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DEPOLYMERIZATION OF COAL BY DIRECT SOLVENT ATTACK

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OBJECTIVES AND SCOPE OF WORK

A. Objectives

To elucidate the mechanisms of coal depolymerization by basic organic solvents.

B. Scope of Work

1. Coal depolymerization in a series of solvents of varying nucleophilicity and basicity will be carried out in order to establish the overall nature of the reaction.
2. Depolymerization kinetics will be studied in several solvents.
3. The dependence of the reaction rates on solvent concentration (the gas density of the supercritical solvents) will be established.
4. Hydrogen transfer reactions will be studied by isotope exchange.
5. In so far as possible, the reaction products will be characterized.
6. Time permitting, relevant model compounds will be studied.

Detailed Description of Technical Program

Introduction

To pursue our first goal - the effect of temperature and nature of the solvent - and establish the extent of solvolytic depolymerization of coal we measured conversion to pyridine solubles in a series of amine solvents having different basicities (pK) and nucleophilicities (Swain-Scott η values). All studies were carried out on Ill. No.6 Coal. It has been shown that the conversion to pyridine solubles is not dependent on solvent basicity (pKa) and/or nucleophilicity (Swain-Scott η value). At 300°C and 350°C with reaction times of 3 hours, the conversions were too high to show any sensitivity to solvent character (Table 1 and 2). The conversions under milder conditions - 250°C and 300°C with reaction times of 1 hour - showed dependency on neither the nucleophilicity nor the basicity of the solvents (Table 3 and 4).

There is a strong effect of temperature on solubilization, leading to complete solubility at 350°C.

Experimental Methods

Coal Preparation. The only coal used in this project was Illinois No. 6 coal (see Table 5 for analysis) obtained from Exxon Research and Engineering Co., Linden, N.J. The coal was stored in a nitrogen atmosphere from the time it was received in the laboratory. The coal was ground to pass a -100 mesh sieve. The coal was dried in a vacuum oven overnight at approximately 105°C. The coal was flushed periodically with nitrogen whenever a sample was removed.

Depolymerization. In all of the experiments, 4.95 g of Illinois No.6 coal and 0.5 mole of the solvent were charged to the autoclave (250 ml, stainless steel, mechanically stirred). After purging the autoclave with N₂, the pressure inside the autoclave was adjusted to one atm with nitrogen. Depending on the experiment, the autoclave was heated to 250-350°C at a rate of 5-10°C/min., and after 1 or 3 hours the reactions were stopped. The autoclave was cooled down to ambient temperature. The contents of the autoclave were taken out and filtered through a cellulose thimble and the residue was extracted with 150 ml of pyridine for one or two days in a Soxhlet apparatus protected with a nitrogen atmosphere. The pyridine-extracted residue was dried to constant weight in a vacuum oven at 105°C. The weight of the residue was used to calculate the percentage of the solubilized coal using the following equation.

$$\% \text{ Conversion (daf)} = \frac{\text{weight of coal} - \text{weight of residue}}{\text{weight of coal}} 100 \times \frac{100}{100 - \% \text{Ash of Coal}}$$

The combined volume of the extraction solution and the filtrate solution was concentrated to 100 ml, then a 50 ml portion was removed and its solvent

evaporated under reduced pressure. The extract was dried to constant weight in a vacuum oven at 105°C. The weight of the extract was used to calculate the concentration of coal in the other half of the solution, which was examined by high speed centrifugation and vapor phase osmometry.

Toluene Extraction. The residue (1 g) obtained when half of the pyridine extraction solution (see above) was evaporated was placed in a cellulose thimble and extracted in a small Soxhlet apparatus with 20 ml of toluene for one day under nitrogen stream. Injection of the toluene into a G. C. gave no peak indicative of the presence of pyridine.

Centrifugation. A Bechman Airfuge Ultracentrifuge capable of 10⁵ rpm (165,000 xg) was used with a rotor with a capacity for six tubes holding 0.17 ml in each. For one measurement, around 0.17 ml of the original pyridine extract combined with the filtrate solution was transferred by syringe to each of six tared tubes. After 3 hours of continuous centrifugation, the supernatant from all of the tubes was combined and saved in a tared weighing dish, then 0.15 ml of fresh pyridine was added to each tube. After a second centrifugation, the solution of the tubes was added to the weighing dish, and its solvent evaporated under stream of nitrogen. The drained tubes and the weighing dish were dried one day in a vacuum oven at 110°C. The ratio in weight change in the six tubes over weight change in the weighing dish was taken as a measure of the colloidal coal particles suspended in the solution (see Tables 1, 2 and 4).

Vapor Pressure Osmometry. To remove colloids and obtain a true solution of the pyridine soluble products, the solutions were filtered through 0.5 μ m millipore filter. Seven solutions were prepared by sequential dilution of the filtered solution. Concentrations used for osmometry were 1.2 to 25 mg/ml. The response as a function of the concentration of the depolymerization

products was analyzed by least squares regression and a number average molecular weight (MW_n) calculated using a calibration constant derived from the osmometer's response with standard solutions of benzil in pyridine (see Table 1 and 3).

Discussion

The chemical conversion of insoluble, solid coal to soluble, smaller fragments involves many factors which are not clear to us at the present time. Our observations clearly proved that depolymerization is not due to the basicity and nucleophilicity of the solvent alone, because the amount of depolymerization is not dependent on either the basicity or nucleophilicity of the solvent. The percentage of depolymerization in the temperature range of 250-350°C for the systems studied are shown in Figure 1.

