Coliquefaction of Waste Rubber Tires with Coal.

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Introduction

There is an interest in the conversion of coal to liquid fuels because of the abundant supply of coal and the diminishing reserves of petroleum. Standard coal liquefaction techniques utilize H_2 gas as a source of hydrogen to cap the radical species produced during liquefaction. Waste materials such as plastics, oils, and rubber tires with a high hydrogen content could be an alternative source of hydrogen that, in principle, could be transferred from the waste materials to the coal during liquefaction. An added benefit of such a program of waste material utilization would be a diminution in materials disposed of in landfills or incinerators.

Rubber tires are approximately one third by weight carbon black. Farcasiu and Smith have shown that carbon black increases yields in coal liquefaction.[1] Since carbon black is one of the top fifty chemicals produced in America during 1993 (3.22 billion pounds)[2] the recovery and reuse of carbon black from tires could become economically attractive. Giavarini has shown in recent work that carbon black could be reclaimed and activated to produce quality carbon blacks after pyrolyzing waste rubber tires.[3] Rubber tires also contain zinc oxide which is added as a filler and also aids in the vulcanization of the rubber.[4] The zinc oxide could play a role as a catalyst in liquefaction reactions. It could also decrease the amount of sulfur that ends up in the coal liquids.

Waste plastics contain many metals used for coloring, waste oils contain metals acquired while used as a lubricant, and waste rubber tires contain zinc. A past investigation suggested that coal undergoing liquefaction may act as a "scavenger" for heavy metals.[5] The ability of coal to trap metals will be discussed in the present paper.

Electron probe microanalysis (EPMA) is a technique which can map the dispersion of an element within a sample by the detection of characteristic X-rays.[6,7] Using EPMA, samples of the insoluble fraction produced by the coliquefaction experiments were analyzed to determine whether several heavy elements of interest were trapped in coal particles.

Experimental

Blind Canyon (Utah) coal (DECS-6, -60 mesh) was obtained from the Penn State Coal Sample Bank and ground under nitrogen to -100 mesh. Waste rubber tire samples were obtained (University of Utah waste material bank) that had been ground to -25 mesh. The catalyst, ammonium tetrathiomolybdate (Aldrich) was used to make an aqueous solution of molybdenum. The ground waste rubber tire and coal were mixed dry (40 % tire and 60 % coal, by weight) with different heavy metals (1 % by weight) (nickel acetylacetonate, vanadium oxide, manganese acetylacetonate, chromium acetylacetonate, and zinc oxide obtained from Strem and Aldrich) and then mixed with 1 % by weight molybdenum using the incipient wetness technique. The mixture was vacuum dried for 2 hours at 100° C. The dried mixture was placed in glass tubes and stoppered with glass wool. The glass tubes were placed in 35 cc tubing bombs, purged with nitrogen, and pressurized to 1000 psig H_2 (cold). Tubing bombs were placed in a fluidized sandbath held at 350° C. The tubing bombs were shaken at 160 rpm for one hour and removed. The tubing bombs were allowed to cool overnight while under pressure. Samples were removed and extracted with cyclohexane using a soxhlet extractor. Products soluble in cyclohexane were isolated using a rotary evaporator and then dried two hours under vacuum at 100° C. The insoluble sample (char/ash) was vacuum dried under similar conditions and then mixed with Petropoxy 154 (Pullman, Washington) and polished with a Syntron diamond paste polisher for eight hours. Micrographs were obtained using a CAMECA Model SX-50 electron microprobe (Courbevoie, France). Two different micrographs are presented: secondary electron images (SEM) and the characteristic X-ray micrograph for a specific element of interest (all micrographs shown are for a 50 μm x 50 μm field of view).

Results

Table 1 shows the percentage (by weight) of gas, cyclohexane solubles (oil), and char produced from coliquefaction of coal and tire samples. Percentages were calculated without including the weight of catalyst, weight of heavy metals added, and the ash weight of the coal (6.6 %). Also not included were the weight of carbon black, sulfur and zinc oxide in the tire sample that together constitute 35 % by weight of a rubber tire.

The oil yields indicate that the addition of zinc oxide and nickel acetylacetonate, in combination with the catalyst ammonium tetrathiomolybdate, have a positive effect on the oil yields. No effect is observed for samples doped with vanadium, manganese, and chromium.

Table 2 contains the elemental analysis of the Blind Canyon (DECS-6) Coal, and the trace analysis of heavy metals naturally found in the coal. EPMA is only sensitive to concentrations of approximately 200 ppm or greater. Therefore, metals in their natural abundance in the coal are undetectable by EPMA.

