

MICROSCALE SIMULATION OF HIGH PRESSURE THERMAL AND CATALYTIC CONVERSION PROCESSES IN COAL AND WASTE POLYMERS WITH ON-LINE GC/MS

Kui Liu, Emma Jakob, William H. McClennen and Henk L. C. Meuzelaar

Center for Micro Analysis and Reaction Chemistry
University of Utah, Salt Lake City, Utah 84112

Keywords:(on-line TG/GC/MS, coal, rubber, hydrolysis)

INTRODUCTION

Over 279 million automotive tires are discarded in the United States each year.¹ These used tires cause serious environmental problems since they are non-biodegradable, occupy considerable land-fill space, and emit noxious fumes when burned. One of the promising approaches to deal with used rubber is the co-processing of it with coal to produce hydrocarbon liquids for use as fuels and specialty chemicals. Recently there have been numerous studies on co-processing of tire rubber and coal since depolymerized rubber has good solvent properties and the carbon black which constitutes of about 20-30% of the rubber is a good catalyst for depolymerization and possibly enhanced coal liquefaction.^{2,3,4,5} Monitoring sample weight loss as a function of temperature with on-line analysis of the evolved products during the co-processing reactions is necessary to elucidate mechanisms and kinetics of the key conversion reactions. Due to the high pressure and high temperature required by some of the most interesting processes, it is difficult to continuously monitor the weight loss and reaction intermediates without interrupting the reactions.

On-line analysis techniques for high pressure conversion reactions have been reported previously,^{6,7} but these systems did not monitor total weight loss vs reaction temperature. They also were not applied directly to coal conversion studies because of the strong potential for plugging of sample orifices with pulverized coal.

Microscale simulation of coal conversion reactions has been performed by high pressure thermogravimetry with on-line combined gas chromatography and mass spectrometry (TG/GC/MS). It requires only a small sample size and can be operated at high temperature and pressure. The weight loss and low molecular weight products can be monitored vs reaction temperature. Analysis of pyrolysis and hydrolysis of coal, rubber and coal with tire rubber, with or without catalyst, by high pressure TG/GC/MS are reported here.

EXPERIMENTAL

High Pressure TG with On-Line GC/MS

The system as shown in Figure 1 consists of the high pressure TG instrument, pressure reduction line, vapor sampling inlet, short GC column and MS detector. A Cahn high pressure TG-151 was used as the reactor. The reactor vessel was made from a quartz tube which is corrosion resistant and has no known catalytic effect on the reaction. This reactor can be operated up to 1000 psi with temperatures up to 1000 C and heating rates ranging

from 0 to 25 C/min. The experiments in this study were operated at 900 psi with a heating rate of 10 C/min up to 600 C followed by a 10 min hold of the final temperature. The reagent gas was either helium or hydrogen. The quartz crucible used for holding the sample was modified as shown in Figure 1. The modified crucible with an open hole at the bottom greatly increased the sensitivity of the GC/MS detection since the vapor products go directly into the quartz sampling tube, which reduced the amount of sample necessary. The coal and tire rubber used were 60 mg each. The pressure of the reactor was kept constant by a back pressure regulator. During operation the reagent gas is flowing continuously through the reactor at 500 ml/min (ambient). A 1 m x 50 μ m i.d. fused silica capillary is used as a pressure reduction line, which carries vapor products to the ambient pressure sampling device. A novel automated vapor sampling (AVS) inlet developed at the University of Utah (U.S. Patent No. 4,970,905), provides automated, repetitive vapor sampling for the GC column. Samples were taken each 73 seconds. The AVS inlet was connected directly to a 2m x 150 μ m i.d. fused silica capillary column coated with methyl silicone (CP-SIL-5CB). The short column was operated isothermally at 90 C and provided rapid separation of the vapor products. The separated products were detected by a small quadruple MS system, the Hewlett Packard model 5971A MSD operating at 70 eV electron energy.

