

## ENHANCED REACTIVITY OF METAL-IMPREGNATED PEAT CHAR AND SEMICOKE DURING GAS PHASE HYDROGENOLYSIS

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### INTRODUCTION

Chars and semicokes of different origins show a definite although moderate reactivity in hydrogenolysis and hydrogenation reactions. Early studies have substantiated this fact (1 - 3). This situation is in contrast with the low reactivity of ordered structures (graphite) as it has been documented by Walker et al. (4). Our attention has focused on the reactivity of peat char and semicoke and more precisely we have tried to improve the hydrogenolysis and hydrogenation of these materials by addition of metals in rather massive amounts (about 15% by weight using the ion exchange properties of humic materials). This follows our previous work on the preparation of finely dispersed metals on peat char and semicoke (5). It was felt that by a proper combination of metal characteristics, dispersion and operating conditions increased amounts of methane could be produced from our preparations even at pressures near atmospheric.

Former work on metal catalyzed hydrogen-char reactions has shown the importance of pretreatment conditions (6). Accordingly our study starts with some considerations on the peat char pretreatment followed by a study on the hydrogen-char reaction with and without addition of metals. Iron, nickel and cobalt have been considered as would-be catalysts for this reaction. The overall reactivity study was carried out using thermogravimetric methods.

### EXPERIMENTAL

The impregnation and the carbonization conditions used were developed in our former study (5). By ammoniation of the peat prior to impregnation the amount of metal which can be incorporated in the peat structure is quite significant. In the present work preparations having 16.1% Ni, 14.9% Co and 17.9% Fe (weight percentage of anhydrous peat) have been achieved. After carbonization of the peat-metal preparations at 540°C specific surface areas of 365, 224 and 364 m<sup>2</sup>/g have respectively resulted. The surface area of the carbonized peat (without any metal added) is only 69 m<sup>2</sup>/g. Yields upon carbonization are of about 40%. The non-impregnated peat char contains 0.02% Fe either as pyrite or oxide.

The devolatilization and H<sub>2</sub> reactivity studies have been carried out in a Mettler thermobalance. 200 to 300 mg of sample were used for each run. Temperature programming was conducted between 2°C/min and 10°C/min with most runs at 4°C/min. H<sub>2</sub> and He flow rates were of 60 mL/min. Both gases were purified by passage through a molecular sieve and a Deoxo unit prior to introduction in the thermogravimetric cell. Atmospheric pressure was used in all the hydrogenolysis experiments. On-stream chromatography allowed intermittent sampling of the gases entering or produced during the reactions.

A typical run consisted of:

- a) Introduction of the sample in the thermobalance cell. Heating at 105°C under vacuum and in the presence of helium to eliminate all traces of moisture.

- b) Heating under helium up to the desired devolatilization temperature.
- c) Return to 20°C under helium, introduction of H<sub>2</sub> and programmed heating up to the desired temperature.

Our criteria for a valid experiment required less than 10% error in the overall material balances.

## RESULTS

### 1. Heating rate effects

Weight losses during hydrogenolysis are strongly influenced by the heating rate. Thus on non-impregnated chars weight losses of 33%, 31.5%, 30.5% and 25.5% accompany heating rates of 2, 4, 6 and 15°C/min respectively for identical devolatilization conditions. On a Ni-doped char the weight losses are of 48% and 33% for 4 and 10°C/min respectively. Two levels of influence seem clear at this point: moderately low heating rates do result in higher overall reacted material as shown in Figure 1 and the presence of the metal enhances considerably the reactivity of the char.

### 2. Devolatilization studies prior to hydrogenolysis

Pretreatment (devolatilization) of the metal-char preparations has an important influence on further hydrogenolysis: when devolatilization under He is conducted at 750°C, 500°C, 250°C and 150°C, weight losses on further hydrogenolysis with programmed temperature up to 1200°C are 8%, 24.5%, 33.5% and 35% respectively.