Table 3 shows an approximate percentage of the components of a tire. The zinc oxide is useful in the EPMA micrographs since it permits the operator to distinguish between tire particles and coal particles.

Figure 1 shows a variety of tire particles and coal particles from a sample that was doped with zinc oxide. The tire particles contain both sulfur and zinc which allows them to be easily distinguished by comparison of the sulfur and zinc micrographs. The particle in the upper right hand corner is a tire particle. Moving from the tire particle towards the lower left hand corner, a roughly circular coal particle can be observed in the sulfur micrograph. The coal particle contains less sulfur than the tire particles. In the zinc micrograph, the coal particle shows that some zinc is found in and around the edges of the coal particle. It appears as if the coal has scavenged some of the artificially added zinc during liquefaction.

Figure 2 shows a tire particle and a coal particle from a sample that has been doped with nickel acetylacetonate. The coal particle is distinguished in the left hand side of the sulfur micrograph and the tire particle in the right hand side of the sulfur micrograph. The nickel micrograph show an outline of nickel around the left hand side of the coal particle indicating the presence of nickel in the borders of the coal particle. Also interesting to note is the presence of zinc in the coal particle even though zinc was not added to this sample. The only source of zinc present is the tire. This further indicates that the coal could be acting as a scavenger for heavy metals.

Figure 3 shows a tire particle and a coal particle from a sample that has been doped with vanadium pentoxide. The coal particle makes up over half of the micrograph on the right hand side of the micrograph. The tire particle, observed in the left hand side of the micrograph, shows an increased sulfur density and is easily distinguished by the zinc abundance shown in the zinc micrograph. The vanadium micrograph shows that there is no evidence of vanadium in the coal particle.

Figure 4 shows a combination of tire particles and coal particles taken from a sample that was spiked with chromium acetylacetonate. The sulfur micrograph shows a coal particle at the center of the micrograph and three other coal particles surrounding the center particle at the 2, 3, and 6 o'clock positions. There are three tire particles. One tire particle is found in the upper right hand corner and the other two are found on the left hand side of the sulfur micrograph. The tire particles are easily distinguished from the coal particles by the presence of zinc observed in the zinc micrograph. The chromium micrograph shows an enhanced presence of chromium in all four coal particles.

Conclusion

Our experiments indicate that zinc oxide, nickel acetylacetonate, and chromium acetylacetonate are scavenged by coal particles during liquefaction. This scavenging effect could decrease the amount of heavy metals that end up in the derived liquids. Further work is needed to determine whether there is a decrease in the amount of zinc, nickel, and chromium found in the derived liquids.

The oil yields indicate an interesting effect arising from mixing zinc oxide or nickel acetylacetonate with the molybdenum catalyst. Further work is needed in order to determine the effect of these two metals on the type of liquids produced from liquefaction.

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References

1 Farcasiu, M.; Smith, C. Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem. 1991, **4**, 1869.

2 C & E News,1994, April 11, p. 13.

3 Giavarini, C. Fuel, 1985, **64**, 1331.

4 Krejsa, M.; Koenig, J. Rubber Chemistry and Technology, 1993, **66**, 377.

5 Sommerfeld, D.; Tuntawiroon, W.; Anderson, L.; Eyring, E. Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem. 1993, **38**, 211.

6 Newbury, D.; Fiori, C.; Marinenko, R.; Myklebust, R.; Swyt, C.; Bright, D. Anal. Chem., 1990, **62**, 1159A.

7 Newbury, D.; Fiori, C.; Marinenko, R.; Myklebust, R.; Swyt, C.; Bright, D. Anal. Chem., 1990, **62**, 1245A.

8 Pennsylvania State University Coal Research Section.

9 Farcasiu, M. Chemtech, 1993, Jan., 23.

Product Distribution of Coliquefaction

Table 1

Composition	Percentage of Gas	Percentage of Oil	Percentage of Char
Tire/Mo/Coal	8.0	35.1	56.9
Tire/Mo/Zn/Coal	5.9	39.0	55.1
Tire/Mo/Ni/Coal	5.7	38.3	56.0
Tire/Mo/V/Coal	5.5	29.5	65.0
Tire/Mo/Mn/Coal	5.7	27.8	66.5
Tire/Mo/Cr/Coal	5.4	27.6	67.0

Blind Canyon Coal Analysis

Table 2 [8]

Elemental Analysis	Percentage
Ash	6.67
Carbon	76.7
Hydrogen	5.80
Sulfur	0.37
Oxygen	9.43

