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SnCl2-catalysed coal hydroliquefaction.

The similarity in the dispersion patterns of $ZnCl_2$ and $SnCl_2$ upon impregnation from solution (*Figures 1* and *2*) suggests that the divergent tar production trends caused by these two Lewis acids[2] (see *Table 1*) must be explained by differing reaction mechanisms. Some recent work on the mechanism of the catalyst-promoted hydrogen/deuterium exchange reaction anthracene/catalyst/D_2O, suggests that $ZnCl_2$ promotes exchange with the central ring, whereas $SbCl_3$, a strong Lewis acid, is considerably less specific[9]. It appears possible that the action of $SnCl_2$ is also more directed towards the side ring[10].

Table 2 Effect of impregnation with 5 wt % $ZnCl_2$ on 4.5 h chloroform extraction yields from Linby coal following slow heating (5°C min⁻¹) to a range of temperatures

	Extraction yield	
Temperature (°C)	Untreated coal, % w/w daf coal	5 wt % $ZnCl_2$ impregnated coal, % w/w dacf[a] coal
279	1.3	0.7
300	1.3	0.6
328	1.1	0.5
350	1.0	0.6
375	1.8	0.8
390	1.8	1.4

[a] dacf = dry ash- and catalyst-free basis. All the catalyst is assumed to remain with the char

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Coal liquefaction yields in tetralin – their prediction from heat measurements of coal hydrogenation in H₂ by DSC

Angel Linares-Solano,* Om P. Mahajan,† Diane Weldon and Philip L. Walker, Jr.

The Pennsylvania State University, Department of Materials Science and Engineering and Coal Research Section, University Park, PA 16802, USA

Given *et al.*[1], in this laboratory, measured the liquefaction behaviour of coals at 673 K in the presence of tetralin but with no added catalyst or molecular hydrogen. Use of a stepwise multiple regression analysis led to a number of linear equations relating liquefaction conversion simultaneously to various coal characteristics. It was concluded that liquefaction yields can only be adequately accounted for by consideration of at least three coal properties. Properties found to be most important were total sulphur, total reactive macerals, and total carbon from ultimate analysis. Concurrently with liquefaction studies, we were measuring in this laboratory exothermic heats involved during hydrogenation of coals in H_2 using differential scanning calorimetry (DSC)[2]. This communication examines the possibility of using d.s.c. to predict coal liquefaction behaviour.

Procedures used in the liquefaction studies were fully described previously[1]. Briefly, the reaction vessel was charged with 10 g coal, 40 g tetralin, and flushed with N_2. The vessel was inserted into a sand bath preheated to 673 K and brought to reaction temperature in about 5 min. Reaction was carried out with continuous rocking of the vessel for 3 h. Product gases were then vented and the

* Present address: University of Alicante, Alicante, Spain.

† Present address: Standard Oil of Indiana, Naperville, IL, USA.

contents were transferred with benzene into an extraction thimble and Soxhlet extracted with benzene for 48 h. From weight of residue remaining, liquefaction yield (defined as conversion to benzene solubles) could be calculated.

Procedures used to measure heats of coal pyrolysis in He and coal hydrogenation in H_2, using DSC, have been fully described[2,3]. Briefly, a DuPont pressure DSC cell was used in conjunction with a cell base Module II and a 990 Thermal Analyser to determine heats of hydrogenation in 5.4 MPa H_2 at 723 K for 2 h. To start a run, the DSC

cell, containing about 10 mg of coal, was filled with 5.4 MPa H_2 at room temperature, heated quickly to 423 K, and held for 10 min to remove moisture from the coal. A heating rate of 50 K min⁻¹ was used from 423 K to 723 K. To evaluate quantitatively the thermal effects involved during hydrogenation of coals, it is essential to correct the DSC output curves for weight losses occurring[2]. To obtain weight losses up to 723 K and during the 2 h run at 723 K, two DSC runs were made. One run was made in the way described above; a second run on a fresh coal