Materials

Blind Canyon (DEC-6), Utah coal (-100 mesh) from the Penn State sample bank was employed in this study. The proximate analysis of the coal is listed in Table I. The experimental procedure for impregnating coal with catalyst is described by Anderson et al.⁸ The catalyst used in the experiments was 1% Fe as iron chloride hexahydrate [$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$] promoted with 0.05% Mo as ammonium tetrathiomolybdate [$(\text{NH}_4)_2\text{MoS}_4$]. The used tire rubber was scraped, cut into small pieces and then ground into fine particles in a cryogenic grinder with liquid nitrogen. The weight ratio of coal to rubber for the mixture was 1:1.

RESULTS AND DISCUSSION

The thermal decomposition of Blind Canyon coal, tire rubber and the mixture of coal and rubber was studied at high pressure under various conditions as seen in Table II. The thermogravimetric profiles are shown in Figure 2 indicating the different course of decomposition of the samples. The complex structure of coal resulted in continuous volatile product evolution up to the final temperature of the experiment (600 C) whereas the flat weight curves of rubber above 500 C suggest that only the relatively inert carbon black and inorganic filling are left and the organic components have been completely devolatilized. Although the volatile evolution of rubber is shifted to somewhat lower temperature in hydrogen atmosphere, the TG profile similarity in helium and hydrogen atmospheres is apparently due to the high inherent hydrogen content of rubber. The effect of hydrogen is clearly visible in the coal decomposition, where a significant increase in volatile product evolution can be observed above 500 C. Adding liquefaction catalyst to the coal and coal + rubber samples increases the total weight loss (Table II) by about 3-4% and the volatile evolution occurs at lower temperature. The effect of rubber on the coal decomposition is not apparent solely by looking at the thermogravimetric results.

Figure 3 shows the average mass spectra of the volatiles evolved from 350 to 600 C from coal and rubber as well as coal + rubber with and without catalyst in hydrogen

atmosphere. The spectrum of the high volatile bituminous coal is dominated by alkene (m/z 41, 55, 69, 83, etc.), and alkane (m/z 43, 57, 71, 85, etc.) fragment ion series as well as aromatic hydrocarbons (m/z 78, benzene; m/z 91, toluene fragment) and phenols (m/z 94, phenol; m/z 107, cresol fragment). The rubber spectrum shows the formation of unsaturated hydrocarbon ions from the butadiene segments of rubber (e.g., m/z 67, methyl butadiene fragment) and aromatic hydrocarbons originating from the styrene moieties (e.g., m/z 91, toluene fragment; m/z 104, styrene). It should be noted that the oil additive of rubber may also release aromatic products. The spectra of the coal + rubber mixture (ratio 1:1) resemble the rubber spectrum at first sight because the rubber releases higher amounts of organic volatiles than the coal. The evaluation of average mass spectra is further complicated by the formation of several common products from coal and rubber (e.g., alkyl aromatics and alkenes). In spite of these difficulties it can be seen that the intensity of several ions is not additive and the presence of catalyst changes the product distribution. More detailed information can be obtained about the effect, of the rubber and catalyst on the coal hydrolysis by using the time resolved data.

As discussed in the experimental section, samples were taken every 1.22 minutes from the volatiles evolved from the TG furnace and analyzed by MS after separation on a short GC column. The total ion intensity profile of coal obtained by this method can be seen in Figure 4a indicating that the maximum rate of decomposition occurs at 480 C. Enlarging one sampling period, the total ion curve shows the separation of several compounds within the 1.22 min interval (Figure 4b). Although the resolution is insufficient in the low MW range due to the relatively high column temperature (90 C), the extracted single ion chromatograms can be used for further analysis. Figures 4c and d show the abundance of characteristic alkene (m/z 55) and alkane (m/z 57) fragment ions revealing the increase of alkene/alkane ratio with decreasing carbon atom number. The intensity profile of a typical alkyl phenol fragment ion (m/z 107) indicates (Figure 4c) that not only different MW compounds (cresol vs. xylcnol), but certain isomers (ethyl phenol vs. dimethyl phenol) can be separated on the short column.