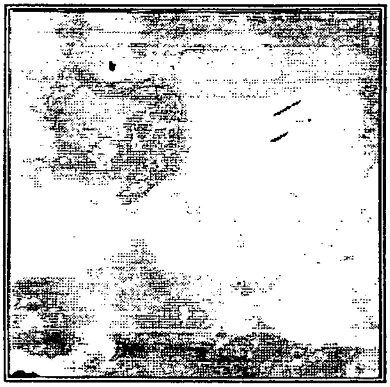
Trace Elements	ppm
Zinc	70
Nickel	25
Vanadium	140
Manganese	155
Chromium	95

Rubber Tire Tread Composition

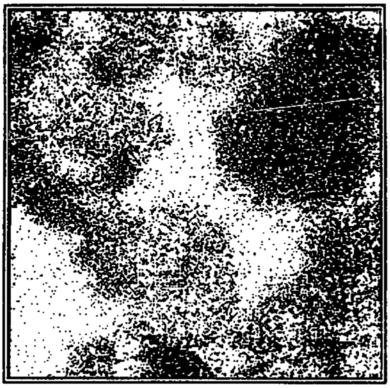
Table 3 [9]

Component	Percentage by weight
Styrene-Butadiene Rubber	35
Carbon Black	33
Aromatic Oil	20
cis-Polybutadiene	8.5
Sulfur	1
Zinc Oxide	1

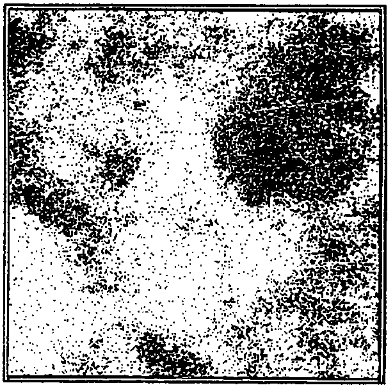
Figure 1
EPMA Micrograph
40 % waste rubber tire mixed with 60 % Blind Canyon DECS-6 by weight
Catalyst: 1 % ammonium tetrathiomolybdate
Doped with: 1 % zinc oxide
Hydrotreated for 1 hour at 350° C under 1000 psig hydrogen (cold)



Secondary Electron Image



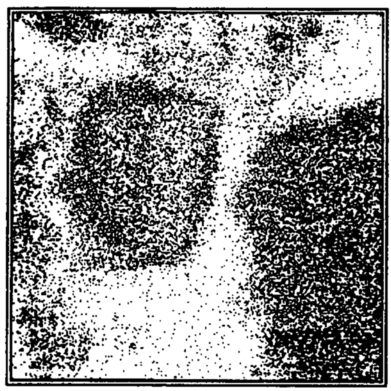
Sulfur K_{α}



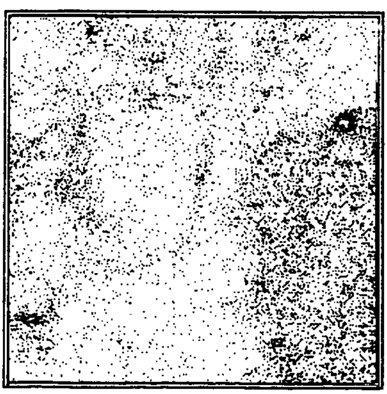
Zinc L_{α}

Figure 2
EPMA Micrograph
40 % waste rubber tire mixed with 60 % Blind Canyon DECS-6 by weight
Catalyst: 1 % ammonium tetrathiomolybdate
Doped with: 1 % nickel acetylacetonate
Hydrotreated for 1 hour at 350° C under 1000 psig hydrogen (cold)

