

# COAL DEGRADATION THROUGH EXTRACTION AND DEPOLYMERIZATION IN A FLOWING SOLVENT UNDER PRESSURE

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## INTRODUCTION

Solubilization and/or depolymerization are the initial steps of coal liquefaction, coking, or pyrolysis. Most of the solubilization/depolymerization experiments performed at rather high temperature in relation to coal liquefaction utilized a batch reactor, the so-called autoclave, where the interaction between the solubilized small molecules and the insoluble macromolecules can not be neglected. Furthermore, it is almost impossible to know the actual extraction yield at a high temperature using autoclave, because we can not separate the fraction which is soluble at the high temperature but is precipitated at room temperature from the residue. The solid recovered at room temperature after experiments is the mixture of the residue and the precipitated solid. Blessing and Ross<sup>1</sup> used a specially designed autoclave which is equipped with a basket assembly. Solvent can penetrate the basket through the glass frits fitted at the top and the bottom of the basket. Coal samples were placed in the basket assembly, and the extract was expected to come out from the basket through the glass frits. Unfortunately this trial was unsuccessful, because the diffusion rate of the deposit through the frit was very small. Flow reactors have been used by several investigators for examining the solubilization/depolymerization behavior of coal at a rather high temperature. Aida et al.<sup>2</sup> tried to extract coal in a flowing stream of solvent with an UV spectrometer as a detector. This enabled them to monitor the products continuously, but detailed analysis of the products has not been performed because of the experimental difficulty. Kandiyoti et al.<sup>3,6</sup> have heated coal up to 450 °C in a flowing stream of solvent to avoid the secondary reaction. They have examined the effect of operating conditions in detail. Their interest was, however, the hydrogenation reaction above 400 °C, because their main research target was to examine the coal liquefaction mechanism.

We have recently found that some bituminous coals can be extracted up to 75 % in a flowing non-polar solvent at 350 °C without appreciable decomposition.<sup>7</sup> At room temperature about a half of the extract were still soluble in the solvent and the rest half precipitated as solid. Both the soluble fraction and the precipitated solid were almost free from mineral matters, suggesting the possibility of preparing clean fuel from coal in high yield.

In this paper the solubilization/depolymerization experiments of eight Argonne premium coals were performed at 350 °C in a flow type reactor, where coal samples were heated in a flowing stream of tetralin. The purposes of this work were to examine the coal structure through detailed analyses of the extract and the residue, and to examine the possibility of preparing clean fuels and/or raw materials for the subsequent conversion. The possibility to decompose further the soluble, the precipitated solid and the residue recovered from Pittsburgh #8 coal was also examined.

## EXPERIMENTAL

**Coal Samples.** Eight coals of the Argonne premium coals were used in this work. The analyses of these coal samples are given in Table 1.

**Experimental Procedure for extraction/depolymerization.** Figure 1 shows a schematic diagram of the apparatus used for extraction and/or depolymerization. 100 to 200 mg of coal samples were placed between two filters (11.2 mm OD and 0.5 mm opening) in a reactor made of Swagelok. Tetralin was supplied continuously using a high pressure pump at the flow rate of 1 ml/min. The pressure was regulated using a pressure regulating valve (TESCOM) at 10 MPa. The reactor was heated at the rate of 5 K/min to 350 °C where it was kept for 0 to 90 min, then it was cooled immediately by a sufficient amount of water to terminate the solubilization and/or depolymerization. The coal fraction extracted and/or depolymerized at the reactor temperature became soluble in the solvent and came out from the reactor with the flowing solvent, but a part of the solubilized components precipitated as solids when the solvent flow was cooled to room temperature. The solid thus precipitated, called "deposit" in this paper, was collected by 3 filters (20, 10, and 2  $\mu$ m openings) placed in series just before the pressure regulating valve. The deposit which passed these filters were collected in a separation trap with the soluble components at room temperature. The components soluble at room temperature are called "soluble" here. Product gas was collected in a gas bag, and analyzed using a gas chromatograph for the components smaller than C<sub>6</sub> hydrocarbons in molecular weight. Thus each coal sample was separated into the residue that is not extracted or depolymerized, the deposit, the soluble, and gaseous components. The weights of the residue and the deposit were directly measured after drying them in vacuo at 70 °C. The weight of gaseous components was calculated from the analysis using the gas chromatograph. The rest of the product was regarded as the soluble.

