

Mild Pyrolytic Production of Low Molecular Weight Compounds from High Molecular Weight Coal Extracts

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Five different rank coals were pyrolyzed at 250 °C for 24 h. Extraction yields using tetrahydrofuran, molecular weight distributions, and average molecular weights of the extracts were determined. The coal extracts obtained before and after the mild pyrolysis were fractionated by using Al₂O₃ into chemical classes, and these fractions were analyzed by using capillary column gas chromatography and gas chromatography/mass spectrometry. The mild pyrolysis results in the production of new molecules in the extract. Two extract fractions containing high molecular weight materials were heated to 250 °C and refractionated. Increased amounts of low molecular weight materials including new compounds were separated, having been produced by the very mild pyrolysis. Pyrolysis at 250 °C is capable of breaking bonds to produce low molecular weight compounds. In a lower rank coal, heating the extract at 250 °C resulted in a molecular weight increase indicative of the occurrence of condensation reactions. In two higher rank coals, no evidence for thermal chemical processes was found. Even heating at 250 °C is capable of causing chemical transformations in coals, but their occurrence is strongly rank dependent.

Introduction

The principal issue addressed in this paper is the origin of the additional extractable material formed when coals are heated. Is the additional extract due to pyrolytic cleavage of covalent bonds liberating more low molecular weight material from insoluble macromolecules, or is inherently soluble but trapped material freed by heat induced changes in the macromolecular structure? This question is directly relevant to the current controversy over the existence of an inherently soluble "mobile phase" trapped within the coal's macromolecular network.

Two experimental approaches are used. In one approach, coal extracts are fractionated by polarity and molecular weight and the low molecular weight components of those fractions are characterized by gas chromatography. The high molecular weight fractions were then pyrolyzed at only 250 °C and the products refractionated and reanalyzed. Since soluble materials are being pyrolyzed, any new compounds formed must be the result of chemical reactions and not the thermal release of physically trapped molecules.

In another approach, coal extracts are fractionated and analyzed by gas chromatography. The coals are then heated at 250 °C for 24 h and extracted as before. The extracts are fractionated, analyzed, and compared to the extracts from unheated coals.

It was first reported by Harger and Illingworth¹⁻³ between 1914 and 1922 that coals preheated at 200-400 °C in an inert atmosphere gave much higher yields of extract than unheated coals. Subsequently, extraction yields and properties of preheated and unheated coals were investigated by several groups.⁴⁻⁸ Ouchi⁴ heated two coals, their pyridine extracts, and residues to several temperatures between 230 and 450 °C at 2 °C/min. He concluded that when the coals are heated to a certain temperature, they begin to melt and bitumen flows out from the interior of each coal particle to the surface and this material can then

be easily dissolved, even by a weak solvent such as chloroform. Sarkar and Krishnan⁵ preheated five kinds of coals at 365-520 °C for 5-80 min before extraction and concluded that the chloroform-soluble substances responsible for the caking properties of coals are the result of mild pyrolysis. Brown and Waters⁶ preheated coals at increasing temperatures and extensively studied their extraction yields and properties. Since the yields and properties of chloroform extracts from preheated coal were closely similar to those of δ -extracts (the chloroform-soluble portion of the pyridine coal extracts), from untreated coals, they suggested that most of the chloroform-extractable material obtained on preheating is present as such in coals and is not a product of pyrolysis. Vahrman⁸ also inferred that readily extractable material was present in large pores and that there was also substantial material present in micropores and/or as clathrates in cages in the macromolecular structure.

Holden and Robb^{9,10} and Herod et al.¹¹ used pyrolysis-mass spectrometry to study compounds released by heating to 250-350 °C. Aliphatic hydrocarbons, alkylbenzenes, and alkylnaphthalenes were released. The observation of similar patterns of mass ranges at different temperatures and even after long heating led to the conclusion that all the components detected were evaporated directly from the micropore structures rather than being formed by thermal decomposition.

