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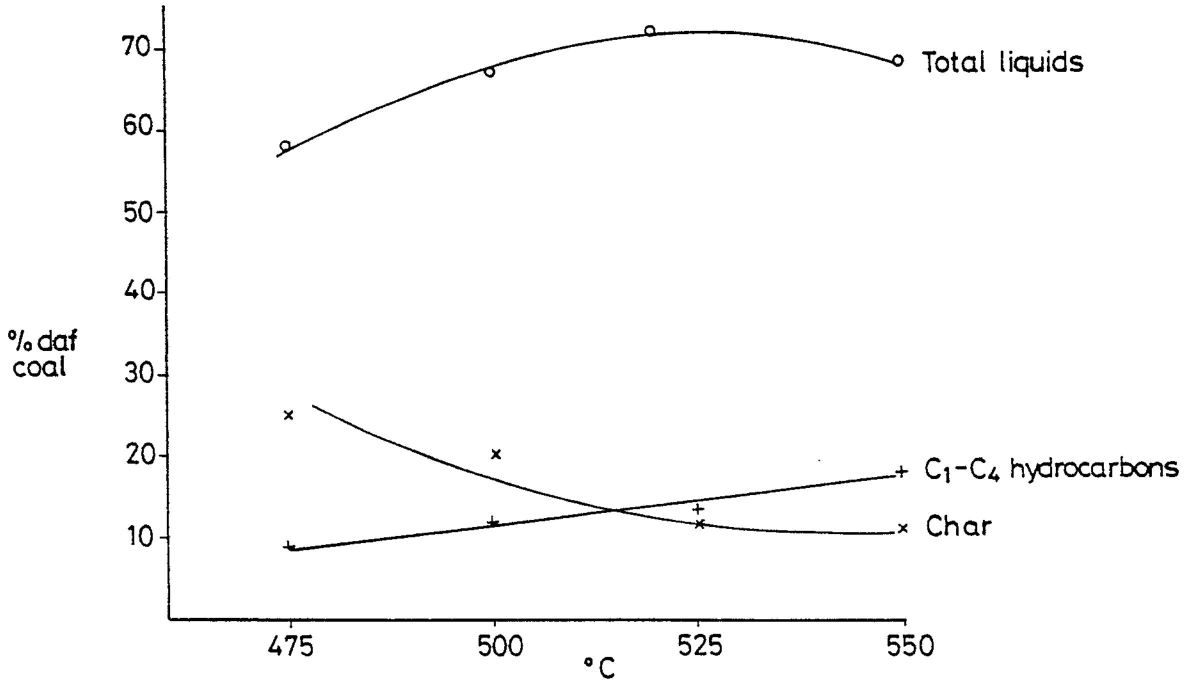
(71) Applicant: Coal Industry (Patents) Limited
Hobart House Grosvenor Place
London SW1X 7AE(GB)

(72) Inventor: Snape, Colin Edward University of Strathclyde
Thomas Graham Building 295 Cathedral Street
Glasgow G1 1XL Scotland(GB)

(74) Representative: Wood, John Irwin et al
Hobart House Grosvenor Place
London SW1X 7AE(GB)

(54) **Improvements in hydropyrolysis.**

(57) A coal is impregnated with 0.01 to 1% by weight of molybdenum disulphide and hydropyrolysed. The products are catalytically hydrocracked. Large yields of valuable liquid products are obtained under moderate conditions, and there is a relatively low production of gas.



EFFECT OF TEMPERATURE ON HYDROPYROLYSIS YIELDS FROM MoS_2 IMPREGNATED LINBY COAL AT 150bar. PRESSURE.

FIG.1.

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IMPROVEMENTS IN HYDROPYROLYSIS

This invention concerns improvements in hydropyrolysis, and more specially it concerns a hydropyrolysis process which yields significant improvements in the yield of liquid hydrocarbon products.

In the art of coal processing, the process of hydropyrolysis is known. We refer by way of example to our prior UK Patent Specification No 2,007,255 B which teaches a non-catalytic two-stage hydropyrolysis process, in which yields of benzene of up to about 10% by weight could be obtained. However, there was a significant increase in methane production at second stage temperatures above about 750°C needed to hydrocrack the primary (first stage) tar into light aromatic compounds.

UK Patent Specification NO 891,971 describes a hydropyrolysis process having the object of producing high yields of liquids and gas, and a single stage of hydropyrolysis is described, with a rapid cooling or quenching of the reaction products. The coal may be treated with ammonium molybdate as catalyst. Yields of gas were indeed high, of the order of 30% or more by weight of the feed coal giving a low selectivity to high value liquid products; gas is of very much lower value than distillable liquids, and such quantities of gas would suggest that the process was not energy efficient for producing liquid products. Publications by the US Bureau of Mines which relate to the process of GB 891,971 indicate that the presence or absence of the catalyst makes very little difference to liquid yields. Some hydropyrolysis processes exist primarily to make high yields of methane.

