LINKS BETWEEN HYDROGENATION BEHAVIOR OF COALS AND THEIR GIESELER-SOLIDIFICATION

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INTRODUCTION

The present study aims at better understanding of links that were found between hydrogen acceptor abilities of coals and their solidification temperatures (1) in search for means of prediction of the development of anisotropic texture in coking coal blends (1).

Our approach is based on the four methodological steps applied to a set of twenty coals that represent a wide range of thermoplastic properties. The steps are: (1) determination of hydrogen acceptor abilities of the coals in reaction with tetralin; (2) determination of Gieseler-solidification temperatures of the coals; (3) characterization of the coals by pyrolysis /Py/-field ionization /FI/ mass spectrometry /MS/ of the coals; and (4) multivariate chemometric evaluation of these three data sets. Specific role of Py-FIMS of coals lies in that the technique displays chemical composition of a part of coal material that is able to diffuse and penetrate coal grains on heating during coal processing; it has been found that this movable part influences coal reactivity in reaction with H-donor (2,3) and in low-temperature pyrolysis (4).

The present paper is aimed at search for structural units of coal material that are active in hydrogen transfer and units that are active in reactions resulting in coal solidification on heating. It is believed that the results can contribute to identification of structures active in liquefaction retrogressive reactions.

EXPERIMENTAL

Coal Samples. Twenty carboniferous coals from Poland were studied. Their basic properties (wt.% daf) are: carbon 85-91; hydrogen 4.3-5.3; oxygen 0.8-7.0; sulfur 0.5-3.8. The petrographic composition (wt.% dmmf) is: vitrinite 63-88; exinite 0.-11; inertinite 7-30. Solidification temperatures of the coals (Table 1) are in the 417-490oC range.

Reaction of Coals with Tetralin. The reaction was carried out at 400oC; 60 min; for coal-tetralin mixture 1:2 w/w. The amount of hydrogen transferred from tetralin to coal material /HTr/ was calculated on the basis of GC determination of unreacted tetralin/naphthalene ratio. Other details were reported earlier (3) except for thermal decomposition of tetralin at 400oC. Tetralin was heated in the autoclave at 400oC/60 min and GC analysed . The result of analysis: 97.8 % tetralin; 1.4 % naphthalene; and compounds of lower and higher retention times 0.5 % and 0.3 %, respectively, were used for calculation of corrected HTr values /shown in Table 1/. The same procedure was

applied in determination of HTr for pyridine /Py/- extractables and Py-residues of the coals.

Py-FI MS and Chemometric Techigues. Both have been previously described in details (2-4).

RESULTS

Hydrogen Transfer to Coal Material. The data in Table 1 show that organic material of Py-extractables as well as of Py-residues react with tetralin. Amount of hydrogen transferred to Py-extractables and to the residues is in the same range from 0.4 to 1.0 grams of H / 100 grams of org. material. If one compares HTr values for a coal, its extracted material and residue, one can say, all cases are observed: some coal samples show the highest HTr; in other coals the highest HTr is found for their extractables or for residues.
The correlation coefficient found between HTr values for the coals and their solidification temperatures is very significant / r = 0.87/. Lower r values were found for the products of extraction.
Hydrogen Transfer and FI Difference Mass Spectrum of Selected Coals. Four most reactive coals /HTr in the range from 0.8 to 1.2/ were selected; their FI mass spectra were normalized and summed. Next, four least reactive coals /HTr in 0.1 - 0.4 range/ were chosen and their spectra were normalized and summed. Figure shows the difference spectrum for the two groups of coals. The upper part of Figure shows FI mass signals whose intensities are higher in the high reactive coals. The lower part shows signals whose intensities are higher in the least reactive coals. Hence, it has been concluded that the composition of the volatilized, in the mass spectrometer, material of coals can supply information about components that are active in hydrogen transfer as well as about unreactive species.

FI Mass Signals Correlated with Hydrogen Transfer. Results of correlation analysis carried out for two sets of data: (a) FI mass signals in the range 158-400 a.m.u. and (b) amounts of hydrogen transferred to the samples of coals, are shown in Table 2. Seventy seven FI mass signals were found to be significantly correlated with the HTr values. A vast majority of the coefficients are highly significant ($r > |0.68|$). This indicates that there is a causitive link between structures represented by the correlated signals and reactivity of the coals in hydrogen transfer.
Out of all the correlated signals, forty seven signals are correlated with positive sign /Table 2;upper/ i.e., the higher the intensities of these signals the higher amount of hydrogen is transferred to the coals. All these signals can be found in the upper part of the difference spectrum /Figure/ .
Thirty signals are correlated with negative sign /Table 2; lower/ which means: the higher the intensities of the signals the lower amount of hydrogen is transferred to the coals. All the signals can be found in the lower part of the difference spectrum.