The role of hydroxyl functional groups in the mechanism of tar evolution was investigated by comparison of original

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Table I. Elemental Analyses of Coals Used^a

coals	element, wt %			
	C	H	N	O + S ^b
Big Brown	73.6	5.8	1.3	19.2
Wandoan	77.4	6.1	1.0	15.5
Illinois No. 6	79.9	5.1	1.8	13.2
PSOC-1309	84.2	5.8	1.4	8.6
PSOC-648	89.6	4.5	2.0	3.9

^a Dry ash-free basis. ^b By difference.

and O-methylated coals by Chu et al.¹² A matrix-isolation FTIR apparatus possessing 60 deposition surfaces was used for pyrolysis studies over a wide range of temperatures. O-methylation of coals was found to cause significant increases in tar yields and a low-temperature fraction, formed between 150–300 °C. A small amount of tar formation was detected at 195–245 °C even from a high-volatile A bituminous coal.

There are two different explanations for the increase in extract caused by heating coals. One holds that the increase is due to pyrolytic bond cleavages generating soluble fragments of the macromolecular network. Alternatively, physical changes in the coal caused by heating make diffusion much easier, and previously trapped material can now be extracted. Obviously, any mixture of these two effects is also an explanation. This issue has gained more attention recently due to the controversial proposal of a two-phase model for coals.^{13–15} This holds that coals consist of an immobile (macromolecular) phase containing large amounts of a mobile (molecular) phase. Relatively small molecules are present in the mobile component of the coal, but cannot be extracted because they are trapped in the network. The issue of the origin of the increase in extract amount caused by heating coals is directly relevant. The mobile-phase model predicts the increase is due to changes in physical structure, not chemical bond breaking.

Experimental Section

Five different rank coals were used, and their elemental analyses are listed in Table I. Big Brown, Wandoan, and Illinois No. 6 coals were obtained from Exxon Research and Engineering Co. (Annandale, NJ), and PSOC-1309 and PSOC-648 were obtained from the Pennsylvania State University Repository. Coal samples were ground, sifted, and stored under an inert nitrogen atmosphere before use. Coal particles of -60 mesh size were used in the experiments.

In these experiments, 2–5 g of sample was extracted with 250 mL of tetrahydrofuran (THF) for 24 h in a Soxhlet apparatus under an N₂ atmosphere. The extracts were fractionated into chemical classes by column adsorption chromatography on neutral alumina.¹⁸ The fractionation scheme is summarized in Figure 1.

Pyrolysis samples were put into Pyrex glass flasks under a dry N₂ atmosphere and were heated at 250 ± 1 °C and about 660 mmHg pressure under N₂ flow in a Forma Scientific high-temperature vacuum oven for 24 h.

A Hewlett-Packard Model 5880 gas chromatograph equipped with a flame ionization detector was used. Sample injection was made in the splitless mode, and helium carrier gas was set at a linear velocity of 80–90 cm s⁻¹. The fused silica capillary tubing (25 m × 0.3 mm i.d.) coated with SE-54 (film thickness of 0.25 μm) was obtained from Hewlett-Packard (Avondale, PA). Com-

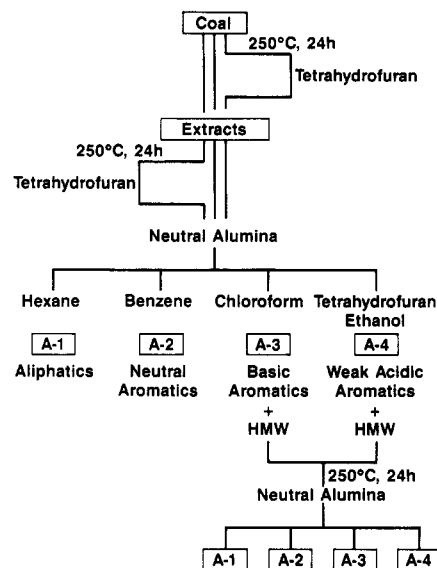


Figure 1. Fractionation and pyrolysis scheme. Key: HMW = high molecular weight compounds.

Table II. Tetrahydrofuran Extraction Yields of Original and Preheated Coals

coals	extraction yields, wt %	
	original coals	coals pyrolyzed at 250 °C
Big Brown	7.2	6.5
Wandoan	13.8	9.7
Illinois No. 6	11.2	13.0
PSOC-1309	4.9	10.4
PSOC-648	1.1	2.3

pounds were identified by comparison of sample component retention data with those of pure standards and gas chromatography/mass spectrometry (GC/MS). A Finnigan 4000 Series GC/MS with electron impact at 70 eV was used for obtaining mass spectra.