During devolatilization under He of the peat chars initially prepared at 540°C only CO<sub>2</sub> and CO appear to be produced. Similar observations had previously been made on graphite where CO requires temperatures of 300°C to be produced (7, 8). With peat chars at temperatures as low as 105°C the presence of CO is easily detected, suggesting weak chemisorption of oxygen and low stability of surface oxides. The higher the temperature of devolatilization, the higher the amount of CO given off and thus the lower the concentration of oxygenated species on the surface. This seems to have a crucial effect on the rate of CH<sub>4</sub> formation upon subsequent hydrogenolysis. Figure 2 illustrates this point. Devolatilization at the lowest temperatures results in higher CH<sub>4</sub> yields. Moreover, the temperature of maximum CH<sub>4</sub> formation is also function of the devolatilization temperature which could be explained by a higher concentration of oxygenated surface species on the samples devolatilized at the lower temperatures.

### 3. Hydrogen reactivity of non-impregnated peat chars

Even on the samples devolatilized at high temperatures (500°C and 700°C) three major species are detected upon subsequent hydrogen-char reactions. CO<sub>2</sub> appears initially at temperatures around 185°C; it reaches a maximum rate of formation at about 390°C and slowly vanishes at about 500°C. Between 400°C and 500°C, CH<sub>4</sub> and CO begin to appear in such a way that the rise in the rate of formation of CH<sub>4</sub> also corresponds to a rise in the rate of formation of CO. Both species follow similar trends although quantitatively CH<sub>4</sub> is present in larger amounts (a factor of 3 to 4 times larger). This trend suggests that the formation of CH<sub>4</sub> from the reaction between peat char and hydrogen (with no O species externally added as O<sub>2</sub> or H<sub>2</sub>O) proceeds via the methanation reaction between CO and H<sub>2</sub> using the O species still present at the surface rather than by direct reaction between the carbon atoms and hydrogen.

### 4. Hydrogen reactivity of peat chars impregnated with Fe, Ni and Co

The catalytic influence of transition metals has been studied following devolatilization at 150°C. Weight losses upon subsequent hydrogenolysis of the samples by temperature programming (4°C/min) up to 1200°C are as follows: uncatalyzed peat

char, 34%; Fe-peat char, 42%; Ni-peat char, 46.5%; Co-peat char, 84%. The case of cobalt is remarkable since it can be concluded that the hydrogenolysis of the organic matter in the char is nearly complete when taking into account the initial ash content of the char (8.5%).

Figure 3 shows the profiles of CH<sub>4</sub> formation during the hydrogenolysis. The reactivity is defined as  $R_s = \text{mg}_{\text{CH}_4} \text{ formed} \times \text{g}_{\text{char}}^{-1} \times \text{min}^{-1}$  in which the  $g_{\text{char}}$  is taken at any time  $t$  during the experiment (and not at initial  $t = 0$ ). For each of the three chars studied, the CH<sub>4</sub> profile shows two maxima: a low temperature peak (625°C for Co and 650°C for Ni and Fe) and a high temperature peak (1010°C for Co, 1020°C for Ni and 1050°C for Fe). In all three cases there is a marked decrease in the temperature of maximum CH<sub>4</sub> formation relative to the non impregnated char (750°C in this case). Furthermore the second peak is absent in the latter samples.

It is important to notice that both maxima are higher for cobalt impregnated chars than for iron or nickel preparations. Also, the effect of iron is more marked at the higher temperatures. Comparatively to observed literature results the impregnated peat chars do present some unique features as shown in Table 1.

Table 1: Temperatures of maximum rate of methane formation			
Metal	Low Temperature Peak (°C)	High Temperature Peak (°C)	Ref.
None	700*		
Fe	650*	1050*, 1020	(9)
Co	625*, 693	1010*, 950	(6), (9)
Ni	650*, 550, 535, 540, 685	1070*, 950, 683	(7), (9) (10), (11)
* - this work			

It is interesting to note that the raw peat char and the Fe preparation show a low temperature peak which has not been previously observed on graphite (9). Also the low temperature peak occurs at lower temperatures on the Co than on the Ni chars, contrary to previous observations on graphite. Metal dispersions might be responsible for this behaviour.