Proposed structures for all correlated signals are shown in Table 3. The structures represent only one of all possible isomers for example, pyrene / m/z 202/ is displayed, although there are three other four-ring aromatic hydrocarbons, all with the same

accurate mass as for pyrene. Isomers not presented in the Table can be found in reference 5.

Structures Active in Hydrogen Transfer /Table 3; upper/. In general, there are two types of compounds that are positively correlated with hydrogen transfer. They are aromatic hydrocarbons and hydroxycompounds. Hydroaromatics seem to be of minor importance for the reactivity of the studied coals, compared with lower rank coals (3,4), since they are represented by a few hydropyrenes.

Aromatic hydrocarbons are represented by 12 classes with respect of number of aromatic rings and mode of their arrangement. They are: 3-aromatic ring hydrocarbon (m/z 190); 4-aromatic ring (m/z 202; 226; 240; 254); 5-aromatic ring (m/z 252; 264; 276; 278); 6-aromatic ring (m/z 302; 328) and 7-aromatic ring hydrocarbon (m/z 300). With respect of alkyl substituents, majority of the hydrocarbons are present as unsubstituted and containing one methyl group. A few hydrocarbons may have C2 and C3 alkyl substituents, for example, accurate masses related to signals m/z 328 and 342 may represent either C2 and C3- coronenes or C0-C1-dibenzochrysenes.

Hydroxycompounds are represented by /OH/- and /OH/2-benzenes;/OH/ and /OH/2-indenes; and /OH/ -naphthalenes, -acenaphthenes, -anthracenes, -fluorenes. No doubt, at least some of the compounds have phenolic OH (m/z 94; 110; 134).

Structures Inactive in Hydrogen Transfer /Table 3; lower/. In contrast to the positively correlated mass signals, the negatively correlated signals represent entirely different structures. None of them can be assigned to unsubstuted aromatic hydrocarbons. Instead of that, the signals represent short alkyl derivatives of naphthalene, fluorene, acenaphthene, anthracene and chrysene, the five classes of aromatic hydrocarbons that are not present at all in the set of active structures. The other aromatics are alkylated, C2-C5, pyrene, perylene, cyclopentachrysene and dibenzopyrene; these aromatics in the positively correlated set are entirely unsubstituted.
A few hydroxycompounds i.e., C4-C7-dihydroxybenzenes were also found to be inactive in hydrogen transfer.

Comparing the present results with results obtained for another set of twenty coals of lower rank (2-4), the major difference is, that in high rank coals much more correlated signals are related to aromatic structures. This refers to the positively as well as negatively correlated signals.

FI Mass Signals and Structures Correlated with Solidification Temperatures. Results of correlation analysis carried out for two sets of data i.e., FI mass signals and temperatures of solidification of coals, Ts, are presented in Table 2. It has been stated that all signals, significantly correlated with Ts, are also significantly correlated with hydrogen transfer, however with opposite sign (Table 2).
This means, the higher the content in a coal of structures shown in upper part of Table 3, the lower is its temperature of solidification and the higher its hydrogen transfer. It clearly indicates a strong link between reactivities of the structures in reactions resulting in solidification and in hydrogen transfer

reactions.
Next, the results of correlation analysis also show: the higher the content in a coal of structures presented in lower part of Table 3, the higher is its temperature of solidification and the lower its hydrogen transfer. Thus, the structures are inactive in solidification as well as hydrogen transfer reactions.

Summing up the results:
- The same structures are reactive in hydrogen transfer from the hydrogen donor and in reactions that result in solidification of coal on its heating. They are: (a) numerous unsubstituted and C1-aromatic hydrocarbons that contain from 3 up to 7 aromatic rings /except for the hydrocarbons quoted in the next para/; a few may have also C2 and C3 alkyls; and (b) C0-C7-alkylated hydroxyaromatic compounds that contain from 1 to 3 aromatic rings.
- Structures that are inactive in hydrogen transfer as well as in solidification reactions, are: alkyl-, up to C3, naphthalenes, fluorenes, acenaphthenes, anthracenes and chrysenes as well as alkyl-, up to C5, aromatic hydrocarbons that have 4 rings (pyrene, perylene, cyclopentachrysene) and 6 rings (dibenzopyrene).

DISCUSSION

The link between H-acceptor capability of coals in reaction with H-donor and their temperature-induced solidification (1) lies in the fact that the same structures that are active in H-transfer from H-donor are also active in thermal reactions resulting in solidification.
Hence, these structures during liquefaction can react via two pathways: they can either react with H-donor or participate in condensation/polymerization reactions. The pathway by which the structure reacts depends on the availability of H-donor molécule or a molecule with which it can condensate or polymerize.