Molecular weight distribution patterns and average molecular weights were obtained on a Waters Associates Model ALC-201 liquid chromatograph equipped with a mass detector (Applied Chromatography Systems Inc., State College, PA). A series of three μ-Styragel columns (30 cm × 7.8 mm i.d., pore size, 100, 500, and 10³ Å) obtained from Waters Associates, Inc., were used with pyridine solvent. Average molecular weights were calculated by using a calibration curve prepared from Illinois No. 6 coal pyridine extracts as reported elsewhere.¹⁷

ACS reagent and HPLC grade solvents were used. THF was distilled before use and others were used without further purification.

Results and Discussion

The evolution of additional extract from coals heated to temperatures between 150 and 250 °C has been documented.^{10,12} Significant direct thermolytic bond cleavage at 250 °C and even chain processes leading to bond scission are expected to be slow for most structures.¹⁸ Therefore, a careful examination of extracts produced after such mild heating is a severe test of the chemical origin of enhanced extractability.

Five different rank coals were heated at 250 °C for 24 h. THF extraction yields of the original coals and the same coals preheated at 250 °C are listed in Table II. Extraction yields of the higher rank coals (Illinois No. 6,

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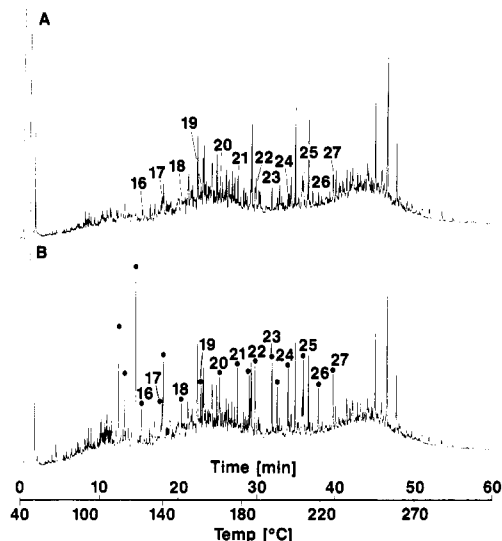


Figure 2. Gas chromatograms of the aliphatic fractions (A-1) of the (A) original and (B) preheated Wandoan THF extracts. Conditions were as follows: 40–100 °C at 10 °C min⁻¹ and 100–270 °C at 4 °C min⁻¹ after an initial 2-min isothermal period. Numbers denote the number of carbons of *n*-alkanes, and dots give increased compounds after 250 °C treatment.

PSOC-1309, and PSOC-648) increased after preheating, while those of the lower rank coals (Big Brown and Wandoan) decreased after preheating. These results can be explained by either chemical or physical changes.

All of the extracts were fractionated by using the procedure diagrammed in Figure 1. All of the fractions were analyzed by gas chromatography, and some extract component structures were tentatively identified by GC/MS. The low molecular weight compounds present in coal extracts have been extensively characterized and identified by GC, GC/MS, and MS.^{19–31} Although relative abundances varied with coal rank, the major components were *n*-alkanes, cyclic isoprenoids, steranes, terpanes, naphthalenes, biphenyls, phenanthrenes, and partly aromatized pentacyclic triterpanes. The rank dependence of the relative abundance of aliphatic compounds in solvent extracts has been reported.^{21,22} The trend in the relative abundances of cyclic alkanes, branched alkanes, and *n*-alkanes with odd and even carbon numbers in the aliphatic fraction (A-1) were the same as previously reported. Major compounds in the lower rank coals (Big Brown and Wandoan) are most probably cyclic aliphatics such as

Table III. Average Molecular Weights of the Wandoan and PSOC-1309 THF Extracts before and after Heat Treatment

extracts	average mol wt	
	M_w	M_n
Wandoan, original	5170	2090
Wandoan, after 250 °C treatment	5730	2310
PSOC-1309, original	2940	1340
PSOC-1309, after 250 °C treatment	3010	1460

mortanes and hopanes, while those in higher-rank coals (PSOC-1309 and PSOC-648) are *n*-alkanes. High molecular weight *n*-alkanes are abundant for PSOC-648 in contrast to PSOC-1309. Both *n*-alkanes and cyclic aliphatics are important compounds in Illinois No. 6 extracts. The aromatic fractions (A-2) of PSOC-1309 and PSOC-648 were mostly composed of simple polycyclic aromatic hydrocarbons (PAH), and that of Illinois No. 6 was composed of PAH and partially aromatized alkyltriterpanes. PAH are not important in extracts of Big Brown and Wandoan coals, and the major compounds are probably hydroaromatic isoprene derivatives. Although the components in A-3 and A-4 could not be identified by GC/MS, these chromatograms were simple and similar for all coal extracts. Furthermore, the chromatograms of A-3 and A-4 from both original and preheated coal extracts were the same.