The present invention provides a two-stage catalytic hydropyrolysis process comprising treating coal impregnated with from 0.01 to 1% by weight of molybdenum disulphide, or a precursor therefore, with hydrogen at a pressure of from 50 to 300 bar and at a temperature of 470 to 550 °C, and catalytically hydrocracking the product therefrom.

The process of the invention permits a significant yield of coal-derived liquid oils, generally in excess of 50% by weight of the coal feed (calculated as dry, ash-free coal), with only low yields of gas(C_1-C_4 hydrocarbons), generally less than 10%. Because of the second stage hydrocracking, the liquid oil products are substantially free of heteroatoms and are low-boiling. Tests involving a substantially deactivated catalyst for the second stage have yielded product material of which over 80% by wt boiled at under 350 °C. The liquid oil products may be processed conventionally to obtain fuels and chemical feedstocks. For example, thermal cracking tests indicated that the liquid oil products give up to 70% by wt if alkylbenzenes and olefins.

The coal starting material is preferably a finely divided (eg - 0.5mm) bituminous coal of high volatile content. High volatile sub-bituminous coals or lignites may also be treated by the process. It is preferred to slurry the fine coal with aqueous solution of ammonium tetra thiomolybdate, formula $(NH_4)_2MOS_4$, or ammonium dioxydithiomolybdate ($(NH_4)_2$ MoO_2S_2), of sufficient concentration to yield the desired catalyst loading. The precursor is converted to MoS_2 by heating, eg during the early stages of the pyrolysis. Preferred catalyst loadings are from 0.1 to 1 by wt.

The temperature and pressure conditions are relatively mild compared to many advocated for hydropyrolysis. Preferred temperatures and pressures are approximately 500 °C and approximately 150 bar for the first stage, and approximately 400°C and 150 bar for the second stage. Suitable residence times are less than 10 sec. and 5 sec. or more respectively, calculated as the gaseous stream.

The second stage is desirably carried out without significant delay on the direct products of the first stage, although the products may be cooled and collected and hydrocracked subsequently. There are many commercially available hydrocracking catalysts available which may be used; in general it has been found that a Ni/Mo on alumina, or Co/Mo on alumina, are suitable for coal-derived liquids. The catalyst may be retained in a fixed bed, or may be used in a moving or fluidised bed.

Although our experiments were carried out using pure hydrogen as the gas feed to the first stage, hydrogen may be in admixture with other gases which do not interfere significantly with the hydropyrolysis, such as steam, CH_4, CO and H_2S.

The invention will now be described by way of example only

EXAMPLE

Coal from Lindby Colliery, England (a high volatile UK bituminous coal of 82% carbon dmmf basis) was crushed to - 0.25 -0.5 mm, and was slurried with an aqueous solution of ammonium dioxydithiomolybdate. The impregnated coal was dried under vacuum at 50 °C to yield a coal material containing 1% by wt MoS_2 (formed in situ), and packed in 5g samples in a fixed bed in an electrically heated tubular reactor. The coal was heated at 2 °C min to the reaction temperature. Hydrogen was passed through the fixed bed at 500 °C. Some tests were carried out on the first stage only, using a dry ice cooled trap for liquid collection, and a pressure let-down valve connected to a gas sampling instrument. In tests using the second stage, a similar tubular reactor was used having a downstream fixed bed of 8g of pre-sulphided commercial Ni/Mo on alumia catalyst, in addition to the coal bed. The first stage was maintained at 500 °C and 150 bar pressure: the second stage was enclosed in an electrically heated furnace, maintaining a catalyst bed temperature of 400 °C, and using the same trap as used in the single stage test.

The results obtained are given in the table below, with results for the crushed Linby coal without catalyst impregnation but otherwise treated in precisely the same manner, given for comparison purposes.

Tests were also carried out to compare the effects on the yields of total liquids (tar and water), gas (C -C_4hydrocarbons) and char residue of varying temperature at a constant pressure and varying pressure at a constant temperature. The results are shown graphically in Figs 1 and 2 accompanying this description.