H-transfer activity of the shown aromatic hydrocarbons (Table 3;upper) can be explained on the basis of mechanism worked out by McMillen, Malhotra et al.(6); the aromatics react with hydroaromatic H-donor and give rise to cyclohexadienyl radicals which in turn, lead to cleavage of single bonds in coal material. The mechanism of solidification reactions of the aromatics can be deduced from studies of carbonization at 430-450oC of model aromatic hydrocarbons (7) showing that they undergo condensation reactions. Hence, it is concluded that the shown aromatic hydrocarbons undergo such condensation during liquefaction and that this constitutes a part of retrogressive reactions in liquefaction.

Assuming that the hydroxycompounds (Table 3; upper) are phenolic compounds, one can explain their activity in H-transfer by several hypotheses (8,9). More obscure is mechanism by which they contribute to solidification, except for dihydroxybenzenes (10).It has been stated that they readily polymerize at 400oC; ionic mechanism was suggested (10). Thus, it is concluded that the hydroxycompounds polymerize in liquefaction and give rise to retrogressive reactions in this way, if H-donor is not available on molecular level.

The inactive structures (Table 3; lower) dilute the concentration

of active species. Hence, the higher the content of inactive ones the longer time is needed for solidification. This has been manifested in the Gieseler-plastometer as the increase of solidification temperature.

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Table 1
BASIC CHARACTERISTICS OF THE STUDIED COALS

COAL No	Wt % daf C	Wt % daf O	SOLIDFTN* Ts; oC	HYDROGEN TRANFER, HTr g of H /100 g org.mat. COAL	RESIDUE	EXTRACT
100	85.0	6.9	433	0.78	0.77	0.68
102	87.3	4.6	417	1.06	0.84	0.83
103	85.9	6.6	428	1.20	0.95	0.85
104	85.3	6.9	451	0.71	0.70	0.86
105	85.7	6.9	440	0.68	0.67	0.91
106	85.7	6.6	451	0.76	0.61	1.01
107	86.4	2.8	464	0.74	0.51	0.95
109	88.4	3.8	471	0.63	0.69	0.61
110	88.3	3.6	458	0.55	0.71	0.55
111	86.7	5.2	465	0.42	0.73	0.60
112	90.6	1.9	478	0.49	0.77	0.49
113	91.9	0.8	487	0.32	0.71	0.47
114	89.4	3.2	490	0.12	0.42	0.44
117	84.5	7.5	454	0.76	1.03	0.81
118	85.7	5.3	448	0.61	0.95	0.72
119	89.5	2.7	479	0.27	0.47	0.41
120	84.5	7.7	430	0.83	1.00	0.72
121	91.4	0.8	488	0.41	0.42	0.50
122	88.7	1.7	490	0.36	0.46	0.97
124	85.1	6.8	430	0.73	1.02	0.62
Range	85-91	0.8-7.7	417-490	0.1-1.2	0.4-1.0	0.4-1.0

*/ Gieseler plastometer; standard method PN-62/G-04536.

Table 2
FI MASS SIGNALS CORRELATED WITH HYDROGEN TRANSFER VALUES /HTr/ AND WITH SOLIDIFICATION TEMPERATURES /Ts/ OF THE COALS

m/z	Corrln coeffnt for HTr	Corrln coeffnt for Ts	m/z	Corrln coeffnt for HTr	Corrln coeffnt for Ts
	Upper Part			Upper Part	
158	.85	-.82	374	.67	-.76
160	.59	-.56	376	.80	-.86
162	.81	-.75	378	.88	-.90
164	.82	-.74	380	.59	-.55
172	.85	-.83	388	.74	-.84
174	.69	-.63	390	.87	-.83
176	.76	-.71	392	.84	-.88
188	.79	-.70		Lower Part	
190	.53	-.59			
200	.70	-.67	166	-.70	.70
202	.54	-.60	168	-.58	.70
212	.91	-.85	180	-.80	.87
214	.80	-.83	182	-.71	.80
224	.50	-.60	192	-.78	.85
226	.93	-.91	194	-.83	.85
238	.82	-.88	196	-.62	.55
240	.91	-.94	206	-.91	.90
250	.82	-.81	208	-.71	.77
252	.81	-.84	218	-.72	.74
254	.77	-.75	220	-.80	.59
260	.57	-.64	230	-.86	.90
262	.72	-.75	244	-.90	.90
264	.85	-.90	256	-.69	.74
274	.73	-.73	258	-.90	.85
276	.76	-.76	280	-.75	.85
278	.88	-.79	284	-.74	.71
288	.69	-.70	294	-.86	.91
290	.68	-.55	298	-.72	.71
300	.62	-.65	306	-.75	.79
302	.87	-.85	308	-.87	.84
314	.86	-.86	318	-.81	.85
328	.79	-.83	320	-.88	.95
338	.81	-.77	322	-.59	.62
340	.64	-.48	330	-.57	.70
342	.83	-.77	332	-.83	.87
350	.71	-.72	334	-.87	.79
352	.90	-.92	344	-.83	.79
364	.85	-.88	346	-.87	.85
366	.88	-.83	358	-.72	.68