The A-1 and A-2 fractions contain aliphatic and aromatic compounds, respectively. The gas chromatograms of these two extract fractions from the original and preheated coals were different for Big Brown, Wandoan, and Illinois No. 6 but were almost the same for PSOC-1309 and PSOC-648. The chromatogram of the A-1 fraction of the Wandoan THF extracts is shown in Figure 2. Relative abundances of *n*-alkanes and other compounds (probably branched alkanes) increased after heat treatment at 250 °C.

The data in the preceding paragraph do not allow a clear distinction between the physical and chemical explanations for the origin of the new extract or the decrease in extract. The identity of the extract from PSOC-1309 and PSOC-648 before and after heating is certainly consistent with the emergence of once trapped material of the same composition as extractable material. If one accepts the idea that the trapped material is homogeneous, then the compositional changes observed with the other coals indicate a chemical origin for the differences. If the trapped "mobile phase" is inhomogeneous, these data do not resolve the issue.

With gas chromatography, only a portion of the extracts is being studied. To rectify this and to bring another probe to bear, molecular weight distributions of the Wandoan and PSOC-1309 THF extracts before and after heat treatment were measured by gel permeation chromatography (GPC). The molecular weight distributions of the PSOC-1309 extracts were essentially the same for both original and preheated samples. There are no indication of any reactions occurring with this coal. Molecular weight distributions of the Wandoan extracts were slightly different. Average molecular weights of these samples measured by GPC are shown in Table III. The average molecular weight of the THF extract of Wandoan coal increased after heating at 250 °C, while those of PSOC-1309 were the same within experimental error (± 100 amu). Taken together with the decrease in the amount of Wandoan extract caused by heating, these data indicate the occurrence on condensation reactions at 250 °C in this coal.

One can only speculate on the origin of this chemistry. Cleavage of even benzylic ethers at 250 °C seems im-

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Table IV. Low Molecular Weight Aromatics Identified in Original and Pyrolyzed Illinois No. 6 Samples

peak no.	molecular ion or major fragment, ^a <i>m/z</i>	possible structure
1	106, 120	C ₂ - and C ₃ -benzene
2	128	2-methylnaphthalene
3	128	1-methylnaphthalene
4	142	C ₂ -naphthalene
5	168	methylbiphenyl
6	182	C ₂ -biphenyl
7	355 (100), 281 (62.5), 221 (44.5), 207 (77.0)	unknown
8	180	methylfluorene
9	178	phenanthrene
10	178	anthracene
11	194	C ₂ -fluorene
12	198	methyldibenzothiophene
13	355 (3.3), 281 (5.3), 223 (10.3), 207 (22.1), 149 (100)	unknown
14	192	methylphenanthrene
15	208	C ₃ -fluorene
16	202	pyrene
17	216	methylpyrene
18	228	benzo[α]anthracene
19	281 (2.0), 259 (3.3), 241 (1.2), 207 (8.7), 147 (14.6), 129 (100)	unknown
20	228	chrysene
21	279 (9.5), 207 (37.8), 167 (30.1), 149 (100)	unknown
22	412 (12.0), 397 (10.4), 384 (6.1), 369 (4.0), 281 (21.9), 207 (100)	alkyl pentacyclic hydroaromatics
23	440 (2.0), 339 (28.3), 281 (22.1), 207 (100)	alkyl pentacyclic hydroaromatics
24	429 (3.4), 415 (3.4), 289 (30.6), 281 (20.5), 207 (100)	unknown

^aNumbers in parentheses denote relative abundances of mass spectra.

probable, and the C-C and C-H bonds thought to be present in coals are quite stable at 250 °C but can react in chain processes in the presence of suitable initiators.³²⁻³⁴ The most likely origin is carboxylate pyrolysis, which has been associated with cross-linking reactions.³⁵

In order to clearly establish whether pyrolytic bond cleavages can occur in coals at 250 °C, portions of the extract from Illinois, No. 6 coal were heated to 250 °C. Clearly any size reduction or new compound formation must be chemical in origin, since physical entrapment is no longer possible.

