------------|------------------------|
| Catalyst                                      | none                   | NiCO <sub>3</sub>      | CoCO <sub>3</sub>      |
| Catalyst (g/100 g coal)                       | 0                      | 0.92                   | 0.92                   |
| Pasting Oil, asphaltene content (wt-%)        | 2— 29.8                | 2— 39                  | 34.8 — 38.8            |
| Gas   | 2/1 H <sub>2</sub> /CO | 2/1 H <sub>2</sub> /CO | 2/1 H <sub>2</sub> /CO |
| Conversion, %                                 | 57.3                   | 88                     | 84                     |
| H <sub>2</sub> Consumption (g/100 g mafcoals) | 6.5                    | 5.9                    | 3.9                    |
| Products (g/100 g mafcoals)                   |                        |                        |                        |
| O in CO <sub>2</sub>                          | 6.8                    | 10.9                   | 8.0                    |
| NH <sub>3</sub>                               | 0.5                    | 0.2                    | 0.4                    |
| H <sub>2</sub> S                              | 0.2                    | 0.6                    | 1.1                    |
| H <sub>2</sub> O                              | 0                      | 0                      | 0                      |
| C <sub>1</sub>                                | 7.8                    | 6.1                    | 4.04                   |
| C <sub>2</sub>                                | 4.4                    | 4.2                    | 3.8                    |
| ) hydrocarbons                                |                        |                        |                        |
| C <sub>3</sub>                                | 3.8                    | 3.4                    | 2.8                    |
| )   |                        |                        |                        |
| i & n C <sub>4</sub>                          | 1.0                    | 1.4                    | 1.2                    |
| )   |                        |                        |                        |
| C <sub>5</sub> - 250°C                        | 6.7                    | 7.5                    | 12.3                   |
| )   |                        |                        |                        |
| Oil   | 4.1                    | 12.4                   | 26.7                   |
| Asphaltene                                    | 27.1                   | 46.0                   | 17.0                   |
| IOM   | 42.7                   | 12.1                   | 16.0                   |
| Unaccounted mafcoals + H <sub>2</sub>         | 1.2                    | 0.9                    | 8.0                    |
|   | <u>106.5</u>           | <u>105.9</u>           | <u>103.9</u>           |
| Ash   | 19.6                   | 12.3                   | 18.7                   |
| Total   | <u>126.1</u>           | <u>118.2</u>           | <u>122.6</u>           |

Mafcoals = mineral and ash-free coal.  
 IOM = insoluble organic matter (coke and unreacted coal).

The asphaltene content of the coal liquid increased progressively through the five cycles, the final value being substantially the steady state value for the catalysed tests. In the  
5 absence of catalyst (Test No. 1) the asphaltene would continue to increase until the slurry could not be handled.

The results in the Table show that the use of nickel carbonate to provide the catalyst gave  
10 the highest conversion of coal to hydrogenated products (88%) and the lowest production of coke.

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Claims

1. A process in which coal or a substance derived therefrom is hydrogenated in the presence of a catalyst, characterised in that the catalyst is provided by the addition of nickel carbonate to the reaction mixture:

2. A process according to claim 1, characterised in that the hydrogenation is carried out at a temperature of from 400 to 450°C under a hydrogen partial pressure of from 3,500 to 35,000 kN/m<sup>2</sup>.

3. A process as claimed in claim 1 or claim 2, characterised in that the hydrogenation products are distilled and the catalyst-containing distillation residue is mixed with further carbonaceous material and subjected to a further hydrogenation step.

4. A continuous process according to claim 3, characterised in that only part of the catalyst-containing distillation residue is recycled, the remainder being bled off and treated to recover its nickel content, and a corresponding amount of nickel carbonate is added to the hydrogenation reaction mixture to maintain its catalyst content.



| DOCUMENTS CONSIDERED TO BE RELEVANT   |   |   | EP 83300973.1  |
|---|---|---|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim   | CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )             |
| A   | <p>GB - A - 1 064 481 (IMPERIAL CHEMICAL INDUSTRIES LIMITED)</p> <p>* Claims; page 1, line 21 - page 2, line 56 *</p> <p>--</p> | 1-4   | <p>C 10 G 1/06</p> <p>C 10 G 47/02</p>                                 |
| A   | <p>US - A - 2 825 700 (ASHLEY, INNES)</p> <p>* Claims; column 1, line 15 - column 4, line 10 *</p> <p>----</p>                  | 1-4   |  |
|   |   |   | <p>TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup>)</p> <p>C 10 G</p> |
| The present search report has been drawn up for all claims  |   |   |  |
| Place of search<br>VIENNA   |   | Date of completion of the search<br>31-05-1983  | Examiner<br>STÖCKLMAYER  |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> |   | <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p> |  |