Table 1 Properties of coals studied

PSOC sample no.	State	Rank	Ash wt % (dry)	VM wt % (dmmf)	Elemental analyses (wt %, dmmf)					Sulphur (wt %, dmmf)	
					C	H	N	S_{org}	O (by diff.)	Pyritic	Total
Eastern and Interior Provinces											
220	KY	HvB	8.0	47.0	79.7	5.8	1.5	3.0	10.0	1.46	4.46
265	PA	HvA	15.5	38.4	86.7	5.4	2.5	0.7	4.7	0.02	0.72
267	VA	HvA	5.9	37.9	79.5	5.2	2.4	1.9	11.0	0.02	2.10
268	VA	HvA	5.1	34.8	86.5	5.4	2.2	1.5	4.4	0.02	1.61
275	OH	HvA	6.6	42.3	83.1	6.0	2.1	0.8	8.0	1.54	2.34
276	OH	HvA	11.2	46.3	83.5	5.6	1.8	1.4	7.7	2.64	4.04
288	IL	HvC	9.0	43.8	79.6	5.2	1.6	2.0	11.6	1.19	3.22
290	IL	HvB	13.9	49.0	82.5	5.4	1.4	2.4	8.3	3.29	5.74
295	PA	HvA	10.8	42.1	84.9	5.5	1.6	1.0	7.0	1.11	2.13
306	OH	HvA	29.3	48.2	84.4	5.8	1.9	1.3	6.4	1.82	3.12
307	OH	HvA	19.3	47.0	83.8	5.8	1.9	1.4	7.1	2.10	3.53
308	OH	HvB	10.2	48.5	79.9	5.7	1.8	1.3	11.3	3.66	5.00
Western Provinces											
95	WA	HvA	21.2	43.7	84.9	5.9	1.1	1.0	7.1	0.83	1.86
235	CO	HvB	7.7	45.0	81.0	5.5	1.6	0.6	11.3	0.10	0.74
237	UT	HvB	12.4	43.3	81.9	5.5	1.8	0.6	10.2	0.06	0.66
238	UT	HvA	9.5	46.9	80.7	6.1	1.7	1.2	10.3	0.83	2.03
249	UT	HvB	10.7	42.0	81.3	5.4	1.5	0.8	11.0	0.36	1.16
250	NM	HvA	9.8	41.2	83.8	5.6	2.1	0.5	8.0	0.03	0.57
309	NM	HvC	20.4	48.9	78.8	4.3	1.4	0.8	14.7	0.44	1.05
310	NM	HvC	8.8	44.6	78.7	5.7	1.7	0.8	13.1	0.20	1.02
311	NM	HvC	17.6	46.6	78.9	4.6	1.5	0.4	14.6	0.12	0.66
312	AZ	HvC	6.6	46.7	78.0	5.3	1.3	0.3	15.1	0.07	0.40
313	UT	HvB	16.1	48.0	81.1	6.1	1.9	0.6	10.3	0.16	0.76
314	UT	HvA	10.0	48.7	81.4	6.1	1.7	0.7	10.1	0.18	0.88
316	CO	HvC	5.2	41.3	79.1	5.5	2.3	0.5	12.6	0.07	0.57

sample was made by only heating to 723 K and then cooling to room temperature.

RESULTS

Twenty-five bituminous coals were studied, twelve from the Eastern and Interior provinces and thirteen from the Western provinces. *Table 1* presents properties of the coals studied. *Table 2* presents the DSC results. Heats evolved are given both on the basis of starting coal weight (Q) and starting sample weight after reaching 723 K (Q'). *Figure 1* summarizes the results for Q versus liquefaction conversion. The fraction of variance (R^2) explained by the linear equation, conversion (%) $= 0.028 Q + 35.5$, is 45.7%. If the two outliers, PSOC 265 and 290, are removed from the plot, R^2 explained by the equation, conversion (%) $= 0.018 Q + 46.8$, increases sharply to 81.0%. If conversion is correlated with Q', R^2 explained by a linear plot of all the data is 47.5%; and with coals PSOC 265 and 290 removed, R^2 is 76.6%.