The hydrolysis of tire rubber results in the formation of a large variety of products, as shown by the total ion current profile in Figure 5a. Figures 5b, c and d display the intensity profiles of three ions representing the three types of products. The butadiene segment of rubber releases primarily butene (m/z 56), exceeding the yield of butadiene, apparently due to the hydrogen atmosphere and high pressure applied. Styrene (m/z 104) is the major product of the polystyrene segments. Various alkyl, alkenyl, alkydicyl benzenes are released containing both building elements of the rubber polymer; m/z 117 (C_3H_5 -benzene) represents a characteristic alkenyl benzene fragment ion in Figure 5d. M/z 104 ion is formed from several compounds beside styrene (Figure 5c). The evolution of styrene starts at lower temperature than the formation of other alkenyl benzenes as shown by the intensity profile of m/z 104 expanded to the whole temperature range in Figure 5c. Although the simple thermogravimetric curve does not reveal the complex reaction route, the different evolution profiles of products suggest a multiple step decomposition mechanism.

The most important products of the thermal decomposition of Blind Canyon coal were presented above. The next Figure (Figure 6) shows the effect of hydrogen reactant gas and a liquefaction catalyst on the evolution profiles of four characteristic products of coal. The TG curve of coal (Figure 2) exhibits two main decomposition regions in hydrogen atmosphere (350-520 C and above 520 C). The rate of volatile evolution up to 520 C is similar in

hydrogen and helium suggesting that hydrogen does not promote the devolatilization significantly in this temperature range. This assumption is confirmed by the intensity profiles of the individual ions in Figure 6. Although there are some variations in the evolution curves the overall difference does not seem to be significant in the lower temperature range. However, the formation of alkyl aromatic products (m/z 92, toluene and m/z 142, methyl naphthalene) is greatly enhanced at high temperature in hydrogen atmosphere. The liquefaction catalyst applied in hydrogen atmosphere increases the yield of each product. Some increase is observed in the high temperature release of alkyl aromatics in comparison with the uncatalyzed coal experiment in hydrogen. Furthermore, the catalyst promotes the formation of alkanes (m/z 43 propyl fragment of C_3-C_9 alkanes) and phenol (m/z 94) as well as methyl naphthalene at lower temperatures.

The mixture of coal and tire rubber (ratio 1:1) was used for simulation of their co-processing under high pressure in hydrogen atmosphere. Figure 7 compares the evolution profiles of m/z 92 and m/z 94 from coal, rubber and the mixture. The absolute intensities cannot be evaluated due to the different experimental conditions; therefore the intensities are scaled for equal height. The toluene evolution profile of the mixture (Figure 7a) appears to be the sum of the individual components. Other hydrocarbons exhibit similar behavior, however, it should be emphasized that this is not a quantitative comparison.

The spectra of both coal and rubber contain the m/z 94 ion, however, it represents two different compounds, phenol and heptatriene, respectively. Due to the chromatographic separation, the intensity profile of each product can be monitored separately in the mixture, as seen in Figure 7b. The heptatriene evolution occurs at about the same temperature from the rubber and the mixture. The rate of phenol formation from coal shows two maxima in hydrogen atmosphere (at about 450 C and 550 C). The presence of rubber significantly promotes the release of phenol in the lower temperature range (350-520 C).

CONCLUSIONS

Simulation of thermal and catalytic coal conversion processes was carried out in inert helium vs hydrogen atmospheres using a high pressure thermobalance coupled on-line to a GC/MS. The weight loss curves and the intensity profiles of products show that the volatile evolution of Blind Canyon coal significantly increases above 500 C in hydrogen atmosphere in comparison with helium due to the release of alkyl benzenes and alkyl naphthalenes. The Fe, Mo liquefaction catalyst increases not only the yield of alkyl aromatics, but enhances the formation of aliphatic hydrocarbons and phenols in the lower temperature range (350-520 C).

The presence of tire rubber appears to promote the phenol formation at 350-520 C, but the evolution profiles of other products seems to be additive in the mixture of coal and rubber. However, further experiments are required to reveal the effect of rubber on the yield of the individual products of coal.

ACKNOWLEDGEMENTS

We would like to thank Professor Larry L. Anderson and W. Tuntawiroon (University of Utah) for providing us with the samples of catalyst impregnated coal. We also acknowledge the U.S. Department of Energy through the Consortium for Fossil Fuel Liquefaction Science and the State of Utah who financially supported this research.