The dried THF extract and a dried mixture of fractions A-3 and A-4 were heated at 250 °C for 24 h and fractionated into chemical classes as shown in Figure 1. Since high-molecular-weight aromatic compounds strongly adsorb on neutral alumina, they are not eluted by benzene but are found in the A-3 and A-4 fractions.³⁶ Figure 3 shows gas chromatograms of the A-2 (aromatics) fractions

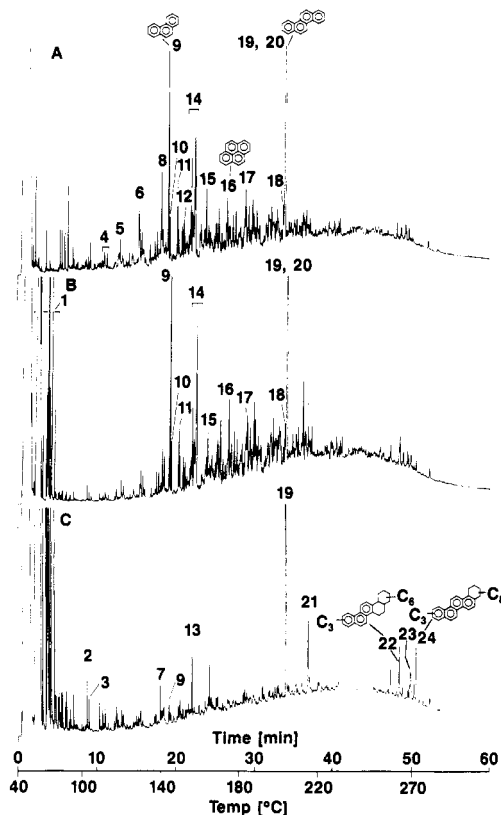


Figure 3. Gas chromatograms of the aromatic fractions (A-2) of the (A) original coal THF extract, (B) heat-treated THF extract, and (C) heat-treated A-3 and A-4 mixture for Illinois No. 6. Conditions were as in Figure 2. Peak assignments are listed in Table IV.

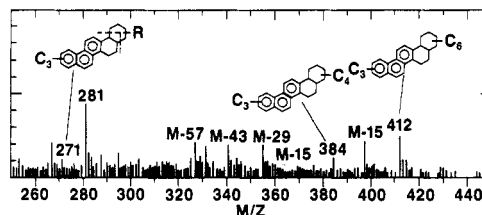


Figure 4. Mass spectrum of peak 22.

Table V. Weight Percent of Each Fraction from a THF Extract of an Original Illinois No. 6, a THF Extract of a Heated Illinois No. 6, and a Heated A-3 & A-4 Mixture of a THF Extract of an Original Illinois No. 6

fraction	A-3 & A-4			
	original coal	coal heated at 250 °C	mixture heated at 250 °C	nonheated A-3 & A-4 mixture
A-1	6.21	4.21	1.20	<0.1
A-2	2.61	1.40	0.50	<0.1
A-3	6.86	5.26	16.9	15.2
A-4	20.3	20.0	24.1	42.0

of these heat-treated samples as well as the A-2 fraction of the original coal extract. Significant amounts of material were found in fractions A-1 and A-2 after heating the extract fractions A-3 and A-4 to 250 °C for 24 h. Simply refractionating a mixture of A-3 and A-4 gave very little material in the A-1 and A-2 fractions (see Table V), so it is clear that the origin of the new compounds is pyrolysis. Furthermore, many new peaks are found in the chromatograms of these fractions. Clearly new compounds are present. Their origin could only be pyrolysis reactions occurring in a coal extract at 250 °C. Among the new compounds are a number of low molecular weight aromatic

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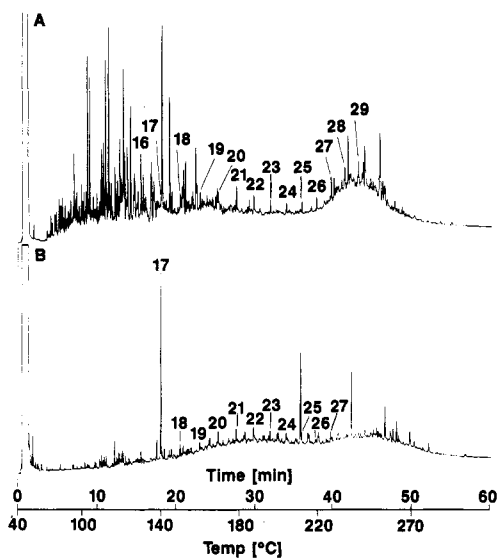