DISCUSSION

Among the key reactions in liquefaction of bituminous coals, whether the hydrogen donor is tetralin (a donor solvent), tetralin plus gaseous H_2, or gaseous H_2 alone, are the following: (i) hydrogenation of aryl hydroxyl groups
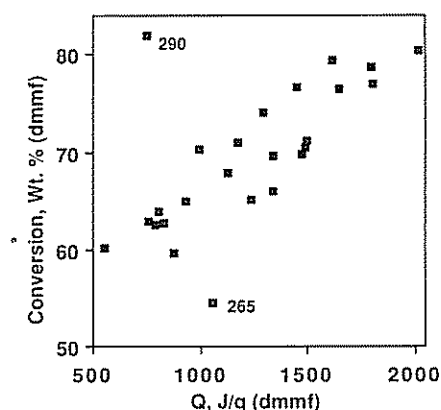

Figure 1 Correlation between liquefaction conversion yield and heat of hydrogenation (Q)

producing water and adding hydrogen to the aromatic ring; (ii) hydrogenation of other aromatic structures to hydroaromatic structures; (iii) carbon–carbon bond breakage of hydroaromatic structures (ring opening) followed by hydrogenation of the radicals formed; (iv) decomposition of partially hydrogenated diaryl ethers. Interestingly, rates of carbon–carbon bond breakage and decomposition of ethers are markedly enhanced by previous conversion of aromatic to hydroaromatic structures, i.e. reactions (i) and (ii)[4,5]. Global heats measured by DSC for hydrogenation of coals depend upon the extent to which the above reactions, and others, occur in 2 h

at 723 K. Qualitatively, the greater the extents (or ease) of the reactions the greater the amount of heat which will be produced during reaction in H_2 and the greater the conversion during liquefaction in tetralin. Thus, a correlation between Q and conversion, as seen in *Figure 1*, could have been expected.

It was of particular interest to understand why coals PSOC 265 and 290 fell so far out of the correlation between Q and conversion. Duplicate runs were made on these samples and agreement between runs was excellent. Why was Q for PSOC 290 so low when conversion was at a maximum and why was Q for PSOC 265 relatively high when conversion was at a minimum? PSOC 290 did have the highest VM and total sulphur contents of all the coals; PSOC 265 had the lowest pyritic sulphur content and a low total sulphur content. However, regression analyses performed between Q and various coal properties listed in *Table 1* exhibited poor correlations, i.e. low R^2 values in all cases. The linear equation showing the best correlation was between Q and VM content; it had an R^2 of 42.1%. Unfortunately, at this time it is not understood why these two samples are such outliers in the Q versus conversion correlation. An understanding of this should clarify whether there are important differences in mechanisms of coal liquefaction using donor solvents H_2.

Table 2 Results of hydrogenation runs from DSC

PSOC sample no.	Weight loss (%, dmmf)			Heat evolved J/g (dmmf)		Liquefaction conversion (wt%, dmmf)
	up to 723 K	at 723 K	Total	Q	Q'	
220	29.9	8.9	38.8	2019	2880	80.4
265	10.9	17.0	27.9	1056	1185	54.5
267	11.8	22.5	34.3	554	628	60.1
268	5.3	26.5	31.8	807	852	63.9
275	13.6	31.7	45.3	1126	1303	67.9
276	22.0	23.2	45.2	1176	1508	71.0
288	26.9	12.3	39.2	1648	2254	76.5
290	20.5	25.3	45.8	749	942	81.9
295	6.9	24.0	30.9	993	1069	70.3
306	19.6	25.6	45.2	1238	1540	65.1
307	15.5	27.1	42.6	1803	2134	76.9
308	25.1	22.8	47.9	1615	2156	79.4
95	9.2	25.1	34.3	880	969	59.7
235	15.2	17.4	32.6	935	1103	64.9
237	10.5	21.0	31.5	1499	1675	71.2
238	23.6	21.4	45.0	1450	1898	76.6
249	17.1	18.2	35.3	834	1006	62.7
250	6.8	23.4	30.2	790	848	62.5
309	26.0	23.4	49.4	1343	1815	66.0
310	28.9	11.1	40.0	1339	1506	69.6
311	22.3	22.3	44.6	1477	1901	69.7
312	19.5	20.5	40.0	1291	1604	74.1
313	17.1	26.9	44.0	1797	2168	78.7
314	29.4	19.2	48.6	1492	2113	70.4
316	20.9	20.0	40.9	757	957	62.9