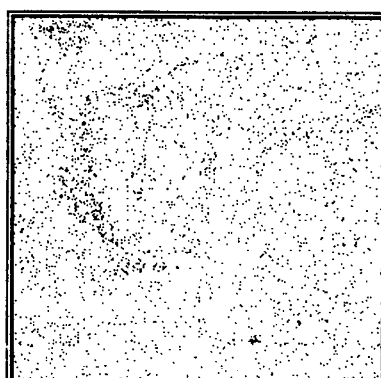
Secondary Electron Image



Sulfur K_α

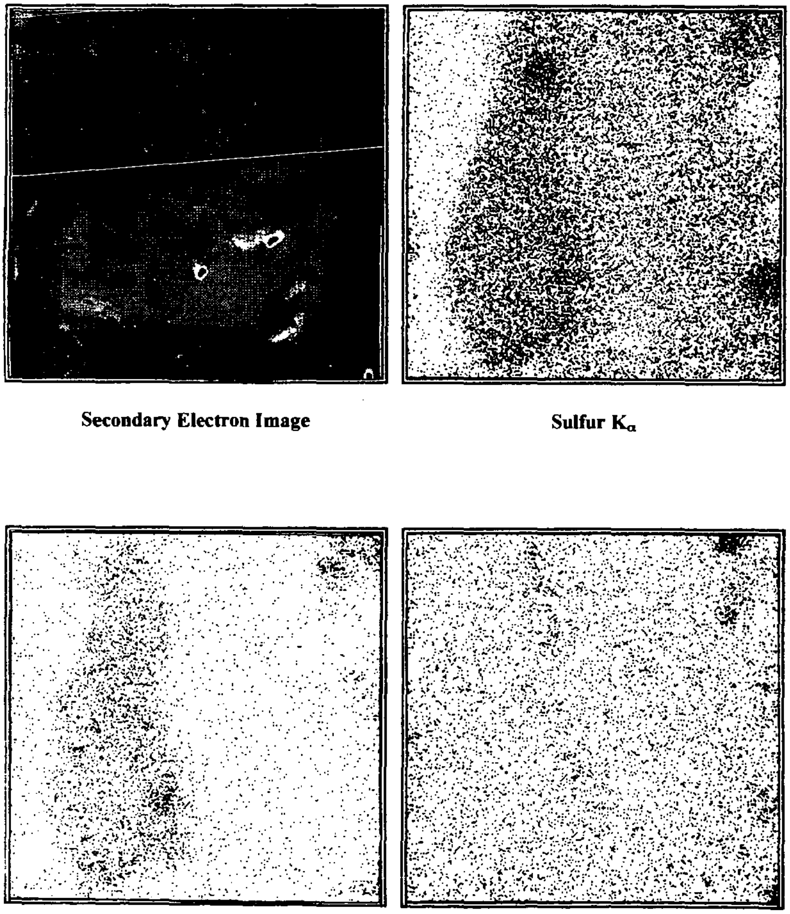


Zinc L_α



Nickel K_α

Figure 3
EPMA Micrograph
40 % waste rubber tire mixed with 60 % Blind Canyon DECS-6 by weight
Catalyst: 1 % ammonium tetrathiomolybdate
Doped with: 1 % vanadium pentoxide
Hydrotreated for 1 hour at 350° C under 1000 psig hydrogen (cold)

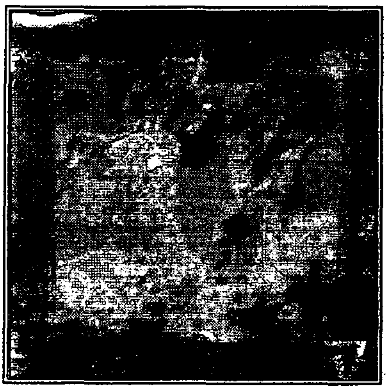


Secondary Electron Image **Sulfur K_α**

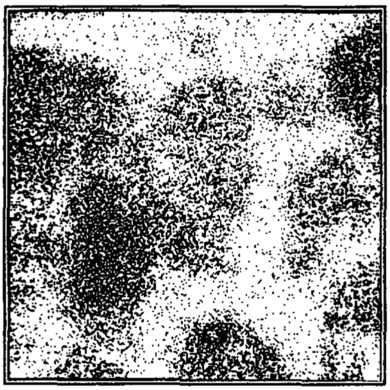
Zinc L_α **Vanadium K_α**

Figure 4
EPMA Micrograph

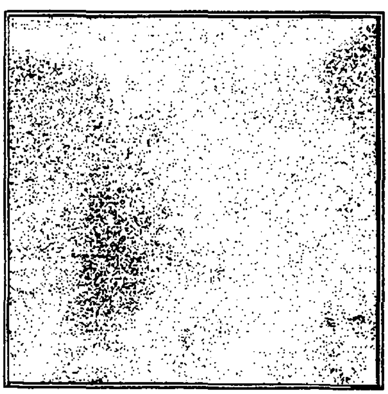
40 % waste rubber tire mixed with 60 % Blind Canyon DECS-6 by weight
Catalyst: 1 % ammonium tetrathiomolybdate
Doped with: 1 % chromium acetylacetonate
Hydrotreated for 1 hour at 350° C under 1000 psig hydrogen (cold)



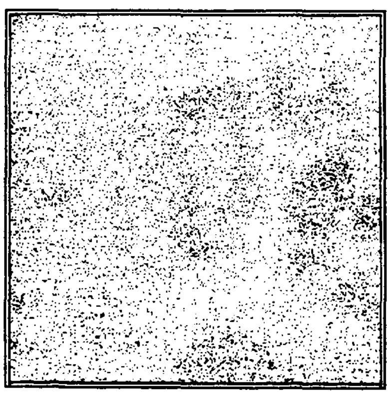
Secondary Electron Image



Sulfur K_α



Zinc L_α



Chromium K_α