**Decomposition of soluble and deposit.** The deposit prepared from PITT was served to the flash hydro-pyrolysis and the pyrolysis in a liquid tetralin to examine the possibility to decompose the deposit further. The flash hydro-pyrolysis was performed using a small scale of batch reactor at 700, 800, and 900 °C at the residence time of 60 s. The decomposition of the soluble, the deposit and the residue in liquid tetralin was performed using a small batch reactor (6 ml in volume). About 50 mg of sample was placed with 5 ml of tetralin in the batch reactor. The whole reactor was immersed in a sand bath regulated at a temperatures between 380 to 450 °C, and kept there for 60 min. The products were separated into hexane-soluble fraction (HS), hexane-insoluble and tetralin soluble fraction (Tets-HI), residue and gas components by a similar procedure presented above.

**Analyses of the products.** The soluble, the deposit and the residue were characterized through various analyses. Ultimate analysis and SPE/MAS  $^{13}\text{C}$  solid NMR analysis<sup>8</sup> of the deposit and the residue were performed using a CHN coder (Yanaco, CHN-500) and a NMR spectrometer (Chemagnetics, CMX-300), respectively. The gel permeation chromatography (GPC) was used to estimate the molecular weight distribution of the deposit, because the more than 95 % of deposit could be solubilized in dimethylformamide (DMF). The packed column used is a Shim-pack GPC-8025 (Shimadzu), and an eluent DMF was supplied at the flow rate of 0.5 ml/min. The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS; Shimadzu/Kratos KOMPACT-MALDI-II) was used to estimate the molecular weight distributions of the soluble, the deposit, the residue, and the raw coal.

## RESULTS AND DISCUSSION

**Changes in yields of soluble and deposit with increasing temperature and extraction time.** Figure 2 shows the changes in the yields of the soluble, the deposit, and the residue with increasing temperature and extraction time for IL coal. The soluble yield increased with the increase of temperature, reached 25% at 350 °C, and finally reached more than 30 % at the holding time ( $t_p$ ) of 30 min at 350°C. On the other hand, the deposit yield was very small up to 350 °C while temperature is increased, but it increased gradually with the increase of holding time at 350°C and finally reached about 40% at  $t_p = 60$  min or so. The increase of the soluble yield is judged to be brought about through the relaxation of coal structure upon heating in solvent, because most of the soluble was produced below 300 °C, in other words, the soluble was not produced through decomposition reaction. By keeping the coal for extended time at 350°C relatively large molecule components that are soluble in tetralin at 350 °C gradually came out from the coal particles. It would be because the intraparticle diffusion rate of the deposit is not so fast.

Figure 3 compares the ultimate product yields at 350 °C, which were arbitrarily defined as the yields at  $t_p = 60$  min, for eight Argonne premium coals. The yields of soluble and deposit for bituminous coals, IL, PITT, and UF coals, were very large. The extract yields for these coals are as follows: 80 % (soluble: 41 %, deposit: 39 %) for UF, 67 % (soluble: 29 %, deposit: 38 %) for PITT, and 63 % (soluble: 27 %, deposit: 36 %) for IL. Surprisingly, 80 % of UF coal were extracted at 350 °C. For the lowest rank coal, ND, the deposit yield was very small and appreciable amount of gaseous components were produced. Both the soluble and the deposit yields were small for the highest rank coal, POC. These results indicate that decomposition reaction occurred for the lowest rank coal ND, but little decomposition reaction occurred for the other higher rank coals. Therefore, most of the soluble and the deposit for the higher rank coals are judged to be relatively small molecule components existent in the original coal. The small molecules could come out because the macromolecular network of coal was relaxed through the heat treatment in the solvent.