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Devolatilization characteristics of single coal particles for combustion in air and pyrolysis in nitrogen

Masahiro Saito, Masayoshi Sadakata, Masayuki Sato and Takeshi Sakai
Department of Chemical Engineering, University of Gunma, Kiryu, Gunma 376, Japan

The devolatilization characteristics of single coal particles were studied experimentally for both combustion in air and pyrolysis in nitrogen. The rate constant in volatile matter combustion was 2–3 times larger than that in volatile matter pyrolysis. The weight loss during the devolatilization in nitrogen gas agreed with the value of proximate analysis. However, in the case of coal combustion, the weight loss during the volatile matter combustion region exceeded the proximate value because the particle temperature became high compared with the surrounding gas temperature.

It is well known that the combustion of a coal particle is a successive two-staged combustion process consisting of gas phase combustion of volatile matter followed by solid combustion of residual char. In general the characteristics of coal combustion are mainly controlled by the burning rate of residual char because its combustion time is considerably longer than that of volatile matter. However, the devolatilization of volatile matter in the coal may characterize the behaviour of the successive solid combustion. Namely, the physical properties, pore structure and specific surface area of the residual char, which is formed after the gas phase combustion, vary with devolatilization conditions such as temperature, pressure, surrounding gas and heating rate. Accordingly, the understanding of the devolatilization characteristics is
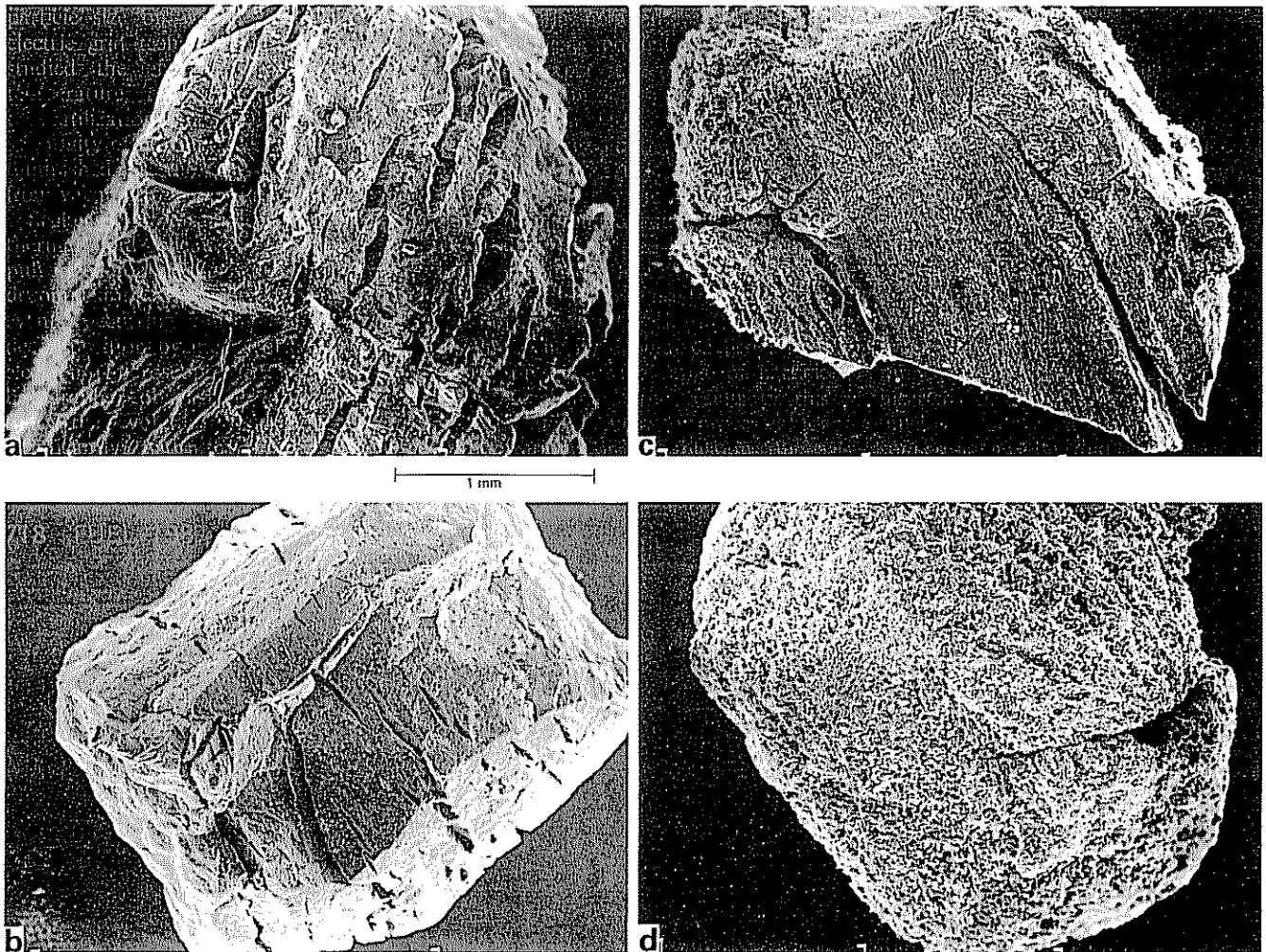
Figure 1 Scanning electron micrographs of the particles quenched during the devolatilization: (a), Taiheiyo char from volatile matter combustion region; (b), Taiheiyo char from pyrolysis in nitrogen; (c), Datong char from volatile matter combustion region; (d), Datong char from pyrolysis in nitrogen