Table 3
STRUCTURES IN THE CORRELATED FI MASS SIGNALS

Upper: FI signals positively correlated with H-transfer and negatively correlated with solidification temperatures
Lower: FI signals negatively correlated with H-transfer and positively correlated with solidification temperatures

m/z					PROPOSED STRUCTURES
					Upper; ACTIVE STRUCTURES
108	122	136	150	164	C_0 – C_5 -hydroxybenzenes*
110	124	138			C_0 – C_2 -dihydroxybenzenes*
146	160	174	188		C_1 – C_4 -hydroxyindenes *
134	148	162	176	190	C_0, C_1 *, C_2, C_3*-dihydroxyindenes
158	172		200	214	C_1 – C_2 and C_4 – C_5 -hydroxynaphthalenes *
198	212				C_2 – C_3 hydroxyacenaphthenes *
224	238				C_3 – C_4 -hydroxyfluorenes * and
					C_1 – C_2 -octahydropyrenes *
190					4H-cyclopenta[def]phenanthrene *
202					pyrene *
250	and	262			C_3 -hexahydropyrene * and C_4 -tetrahydropyrene *
226	240	254			C_0 – C_2 -benzo[ghi]fluoranthenes *; C_0 – C_1 -cyclo
					penta[def]chrysenes *; C_0 -cyclohexa[def]chrysene *
252					perylene *
260	274	288			$C_n H_{2n} - {}_{20} N_2$ *
264	278				C_0 – C_1 -11H-cyclopenta[ghi]chrysene *; C_0 -picene *;
					C_5 – C_6 -hydroxyanthracenes *
276	290				C_0 – C_1 -anthanthrenes *
302					C_0 -dibenzopyrene *; C_6 – hydroxypyrene *
300	314	328	342		C_0 * , C_1 * , C_2 * , C_3 -coronenes;
					C_0 * – C_1 -dibenzochrysenes
340					C_1 -dibenzocyclopenta[cd]pyrene
350	364	378	392		C_0 – C_3 -benzocoronenes; C_0 – C_1 -tribenzochrysenes
352	366	380			C_0 – C_2 -tribenzopyrenes
374	388	and	376	390	?

Lower: INACTIVE STRUCTURES

142	156			C_1 – C_2 -naphthalenes *
166	180	194	208	C_4 – C_7 -dihydroxybenzenes * a. C_1 – C_3 -fluorenes *
192	206	220		C_1 – C_3 -anthracenes *
218				C_2 – 4H-cyclopenta[def]phenanthrene
168		196		C_1 , C_3 -acenaphthenes * and $C_{13}H_{12}N_2$ *
230	244	258		C_2 – C_4 -pyrenes
256		284	298	C_2 , C_4 *, C_5 -chrysenes
280	294	308	322	C_2 *, C_3 *, C_4 , C_5 -perylenes
306	320	334		C_3 , C_4 , C_5 * -11H-cyclopenta[ghi]chrysenes
304	318	332	346	C_2 – C_5 -anthanthrenes
330	344	358		C_2 *, C_3 , C_4 -dibenzopyrenes

* the assignments have been confirmed by high res. and accurate mass measurements

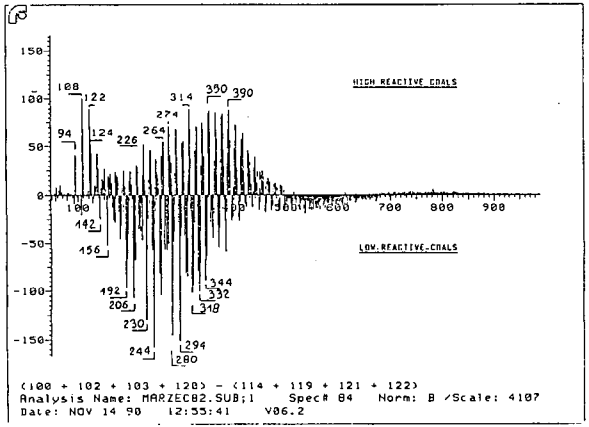

Figure.

FI Difference Mass Spectrum nf Selected Coals showing high and low reactivity towards the H-donor. See Table 1 for coals No. 100, 102, 103, 120 and 114, 119, 121, 122.