REFERENCES

1. Hearing before the Subcommittee on Environment and labor and Subcommittee on Regulation, Business Opportunities and Energy of the Committee on Small Business: House of Representatives, April 18, 1990. *Scrap Tire Management and Recycling Opportunities*, Serial No.101-52.
2. Farcasiu, M.; Smith, C. M. *Fuel Chem. Preprints. Am. Chem. Soc.* 35 (1990), 404.
3. Farcasiu, M.; Smith, C. M.; Hunter, E. A. *Proc. 1991 Conference on Coal Science*, IEA Coal Research Ltd. (Ed.), Butterworth: Heinemann Ltd., 1991, p. 166.
4. Farcasiu, M.; Smith, C.M. *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem.* 37 (1992), 472.
5. Farcasiu, M. *Chem TECH*, January (1993), 22.
6. Huai, H.; Tsai, C.H.; Shabtai, J.S.; Meuzelaar, H.L.C., *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem.* 37 (1992), 925.
7. Dworzanski, J.P.; Chapman, J.N.; Meuzelaar, H.L.C., *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem.* 37 (1992), 424.
8. Anderson, L.L.; Yuen, W.H.; Jaturapitornsakul, J., *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem.* 38 (1993), 142.

Table I. Proximate Analysis of Blind Canyon (DEC-6) Coal

	as received
Moisture (wt.%)	4.73
Volatile matter (wt.%)	42.40
Fixed carbon (wt.%)	47.31
Ash (wt.%)	5.56

Table II. Weight Loss Data from High Pressure TG

	Fe, Mo Catalyst	Reactant Gas	Weight Loss, %
Coal	No	He	36.6
Coal	No	H ₂	54.7
Coal	Yes	H ₂	57.9
Rubber	No	He	66.6
Rubber	No	H ₂	67.5
Coal + Rubber	No	H ₂	57.7
Coal + Rubber	Yes	H ₂	61.8

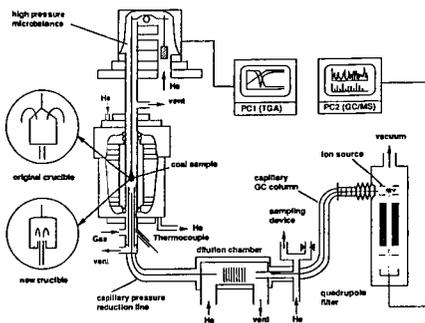


Figure 1. Schematic of the TG/GC/MS system.

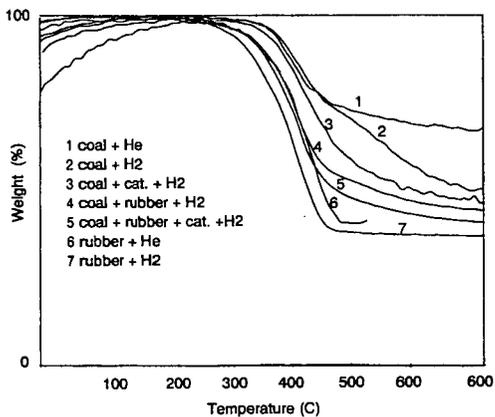


Figure 2. TG curves of coal and rubber under various conditions at high pressure (900 psi).

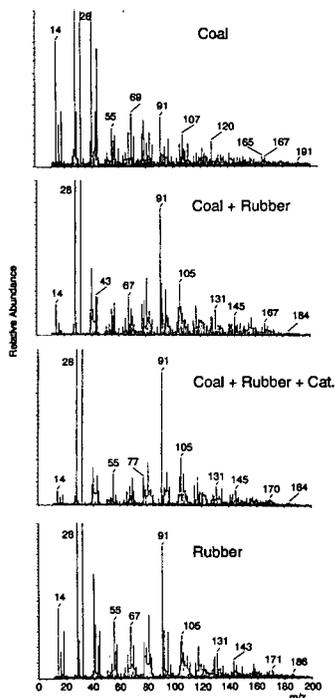


Figure 3. Average mass spectra of hydrolysis products of coal, rubber and coal + rubber with and without catalyst from 350 C to 600 C. (m/z 14, 28, 32, 40 are background peaks.)