Figure 5. Gas chromatograms of the aliphatic fractions (A-1) of the (A) original coal THF extract and (B) heat-treated A-3 and A-4 mixture for Illinois No. 6. Conditions were as in Figure 2. Numbers denote the number of carbons of *n*-alkanes.

compounds such as alkylbenzenes, alkyl naphthalenes, phenanthrene, and alkyl hydroaromatic triterpanes, presumably formed by pyrolysis of the high molecular weight fractions. Figure 4 shows a mass spectrum which was tentatively identified as alkyl pentacyclic hydroaromatics.

The gas chromatograms of the A-1 fraction of the original coal extract and of heat-treated A-3 and A-4 mixtures are shown in Figure 5. The differences between the chromatograms demonstrate the occurrence of pyrolysis reactions.

We have shown that low molecular weight compounds are produced by very mild pyrolysis of some coal extracts. They were not physically trapped in the coal but are formed by decomposition of higher molecular weight compounds. While we have not demonstrated that the increase in extractability caused by mild heating of coals is due to pyrolyses, we have demonstrated that it *may be* due to pyrolysis in *some* coals. The relatively small molecules (a mobile phase) isolated after pyrolysis need not be present as clathrates inside cages in the macromolecular network (an immobile phase). Our data are clearly inconsistent with the claim that no coal pyrolysis occurs at temperatures below 350 °C.³⁷ Coal pyrolysis can begin at temperatures as low as 250 °C and is presumably continuous above that temperature. Unimolecular bond scission of single σ bonds is improbable at this temperature, and the low-temperature processes probably involve chain reactions and/or electrocyclic processes.

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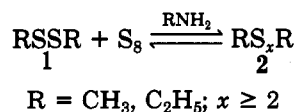
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Communications

Ultrasound-Assisted Regeneration of Sulfur Solvents Used in Sour Gas Production

Sir: Sulfur deposition in production tubulars has become a more common occurrence as higher H_2S containing natural gas reservoirs are developed.¹ These reservoirs are important new sources of elemental sulfur produced from H_2S by the Claus process. So-called supersour (>60% H_2S) gas reservoirs likely cannot be produced without use of a suitable solvent to dissolve elemental sulfur that is precipitated as the pressure and temperature along the production flowpath decrease.

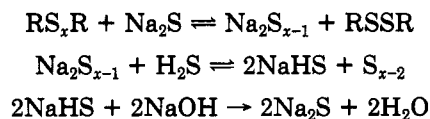
At present, when a well plugs with sulfur, dimethyl disulfide or a mixture of alkyl disulfides (1) is displaced down the well string. These materials react with sulfur in the presence of basic catalysts, producing liquid polysulfides that can be flowed from the well:



For sour gases containing <60% H_2S , the degree of sulfur plugging is such that it is uneconomic to recover the dialkyl polysulfides and regenerate the disulfides (1) for recycling. However, because supersour gases can carry and subsequently deposit large amounts of sulfur (15–75 kg 10^3 m of gas for 50–90% H_2S concentrations), it will be nec-

essary to circulate sulfur solvents on a continuous basis and regenerate the materials when they are close to sulfur saturation.

Regeneration. Previously,² we had developed a procedure for the regeneration of dialkyl polysulfides using aqueous sodium sulfide and related materials. The basic chemistry is



Industrially, the scheme has several advantages since it uses inexpensive chemicals, it produces salable sulfur as well as the disulfide, and it also forms excess sodium sulfide to overcome the inevitable process losses. However, the first stage, which requires efficient mixing of organic alkyl polysulfides with aqueous sodium sulfide, is difficult to accomplish industrially because these two materials are immiscible with one another. Mixing difficulties are compounded by the considerable density difference for the two fluids (1.5 M Na_2S (1.11 g/cm³) and $\text{CH}_3\text{S}_x\text{CH}_3$ (1.38 g/cm³), x = average of 5). Thus, commercially expensive tank mixers are required.

In the present study, a mixture of dimethyl polysulfides (dimethyl disulfide reacted with 100 wt % of sulfur) and

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