To emphasize the distinct behaviour of peat chars, Table 2 shows the percentage of reacted char (% conversion) as a function of selected temperatures. Appropriate literature references have also been included (9, 11).

Table 2: Percentage of reacted peat chars during hydrogenolysis at a programmed temperature of 4°C/min and 1 atm.

Metal	650°C		750°C		950°C		1050°C	
	(11)	this work	(9)	this work	(11)	this work	(9)	this work
None	0	21	0	26	2	29	8	31
Fe	0	22	0	27	3	33	9	37
CO	0	68	0.1	74	5	76	25	79
Ni	2	20	36	29	7	37	62	41

Differences between literature values used for comparison reflect distinct carbon structures (9, 11). It is important to realize that in all cases, except for Ni, peat chars, impregnated or not, show higher conversion figures at a given temperature. Although differences between the heating schedules might be partly responsible for the observed results, we favor nevertheless an explanation based on the concentration of oxygenated species in the chars. Thus, peat chars contain >10% oxygen. Whereas the carbons used as comparison range from 6.2% (9) to 1.4% (11). Moreover, a unique metal effect is observed in the sense that CO catalyzes the hydrogenolysis reaction in a very efficient way. Such catalytic action could be explained by the state of the metal on the carbon support. In fact X ray studies on the sample have shown that CO is present as a highly dispersed metal not having achieved a definite crystal structure. Ni is present as a crystalline metal whereas Fe is present both as a metal and as a mixture of oxides. Thus it is quite probable that the highly dispersed "amorphous" cobalt acts as a nucleus both for H<sub>2</sub> chemisorption and its subsequent dissociation and also its reaction with surface carbonyls or formed CO to produce methane.

Since the maximum rate of CH<sub>4</sub> formation takes place in between 625°C and 700°C a series of runs was carried out by programming the temperature (4°C/min) up to 700°C and letting the chars react at this temperature until no methane was evolved. Maximum reactivity values were very similar to those shown in Figure 3. Total conversions were: 77.5%, 31.0%, 25.0% and 24.5% for CO, Ni, Fe and raw char respectively. The significance of CO in hydrogenolysis of peat chars is thus again emphasized.

Modelling of the conversion vs time profile was attempted using the generalized model put forward by Chornet et al. (12). The parameter  $\tau = t/t_{0.5}$  as defined by Mahajan et al. (13) could only be applied to the CO-char preparation since it was the only sample which resulted in  $f > 0.5$ . The generalized kinetic expression is:  $df/dt = kf^a(1-f)^b$ , where  $f$  is the conversion;  $t$ , the hydrogenolysis reaction time and  $k$ ,  $a$  and  $b$  are constant characteristics of a particular reaction. For the CO-peat char sample and using the experimental run in which the temperature is held constant at 700°C a computer simulation yields the following values:  $k = 1.65 \text{ min}^{-1}$ ,  $a = 0.5$  and  $b = 0.4$ , with a correlation coefficient of 0.95 between the experimental values and those derived from the model. Evidence of the excellent fit for CO is presented in Figure 4. Similar profiles were also obtained for the other samples. No attempt has been done so far to interpret these profiles which

suggest some sort of autocatalytic reaction sequences.

#### DISCUSSION

Proposed mechanisms of direct  $\text{CH}_4$  formation from carbon and hydrogen are numerous (1, 14, 16). The existence of two distinct reaction paths as evidenced from the two peaks observed in the present work on peat chars has also been documented on other carbon supports (1, 8, 9, 17). Its explanation is still a challenging problem. Several authors have suggested that the heterogeneity of the carbon surfaces may be responsible for the presence of two or several peaks during the hydrogenolysis: first the reaction focusses on the amorphous fractions, later on the crystalline sections (7, 9, 17, 8, 18, 11). Dissociation of hydrogen on the surface and further reaction with surface carbon atoms has been mainly proposed as the dominant mechanism (9, 19, 20). Direct reaction between weakened surface carbon atoms and gaseous hydrogen has also been considered (21).