These results suggest that the structure of the bituminous coals used in this work is rather close to the model B of Nishioka (physically associated model).<sup>9,10</sup> The soluble and the deposit are assumed to be physically associated each other and/or with the residue in the raw coal.

**Ultimate analysis and  $^{13}\text{C}$  NMR analysis.** The above discussion clarified that 50 to 80 % of coal can be extracted with little decomposition by tetralin at 350 °C for bituminous coals. Then the solid products, the deposit and the residue, were characterized by various analyses to examine the change accompanying the extraction. Table 2 compares the ultimate analysis and ash content of the raw coal, the residue, and the deposit prepared at  $t_p = 60$  min at 350°C for PITT and IL coals. Since the soluble concentration was very small and hence could not be subjected to the analyses, the numbers for the soluble in Table 2 were calculated by the proportional allotment from the data for the raw coal, the residue and the deposit using their yields given in Fig. 3. Although the ultimate analyses were not significantly different among the raw coal, the deposit, and the residue, the hydrogen content and the atomic H/C ratio of the residue were appreciably smaller than those of the raw coal and the deposit. As a result of this difference, the atomic H/C ratio of the soluble was the highest. This indicates that the soluble is richer in hydrogen than the other fractions. The most distinguishing result is that the soluble and the deposit contain little ash, which means most of ash remains in the residue. This presents the possibility to prepare clean fuel or clean raw materials in a high yield from bituminous coals by simple extraction.

Figure 4 compares the  $^{13}\text{C}$  NMR spectra among the raw coal, the residue, and the deposit prepared at  $t_p = 60$  min at 350°C for PITT. The carbon distributions estimated from these spectra are given in Table 3. Again the carbon distribution for the soluble was calculated by the proportional allotment from the distributions for the raw coal, the residue, and the deposit by assuming that no decomposition reaction occurred during the extraction. Although the distributions for the raw coal, the residue, and the deposit are rather close, the proportions of methyl groups ( $-\text{CH}_3$ ) and methylene bridge ( $-\text{CH}_2-$ ) are smaller and the proportions of the bridgehead carbon (Bridgehead) are larger in the deposit and the residue than in the raw coal. These differences reflected on the difference in the values of the aromaticity index,  $f_a$ , of the raw coal, the residue, and the deposit: they are 0.733, 0.785 and 0.782, respectively. The calculated carbon distribution for the soluble shows that the soluble is rich in methyl groups and methylene bridge and the proportions of the bridgehead carbon is small, resulting in the small  $f_a$  value of 0.650. These results are consistent with the ultimate analyses shown in Table 2.

Above results suggest that soluble is the fraction consisting of small and more aliphatic molecules in the original coal, and that the average chemical structure of the raw coal, the residue, and the deposit are very close. This circumstantially supports the above discussion concluding that bituminous coals were extracted with little

decomposition below 350 °C. Then the detailed analyses of the soluble, the deposit, and the residue will give us a more realistic picture of bituminous coals.

**Molecular weight distribution of soluble, deposit and residue.** We have clarified that the molecular weight distribution (MWD) can be well estimated by the MALSI-TOFMS method for molecules less than 5000 in molecular weight by comparing the MALDI and the GPC measurements for a deposit solubilized in dimethylformamide (DMF).<sup>7</sup> Then Figure 5 compares the MWDS measured by the MALSI-TOFMS method for the soluble, the deposit and the residue prepared from PITT at  $t_f = 60$  min at 350 °C with the MWD of the raw PITT coal. The MWDS for the raw coal, the residue and the deposit are all bimodal having peaks at  $M_w = \text{ca. } 300$  and  $\text{ca. } 2200$ . The  $M_w$  of the peak position for the larger molecules in the deposit seems to be slightly smaller than that in the residue. On the other hand, the soluble consists of only small molecules of less than 600 in  $M_w$ , and the peak position almost coincides with the peaks of smaller  $M_w$  in the raw coal, the residue and the deposit. These results again support the model B of Nishioka for the structure of PITT. The deposit and the residue still contain the small molecule components which could not be dissociated at 350 °C.

