# Hydrogasification of Carbons from Coals to Produce Methane:
# Kinetics and Catalysis

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Abstract. Carbons (chars) were prepared from three coals.
Rates of hydrogasification, 1073-1273 K, were all comparable:1.1
to $1.7 \times 10^{-3}$ ml $min^{-1}m^{-2}$ at 1266 K. Iron and nickel additives
to coals were catalytic, potassium only influencing the carbon-
ization process. Carbonization in hydrogen enhanced surface
areas but not reaction rates per unit of surface area. Increas-
ing pressure and heating rate of coals reduce rates of reaction
for carbons prepared in the dilatometer.

## Introduction

Because reserves of natural gas (methane) are
finite, attention is being directed to possible
routes for producing a Substitute Natural Gas (SNG)
from coal. One route is through the direct gasifi-
cation of coal or coal carbon (char) with hydrogen
(hydrogasification) to form methane. The early
work of Blackwood et al. (1) established that
carbons from a range of coals and coconut had
similar reactivities during hydrogasification.
Johnson (2) studied about 30 carbons, the reactivi-
ties of which varied by a factor of 4, increasing
with increasing oxygen content. Tomita et al. (3)
showed a wider scatter of reactivities (factor of
15 (4)).

Huttinger et al. (5) using six coals, noted
similar reactivities to 850°C, thereafter catalysis
by iron produced variations in reactivities. The
order of reaction with respect to hydrogen has been
reported as 0 to 2 commonly 1 to 1.5. The activa-
tion energy is between 70 and 210 kJ $mol^{-1}$ for coal
carbon and increases with burn-off (3, 6). Hydro-
gasification of pure carbon is unacceptably slow
and catalysis is required. Tomita et al. (7, 8)
and McKee (9) report catalysis by Group VIII metals.
Gardner et al. (10) report catalysis by potassium
and Cypres et al. (11) by iron pyrites. Walker
et al. (12) consider calcium to be ineffective.
Baker et al. (13) observed catalytic channelling by
nickel on graphite surfaces. Tomita et al. (14)
suggest reaction mechanisms for hydrogasification.

The objectives of this study are (a) to
measure rates of hydrogasification of coal carbons
in units of ml $min^{-1}$ $m^{-2}$ of surface (b) to note
effects of carbonization procedure (c) to note
effects of 'catalytic' additives and (d) to note
effects of carbonizing in a dilatometer.

Materials Used. Three coals, Markham Main (MM)
NCB CR 702, Gedling (G) 802 and Snibstrom (S) 902
were used. The 'catalytic' additives were ferric
acetylacetonate (FA), nickel acetylacetonate (NA)
and $K_2CO_3$ and were added to the coal from solution
(12.9 wt% of FA, 9.3 wt% of NA, 2.5 wt% of $K_2CO_3$).

Experimental. The coals were carbonized in
nitrogen to 1073 K and then in hydrogen or in
nitrogen to 1273 K, 5 K $min^{-1}$, 1 h soak. The 500-
250 μm particle size fractions were gasified with
hydrogen (150 ml $min^{-1}$) 1073 K to 1273 K and the
product methane analyzed using a Perkin Elmer F17
gas chromatograph, the column packed with Poropak Q,
with a flame ionisation detector. Surface areas
were calculated from isotherms of adsorption of
carbon dioxide at 273 K. Topography was assessed
by scanning electron microscopy. In the dilatometry
studies a coal pencil was heated at one of four
rates, 3, 10, 20, 40 K $min^{-1}$ to 823 K (550°C) under
pressures of nitrogen 0.1 to 6.0 MPa to produce the
appropriate carbon, then gasified at 1266 K.

Results. The results are listed in Tables 1, 2.

Conclusions. (i) Rates of hydrogasification of all
coal carbons closely approximate to each other (1.1
to $1.7 \times 10^{-3}$ ml $min^{-1}$ $m^{-2}$). (ii) Coal carbons
pyrolyzed in hydrogen, 1073-1273 K, have higher
surface areas but similar rates. (iii) All additives
enhanced rates of reaction, the Fe and Ni being
catalysts as seen by SEM, the K enhancing surface
areas. (iv) Activation energies are similar for
non- and catalysed reactions. (v) Increasing
pressure and heating rate reduce rates of hydro-
gasification for MM carbons prepared in the
dilatometer. (vi) Activation energies for hydro-
gasification of carbons prepared by carbonizing
in hydrogen, 1073-1273 K, were relatively low,
21-48 kJ mol $^{-1}$.

## Table 1

### Kinetic Data of Hydrogasification of Coal Carbons

| Coal Carbon, HTT 1273 K in $N_2$ | Surface Area/ $m^2g^{-1}$ | Rates of Reaction at 1266 K/ | | Activation Energy/ $kJ\ mol^{-1}$ | Pre-exponential Value/ $\ln A*$ |
|---|---|---|---|---|---|
| | | $ml\ min^{-1}\ g^{-1}$ | $ml\ min^{-1}\ m^{-2}\ x\ 10^3$ | | |
| MM | 50 | 0.079 | 1.6 | 110 | 7.48* |
| G | 55 | 0.068 | 1.7 | 110 | 7.7* |
| S | 150 | 0.17 | 1.1 | 130 | 10.6 |
| MM + Fe | 160 | 0.52 | 3.3 | 180 | 16.5 |
| MM + Ni | 150 | 0.56 | 3.7 | 100 | 9.1 |
| MM + K | 105 | 0.17 | 1.7 | 140 | 11.7 |
| S + Fe | 50 | 0.54 | 11.3 | 155 | 14.0 |
| S + Fe/K | 105 | 0.56 | 5.4 | 155 | 14.1 |
| S + Ni | 220 | 0.59 | 2.7 | 140 | 12.9 |
| S + K | 180 | 0.26 | 1.5 | 120 | 10.0 |
| HTT 1073 K (under $H_2$ to 1273 K) | | | | | |
| MM | 120 | 0.17 | 1.4 | 32 | 1.1 |
| G | 120 | 0.20 | 1.7 | 21 | 0.3 |
| S | 160 | 0.28 | 1.7 | 48 | 3.0 |

$*\ln$ of $ml\ min^{-1}g^{-1}$

## Table 2

### Kinetic Data of Hydrogasification of Coal Carbons from Dilatometer

| Coal Carbon HTT 1273 K in $N_2$ | Pressure of $N_2$/MPa | Heating Rate/ $K\ min^{-1}$ | Rate of Reaction at 1266 K $ml\ min^{-1}\ g^{-1}$ |
|---|---|---|---|
| MM | 0.1 | 3 | 0.16 |
| MM | 0.1 | 40 | 0.11 |
| MM | 6.0 | 40 | 0.07 |
| MM + Fe | 0.1 | 3 | 0.62 |
| MM + Fe | 0.1 | 40 | 0.51 |
| MM + Fe | 4.0 | 40 | 0.35 |
| MM + K | 0.1 | 3 | 0.46 |
| MM + K | 0.1 | 40 | 0.53 |
| MM + K | 6.0 | 40 | 0.10 |

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