In this study the role of oxygenated species present in the char is of paramount importance. The indications derived from our experiments can be summarized as follows: a) influence of the heating rate on  $\text{CH}_4$  formation: a higher rate of  $\text{CH}_4$  formation at the low heating rates is a consequence on increased surface reaction times which result in more CO reacted; b) the negative role of higher devolatilization temperatures on the rate of  $\text{CH}_4$  formation is a result of a lower concentration of oxygenated surface species; c) the decrease in the formation of  $\text{CO}_2$  is accompanied by an increase in CO; and d) the simultaneous presence of  $\text{CH}_4$  and CO in the first reaction stage, tends to indicate that  $\text{CH}_4$  formation is closely linked to the presence of CO.

A tentative reaction sequence consistent with the observed results can then be suggested as follows:

- 1- Decomposition of basic surface oxides (carbonyl or ether types) with formation of  $\text{CO}_2$  starting at about  $150^\circ\text{C}$ , as suggested by Boehm and co-workers (22, 23).
- 2- Reaction between the  $\text{CO}_2$  formed and the char to yield CO as proposed by Shaw (24). Some CO is probably also present as surface carbonyl.
- 3- Reaction between the surface CO and hydrogen as a true methanation step (25, 26). The in-situ production of steam during this reaction will allow regeneration of the oxygenated surface species via its subsequent interaction with the surface carbon atoms and eventually produce either  $\text{CO}_2$  (27) or CO (24, 28). It is during this step that the impregnated metal plays a major role since Fe, Ni and Co are excellent catalysts for the methanation reaction when present in a peat-derived carbon matrix (28).
- 4- At high temperatures ( $>>700^\circ\text{C}$ ) direct reaction between hydrogen and the char takes place, the metal probably facilitating the dissociation of the incoming hydrogen and its migration toward adjacent carbon atoms for further methane formation.

#### CONCLUSIONS

In the present study, the gas phase hydrogenolysis of peat chars prepared at about  $540^\circ\text{C}$  and previously impregnated with Fe, Ni and Co has been investigated. The following points summarize the main findings of this work:

devolatilization of the char is an important factor for its subsequent reactivity toward hydrogen. The lower the devolatilization temperature prior to hydrogenolysis, the higher the rate of methane formation during hydrogenolysis.

- the catalytic effect of the metals is important at two levels: higher conversions to methane and lower temperatures of maximum rate of methane formation.
- the conversion versus time profiles can be very well fitted by the following expression  $df/dt = k f^a (1-f)^b$  suggesting a kinetic sequence closely related to autocatalytic steps.
- the oxygenated surface species play a major role in the methane formation, which probably takes place at the lower temperatures (625-700°C) via reaction between surface CO and chemisorbed hydrogen catalyzed by the metals. CO is the very most active of the metals at this level. At higher temperatures (>700°C), direct reaction of hydrogen with the surface carbon atoms also seems to occur.

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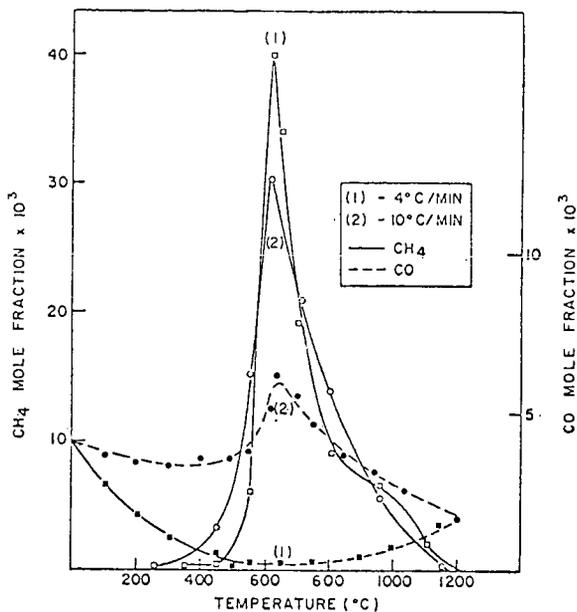