**Decomposition of soluble, deposit and residue in tetralin.** The soluble, the deposit and the residue prepared from PITT were heated in tetralin at 380 to 450 °C in the batch reactor to decompose them further. Figure 6 shows the product distribution through the decomposition for the deposit. The yields of oil (HS) and TeS-HI fraction increased with increasing temperature up to 420 °C monotonously and the sum of the two yields reached 78 wt %. By further increasing the temperature up to 450 °C a part of the TeS-HI fraction were decomposed into oil fraction, and the yields of oil and TeS-HI reached 56 wt % and 22wt%, respectively. Figure 7 compares the MWDs of the products at 450 °C, which were measured by the MALDI-TOFMS method. Comparing with the MWDs of the soluble and the deposit, the oil fraction consists of the components smaller than these in the soluble, the components in TeS-HI fraction are similar to those in the soluble, and the TeI fraction consists of the components smaller than those in the deposit. These results show that the deposit can be further decomposed into small molecule compounds just by heating it in tetralin at 450 °C. Figure 8 enlarges the MWD of the oil fraction so as to identify the components more easily involved. Most of the oil fraction consists of the components of  $M_w = 250$  to 350. These components were judged to be dimers of two aromatic ring components from the <sup>13</sup>C NMR analysis.

Figure 9 compares the product distributions through the decomposition of the soluble, the deposit and the residue at 450 °C. Since 72 wt % of the soluble consisted of oil, the oil yield increased by only 9 % for the soluble through the decomposition. A small amount of gaseous components (CH<sub>4</sub> and CO are main components) were simultaneously produced. This indicates that the soluble fraction is hardly decomposed at 450 °C. The residue was converted into 32 wt % of oil, 1 wt% of gaseous components and 67wt % of TeI and residue. Figure 11 shows that more than 52 wt % of PITT coal (d.a.f. basis) are converted into oil fraction through the combination of extraction at 350 °C and the decomposition at 450 °C in tetralin. This is very attractive as a coal conversion process, since this conversion process does not require expensive gaseous hydrogen. These results with the detailed analyses of the soluble, the deposit, and the residue given above clearly show that the unit components composing the soluble, the deposit, and the residue are similar.

**Flash hydrolysis of deposit.** The above results and discussion showed that the unit structures of the deposit produced from PITT coal are two aromatic ring components. Then the flash hydrolysis of the deposit was performed to examine the possibility to convert most of the deposit into two aromatic ring components such as naphthalene, methylnaphthalenes, etc. Figure 10 shows the effect of temperature on the product yields for the flash hydrolysis of the deposit. Main products were, unexpectedly, CH<sub>4</sub> and benzene, and the total conversion to volatiles was less than 50 % even at 900 °C. Flash hydrolysis over 700 °C seems to be too severe to preferentially obtain two aromatic ring components. We are now examining the possibility of milder hydrolysis conditions for this purpose.

## CONCLUSION

Eight Argonne premium coals were extracted in a flowing stream of tetralin under 10 MPa at 350 °C. Bituminous coals, Illinois #6, Pittsburgh #8, and Upper Freeport, were extracted by 65 to 80% at 350°C, and the extract was divided into about 30 to 40 % of soluble (soluble) at room temperature and 25 to 40% of precipitated solid (deposit) at room temperature. The contribution of the decomposition reaction on the extraction yield is judged to be neglected for these coals. The extraction yields of lower rank coals, Beulah-Zap was not so large as those for the bituminous coals. At 350°C appreciable gas formation was observed, indicating that the decomposition reaction as well as the extraction proceed for these coals. The extraction yield of the highest rank coal, Pocahontas, was also small reflecting its structure. Since both the soluble and the deposit were almost ash free, they will be well utilized as a starting material of subsequent upgrading processes such as liquefaction, pyrolysis, and coking.