To detect the effect of solvent polarity, the percentage of conversion was examined as a function of the dielectric constant (a macroscopic property). See Table 4 and Figure 2. It was found that the polarity of the solvent has an effect at both reaction temperature of 250 and 300°C, but the relationship has a maximum for n-Bu NH₂ with $\epsilon = 4.88$. After that the higher the dielectric constant the lower the conversion.

As expected, conversion decreases as the temperature of the reaction is reduced (see Figure 1). The lower the reaction temperature, the higher the percentage of nitrogen in the products (see Table 5). The relative importance of this solvent attack and thermal depolymerization is not yet clear.

To determine the mode of adduction or to study the chemical bond attachment including molecular interaction and hydrogen bonding, the reaction of Et₃N with Illinois No.6 coal at 300°C for 1 hour was investigated. The molecular weight distribution was obtained by VPO along with the elemental analysis. Indications are that at the lower temperature, lower average molecular

weights and higher percentages of amine incorporation result. The vacuum dried pyridine soluble products were extracted with toluene and checked by G.C. in order to see if any non-bonded pyridine was retained in the products. The extracts contained no pyridine and we assume the increase in nitrogen is due to triethylamine incorporation.

We have made a change in the direction of this project and are now carefully studying the structure of the soluble products, with emphasis on the nature of the incorporated nitrogen.

TABLE 1. AVERAGE MOLECULAR WEIGHT OF PYRIDINE-SOLUBLE PRODUCT OF DEPOLYMERIZATION OF ILL. NO.6 COAL AFTER HEATING 300°C FOR 3 HOURS

Solvent	η	pK_a	Conver- sion (wt% coal, daf)	% colloi- dal parti- cles	Pyridine- soluble product (MW_n)	Mass- balance (%)
Et ₃ N	3.98	11.01	87.7	0.0	790	127
Pyridine	4.27	5.25	31.0	5.1	-	185
Morpholine	5.13	8.33	87.8	0.2	360	249
n-BuNH ₂	5.13	10.77	80.5	0.8	520	148
Pyrrolidine	5.67	11.27	84.7	0.8	230	297

TABLE 2. DEPOLYMERIZATION AT 350°C and 3 HOURS

Solvent	n	pK_a	Conver- sion (wt% coal, daf)	% colloidal Particles	Mass- balance (%)
Et ₃ N	3.98	11.01	93.4	1.1	164.8
Pyridine	4.27	5.25	35	-	-
Morpholine	5.13	8.33	90.9	2.5	397
n-BuNH ₂	5.13	10.77	94.5	0.7	142
Pyrrolidine	5.67	11.27	94.12	0.3	414.5
Triethylenediamine	-	8.60 2.95	93.87	0.6	215.5

TABLE 3. DEPOLYMERIZATION AT 250°C AND 1 HOUR

SOLVENT	n	pK _a	Solubility Parameters (δ)	Solubility Parameters (δ_h)	Dielectric Constant ϵ	Conver- sion (wt% coal, daf)	Pyridine- soluble product (MW _n)	Mass- balance (%)
Et ₃ N	3.98	11.01	-	-	2.42	18.6	468	119
Pyridine	4.27	5.25	10.7	2.9	12.3	21.4	-	108
Aniline	4.35	4.63	10.3	5.0	6.89	37.0	606	130.6
Morpholine	5.13	8.33	10.8	4.5	7.33	36.4	-	132.6
n-BuNH ₂	5.13	10.77	8.7	3.9	4.88	49.1	-	130
Pyrrolidine	5.67	11.27	-	-	-	33.9	-	150
Et ₂ NH	-	10.49	-	2.0	3.58	20.1	-	117.1
Pr ₂ NH	-	10.96	8.0	3.0	3.07	24	-	123.5

∞

TABLE 4. DEPOLYMERIZATION AT 300°C AND 1 HOUR

SOLVENT	n	pK _a	Experi- mental pressure (psig)	Conver- sion (wt% coal, daf)	% colloidal particles	Mass balance (%)
Et ₃ N	3.98	11.01	650	69*	3.8	123.8
Pyridine	4.27	5.25	520	37.4	0.5	110
Aniline	4.35	4.63	370	83.5	11.0	129
Morpholine	5.13	8.33	500	75.4	0.9	189
n-BuNH ₂	5.13	10.77	740	89.4	0.0	148
Pyrrolidine	5.67	11.27	690	63*	1.2	199

* The average of two experiments.

TABLE 5. ANALYSIS OF Et₃N REACTION WITH COAL

COMPOUND	%C	%H	%N	%S	%Ash
Ill. No.6 Coal	68.40	5.23	1.26	4.38	10.26
" (daf)	(76.22)	(5.83)	(1.40)	(4.88)	-
Py [*] -soluble product at 250°C/1 hr.	74.44	7.13	4.00	2.43	0.18
Py-soluble Product at 300°C/1 hr.	77.76	7.13	3.09	2.55	1.12
Py-Soluble Product at 350°C/3 hr.	83.07	8.56	3.23	1.45	0.5

* Py = pyridine

SEMI-ANNUAL SUMMARY

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SUMMARY

The depolymerization of Illinois No. 6 coal by a series of solvents having different basicities (pK_a) and nucleophilicities (Swain-Scott n values) showed no dependence on either the basicity or nucleophilicity of the solvents. As expected, the conversion decreases as the temperature of the reaction is reduced, but the lower the reaction temperature, the higher the percentage of amine incorporation becomes in the products.

Figure 1 The % of depolymerization vs temperature

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