TABLE

Coal	Comparison	Ex1	Ex2	EX3
MoS_2 Precursor	None	$(NH_4)_2MoO_2S_2$		$(NH_4)_2$ Mo
	Single Stage			Two Stage
Product wt% daf coal				
CH4	4.5	5	5	3.4
Total C_1-C_4 gases	9.5	11	11	8.5
Total gas+	13	13	13	10
Char	57	20	21	23
Tar + 6% water	32	65	65	59*
% Aromatic hydrogen of total hydrogen in tar	36	ND	33	ND

Notes *a proportion of light product believed to have been lost
ND = Not Determined
+ gas contains approx 2% CO and CO_2.

Claims

1. A two-stage catalytic hydropyrolysis process comprising a first stage of treating coal impregnated with from 0.01 to 1% by weight of molybdenum disulphide, or a precursor therefore, with hydrogen at a pressure of from 50 to 300 bar and at a temperature of 470 to 550 °C, and catalytically hydrocracking the product therefrom in a second stage..

2. A process according to claim 1, wherein the coal is a finely divided high-volatile bituminous or sub-bituminous coal.

3. A process according to claim 1 or 2, wherein the concentration of molybdenum disulphide is from 0.1 to 1% by weight.

4. A process according to claim 1, 2 or 3, wherein the first stage temperature is approximately 500 °C.

5. A process according to any one of claims 1 to 4, wherein the first stage pressure is approximately 150 bar.

6. A process according to any one of the preceding claims, wherein the second stage catalyst is Ni/Mo on alumia or Co/Mo on alumia.