The treatment of the extraction products prepared from PITT coal were performed in tetralin at 380 to 450 °C to examine the possibility to decompose the fractions under mild conditions. Through the extraction and the heat treatment at 450 °C Pittsburgh #8 coal was converted into 52 wt % of oil (hexane soluble). This is very attractive as a coal conversion process, since this conversion process does not require expensive gaseous hydrogen. The detailed analyses of the extraction and the decomposition products clearly showed the structure of PITT coal is represented by the model B of Nishioka (physically associated model).

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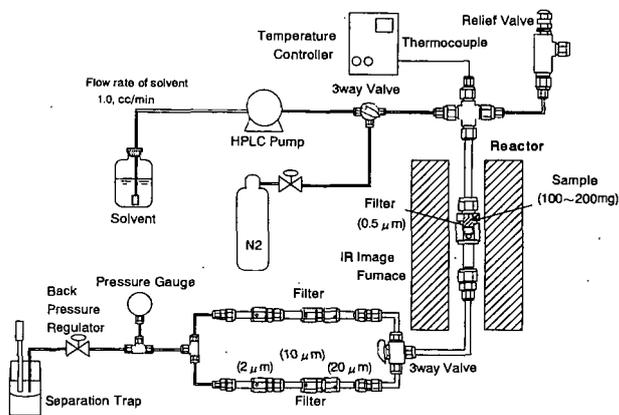
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**Table 1. Ultimate and proximate analyses of coals used [wt%]**

Coal	Ultimate analysis [da.f]				Prox. analysis [db.]		
	C	H	N	O(dff)	FC	VM	Ash
Boublik-Zap (ND)	72.9	4.8	1.2	20.1	45.3	44.9	9.7
Wyosick (WY)	73.0	5.4	1.1	18.5	46.5	44.7	8.8
Illinois#6 (IL)	77.6	5.0	1.4	16.0	44.4	40.0	15.4
Blind Canyon (UT)	80.7	5.8	1.6	11.9	49.5	45.8	4.7
Levinston-Stockton (ST)	82.5	5.3	1.6	10.6	49.9	30.1	19.8
Pittsburgh#1 (PITT)	83.2	5.3	1.6	9.9	52.9	37.8	9.3
Upper Freeport (UF)	85.5	4.7	1.6	8.2	59.3	27.4	13.1
Pocahontas (POC)	91.0	4.4	1.3	3.3	76.6	18.6	4.8

**Table 2. Analyses of the deposit and the residue produced from PITT.**

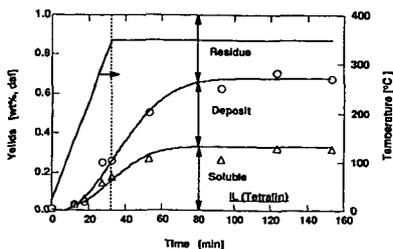
	Ultimate analysis [wt%, da.f]				Ash	taric ratio [-]	
	C	H	N	O(dff)		H/C	O/C
PITT							
Raw	80.6	5.4	1.8	12.2	7.3	0.81	0.11
Residue	80.8	4.8	2.0	12.4	21.3	0.71	0.12
Deposit	81.4	5.4	2.2	11.0	0.8	0.80	0.10
Soluble	79.8	5.9	1.3	12.4	=0	0.89	0.12
(Calculated)							
IL							
Raw	77.6	5.0	1.4	16.0	15.5	0.77	0.15
Residue	77.4	4.6	1.5	16.6	32.1	0.71	0.16
Deposit	79.2	5.3	1.8	13.7	0.1	0.80	0.10
Soluble	75.7	5.1	0.7	18.2	0.3	0.81	0.18
(Calculated)							



**Figure 1. Schematic of experimental apparatus used for extraction/depolymerization in a flowing solvent.**

**Table 3. Carbon distribution in the raw coal, the residue, and the deposit prepared at 350 °C ( $t_f = 60$  min) for PITT.**