important in order to clarify the coal combustion and carbonization processes.

Recently, many studies on coal devolatilization have been reported by using various methods such as thermobalance[1], electric grid[2-8], fluidized bed[8,9], entrained flow[10], and flow furnace[11-13]. Anthony et al.[2] studied the effects of residence time, temperature and particle size on weight loss using an electric grid technique. Niksa et al.[6,7] studied the effects of heating rate, temperature and pressure on coal devolatilization. The results showed the sensitivity of heating rate to weight loss diminished as the pressure increased from vacuum to 0.19 MPa.

Seeker et al.[11] examined the physical, thermal and chemical behaviour of pulverized coal particles during thermal decomposition and observed the physical events occurring during the thermal decomposition by means of a scanning electron microscope (SEM) and a holograph. Kobayashi et al.[13] reported that the volatile yields increased significantly with temperature, from about 30% (d.a.f.) at 1260 K to 63% at 2100 K. Most studies on devolatilization have been carried out separately with regard to the devolatilization process of coal in the inert gas atmosphere or volatile matter combustion in oxidizing gas.

In this study, the authors used the mutual relation of devolatilization characteristics between coal combustion in oxidizing gas and coal pyrolysis in inert gas. The paper reports the results for devolatilization of two coals at temperatures between 1123 and 1373 K. The particle sizes used in the experiment were 2.42–3.81 mm. Particle size is especially important since various reactor types demand different coal diameter: fixed bed (10–100 mm), fluidized bed (0.1–10 mm) and entrained flow (1–100 μm). In general, coal of sizes used in pulverized fuel boilers is 70–80% through 200 mesh (74 μm). The fixed/fluidized bed allows utilization of a wide range of particle sizes. Accordingly, the results of this study relate directly to processes for carbonization or combustion in a fixed/fluidized bed.

The main purpose of the present study was to clarify the difference of devolatilization characteristics between (1) devolatilization during coal combustion in high temperature air and (2) coal pyrolysis in high temperature nitrogen gas.

EXPERIMENTAL

The captive sample technique was used in this experiment. A single coal particle in a basket was rapidly inserted into a porcelain tube (i.d. 22.5 mm) located within an electric furnace and was burned or pyrolysed. High temperature gas was flowing in the porcelain tube at a constant flow rate of 0.76 kg m^{-2} s^{-1}. The gases used in this experiment were air for coal combustion and nitrogen gas for coal pyrolysis. The gas was heated electrically to the desired temperature within the range 1123–1373 K. The coal particle inserted into the porcelain tube was quickly withdrawn from the furnace after some residence time and the reaction was