Figure 1 Heating rate effects on Ni-peat char hydrogenolysis as measured by the CH<sub>4</sub> mole fraction in exit gas

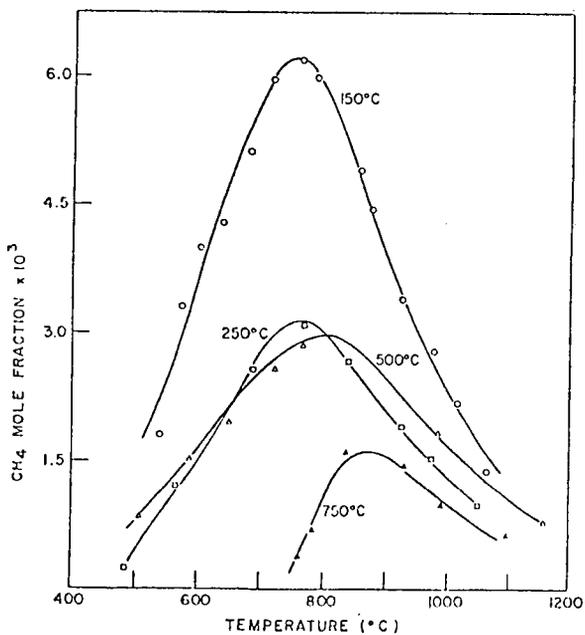


Figure 2 Methane formation during hydrogenolysis of peat char as a function of devolatilization temperature

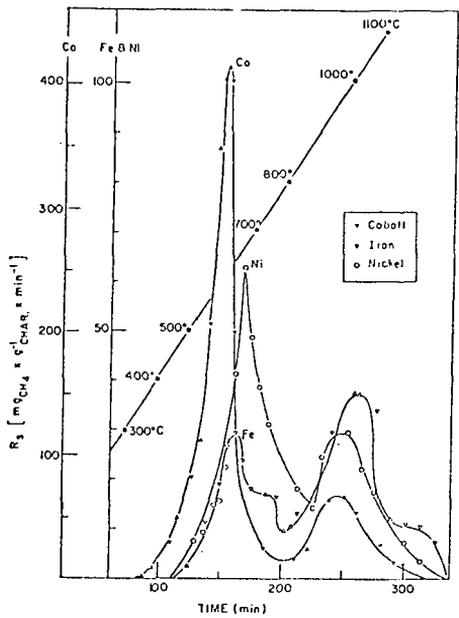


Figure 3 Hydrogen reactivity of metal impregnated peat chars as measured by  $\text{CH}_4$  formation

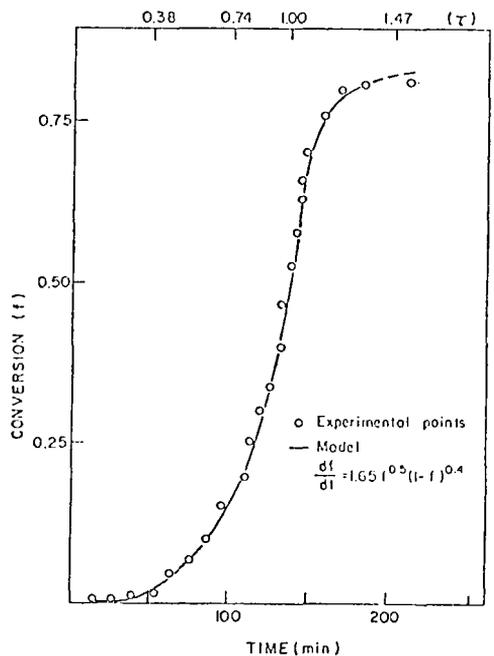


Figure 4 Conversion,  $f$ , as a function of time,  $t$ , and standardized time  $\tau = t/t_{0.5}$  for the hydrogenolysis of Co-impregnated peat chars