Carbon type	Raw Coal	Residue	Deposit	Soluble (Calculated)
Aliphatic carbon				
-CH <sub>3</sub>	0.069	0.047	0.049	0.103
-CH <sub>2</sub>	0.168	0.154	0.158	0.188
-OCH <sub>3</sub>	0.013	0.008	0.010	0.020
-CO-C, R-OH	0.017	0.006	0.001	0.039
Aromatic carbon				
A-H	0.328	0.336	0.323	0.325
Bridgehead	0.299	0.336	0.337	0.238
A-OH, -OCH	0.092	0.105	0.120	0.054
-COOH	0.014	0.008	0.002	0.028
Aromaticity index, $f_a$	0.733	0.785	0.782	0.650



**Figure 2. Change in the yields of soluble, deposit and residue with the increase of the holding time at 350 °C for IL.**

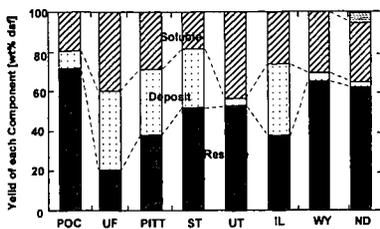


Figure 3. Yields of soluble, deposit and residue for Argonne premium coals (350 °C,  $t_f=60$  min).

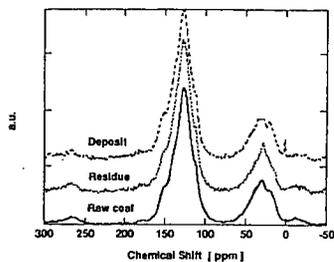


Figure 4.  $^{13}\text{C}$  NMR spectra for the raw coal, and the deposit and the residue prepared at  $t_f=60$  min at 350 °C for PITT.

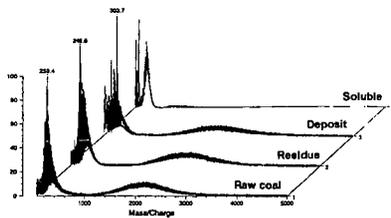


Figure 5. MWDs of the raw coal, and the residue and the deposit prepared at  $t_f=60$  min at 350 °C for PITT (MALDI-TOFMS).

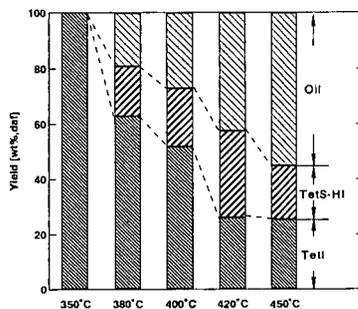


Figure 6. Product distributions through the decomposition of the deposit at different temperatures (PITT).

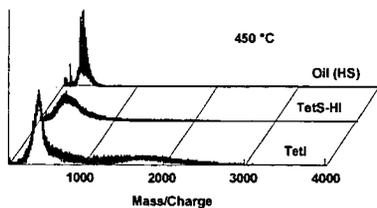


Figure 7. Comparison of the MWDs of the decomposition products from the deposit at 450 °C (PITT).

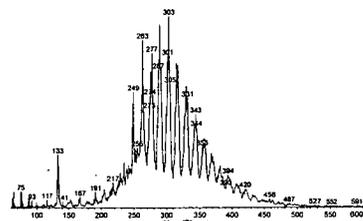


Figure 8. MWD of the oil fraction produced by the decomposition of the deposit at 450 °C (PITT).

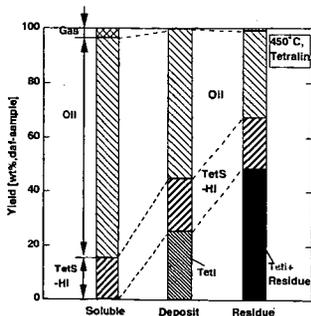


Figure 9. Product distributions through the decomposition of the soluble, the deposit and the residue at 450 °C (PITT).

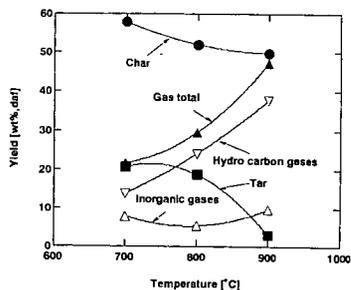


Figure 10. Effect of temperature on the product yields for the flash bydropyrolysis of the deposit (PITT).