

SHORT COMMUNICATIONS

HYDROGEN PRESSURE AND THE TWO-STAGE MECHANISM FOR THE HYDROGENATION OF COAL TO METHANE†

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Evidence for a two-stage mechanism for the production of methane by the hydrogenation of coal at elevated temperatures and pressures has already been presented.¹ The first stage is a rapid reaction which appears to occur between the hydrogen and the parts of the coal structure closely associated with those which contain oxygen,² while the second stage is a relatively slow reaction between hydrogen and the residual char. The results of various workers^{3,4} have shown that the first-stage reaction can be considered to be instantaneous where the residence time of solid is greater than approximately 1 min. The results of Moseley and Paterson,⁵ for experiments where the residence time of solids was less than 1 sec, show that the first-stage reaction has a finite rate and that the rate decays approximately exponentially with time. Factors affecting the reactivity of the residual char to hydrogen, after devolatilization of the coal, have also been discussed.⁶ Further evidence will be given below to show that considerable variation may be expected in the relative magnitudes of the two stages, depending on the hydrogen pressure.

The overall mechanism in a flow reactor at low methane concentrations, can be expressed by the equation:¹

$$R_{\text{tot}} = kFf(p) + M_c pk^*$$

where R_{tot} is the total rate of formation of methane, k is a constant of proportionality, F is the coal feed rate, $f(p)$ is some function of hydrogen pressure, M_c is the mass of fixed carbon in the reactor, p the hydrogen pressure, and k^* is a rate constant.

The form of $f(p)$ has been determined for brown coal in the pressure range 1–36 atm and the temperature range 700–950°,¹ and is closely approximated by a square root law. Further data from other sources^{3–5} have now become available for the reaction with hydrogen of lignites of similar composition to the above brown coal, in the pressure range 100–350 atm. The data for 100 atm were obtained with a reactor using a batch of coal with continuous gas flow^{3,4} and those for 350 atm with a horizontal continuous entrainment reactor.⁵

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¹ Blackwood, J. D., and McCarthy, D. J., *Aust. J. Chem.*, 1966, **19**, 797.

² Birch, T. J., and Blackwood, J. D., *Nature*, 1964, **201**, 797.

³ Feldkirchner, H. L., and Linden, R. H., *Ind. & Engng Chem.—Process Design & Dev.* 1963, **2**, 153.

⁴ Wen, C. Y., and Huebler, J., *Ind. & Engng Chem.—Process Design & Dev.*, 1965, **4**, 142

⁵ Moseley, F., and Paterson, D., *J. Inst. Fuel*, 1965, **38**, 378.

⁶ Blackwood, J. D., Cullis, B. D., and McCarthy, D. J., *Aust. J. Chem.*, 1967, **20**, 1561.

The results of these authors have been examined on the basis of a two-stage mechanism as discussed by Blackwood and McCarthy.¹ In order to put all the results onto a comparable basis, rates for the second-stage reaction in the above equation have been calculated using the value of k^* found from the work of Feldkirchner and Linden³ and Wen and Huebler.⁴ These values have been subtracted from the total rates R_{tot} , and the resultant rates converted to yields of methane per pound of coal. The results of Moseley and Paterson⁵ have been analysed in a similar way using their terminal char composition and the appropriate rate constant as determined by Blackwood and McCarthy.¹

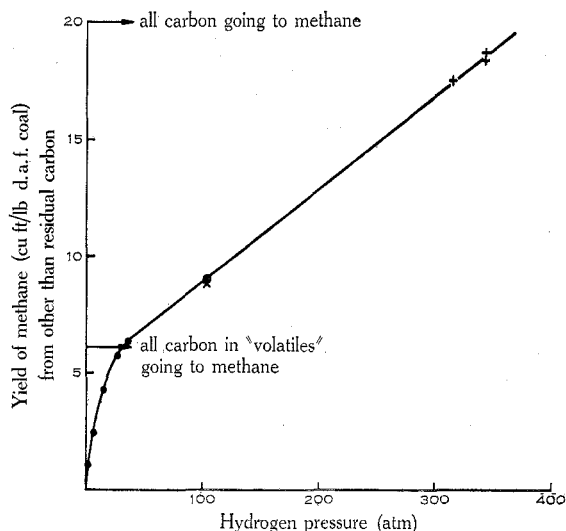


Fig. 1.—Relationship between yield of methane, from carbon gasified by the fast first-stage reaction, and hydrogen pressure.

● Blackwood and McCarthy;¹
 × Feldkirchner and Linden³
 (9.0 and 8.8);
 ○ Wen and Huebler⁴ (9.0);
 + Moseley and Paterson.⁵

The collected results showing the yield of methane due to the first stage of the reaction as a function of the hydrogen pressure are shown in Figure 1. It has been shown¹ that the results up to 40 atm hydrogen are consistent with a postulated two-stage mechanism. Further, it is apparent that the additional results at higher pressures are also consistent with this mechanism, but that $f(p)$ becomes linear in p so that the contribution from the first stage becomes more important at higher hydrogen pressures. This appears to occur because, as the hydrogen pressure is increased, a point is reached where the amount of carbon gasified by the rapid first stage is in excess of that given by the conventional "volatiles" of the proximate analysis. As a consequence there is a change in slope of the line in Figure 1 at this point, the term $f(p)$ then following a linear law at high pressures. It can therefore be inferred that above approximately 40 atm of hydrogen there is a change in mechanism of the attack of hydrogen on the coal structure so that the contribution from the rapid first stage becomes predominant.