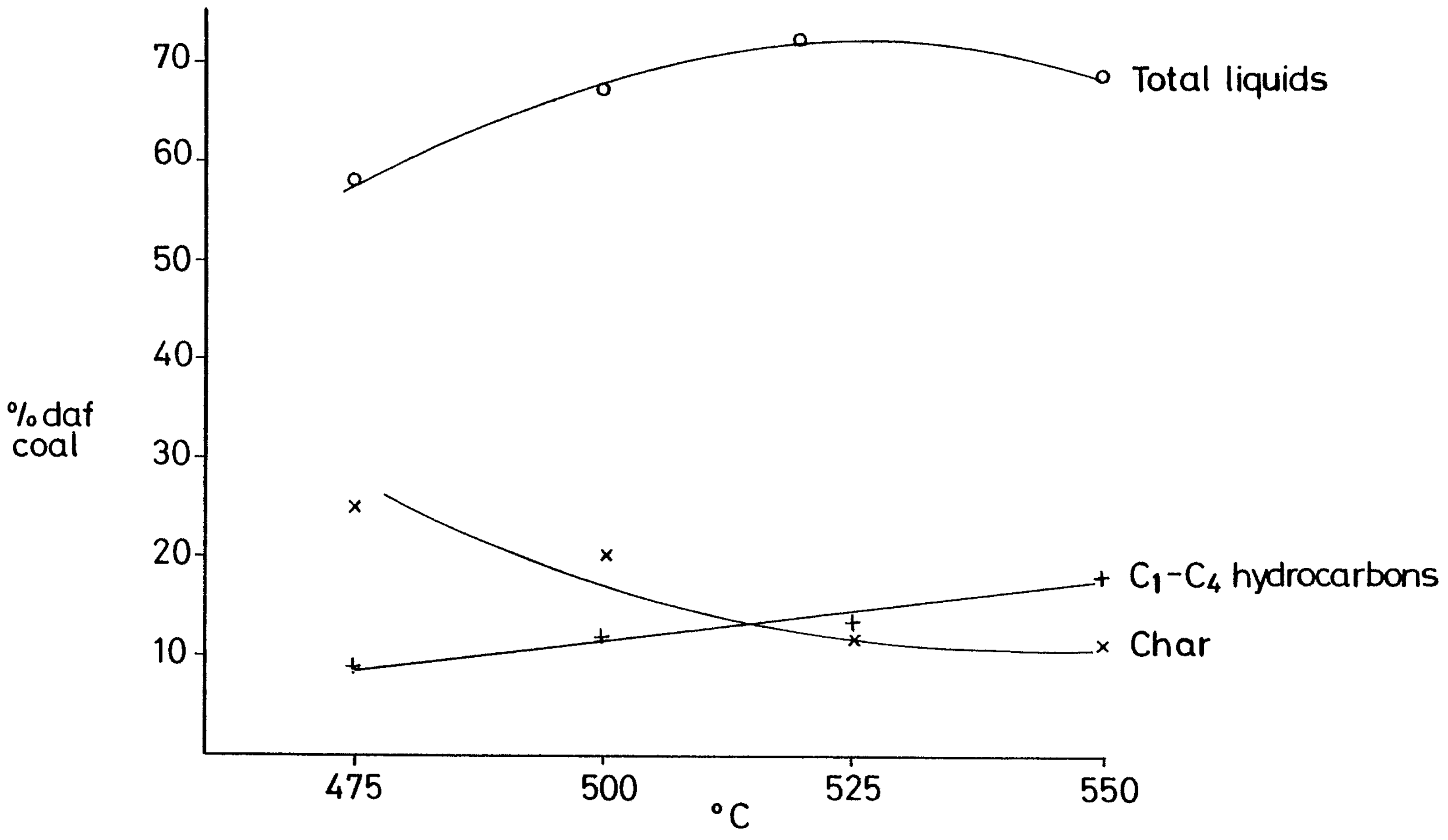

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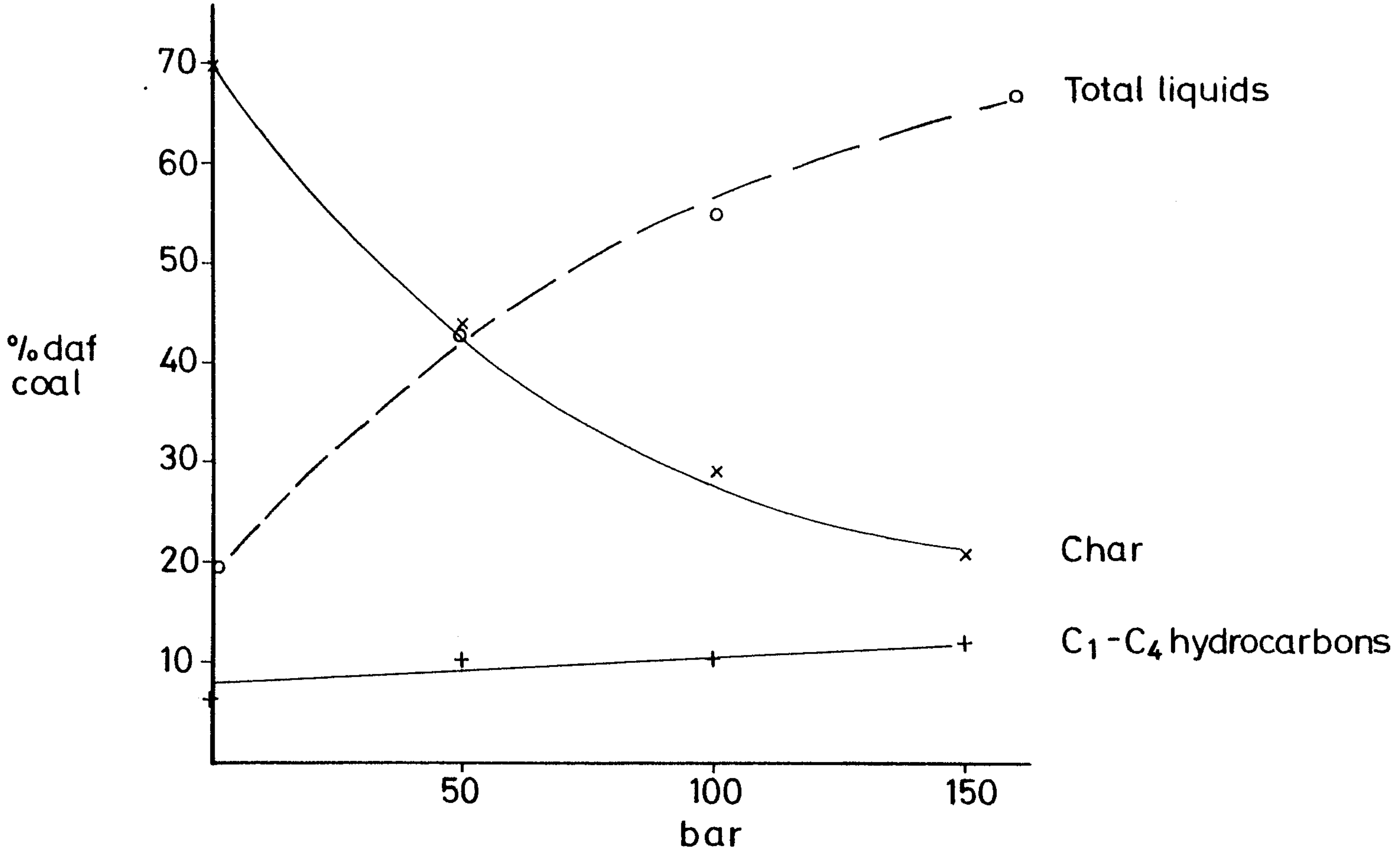
FIG.1.



EFFECT OF PRESSURE ON HYDROPYROLYSIS YIELDS FROM MoS_2 IMPREGNATED COAL AT 500°C.

FIG. 2.