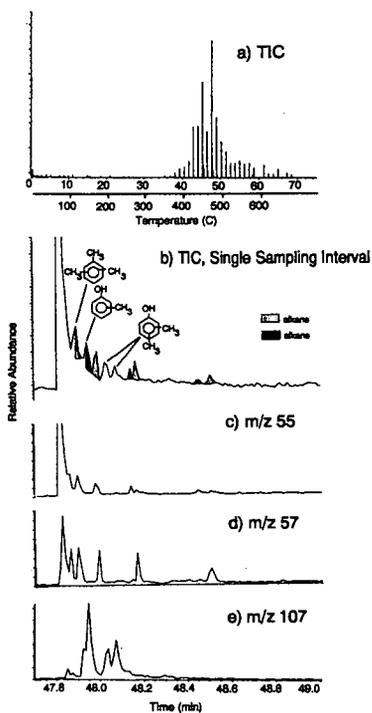


Figure 4. Thermal decomposition of coal in helium atmosphere. a) Total ion intensity; b) in a single sampling interval. Ion intensity of c) m/z 55, alkene; d) m/z 57, alkane; e) m/z 107, cresol fragment.

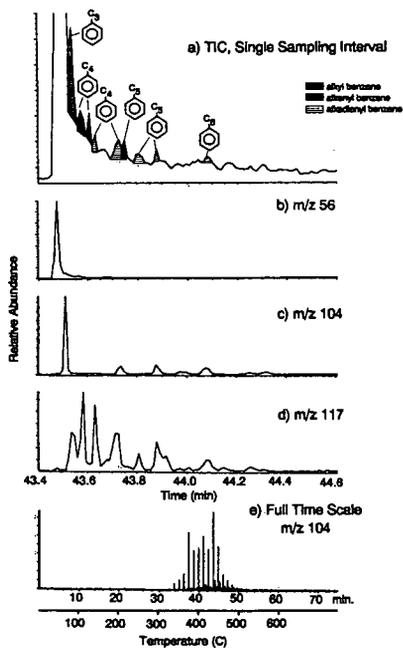


Figure 5. Decomposition of rubber in hydrogen atmosphere. a) Total ion intensity; ion intensity of b) m/z 56, butene; c) m/z 104, styrene; d) m/z 117, C_3H_4 -benzene fragment; e) m/z 104 in the whole temperature range.

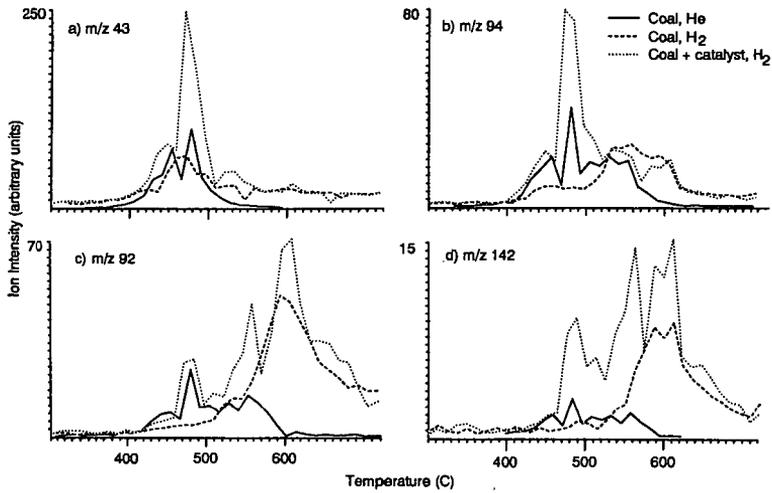


Figure 6. Effect of hydrogen and catalyst on evolution profile of coal decomposition products. a) m/z 43, propyl fragment, b) m/z 94, phenol; c) m/z 92, toluene; d) m/z 142 methyl naphthalene.

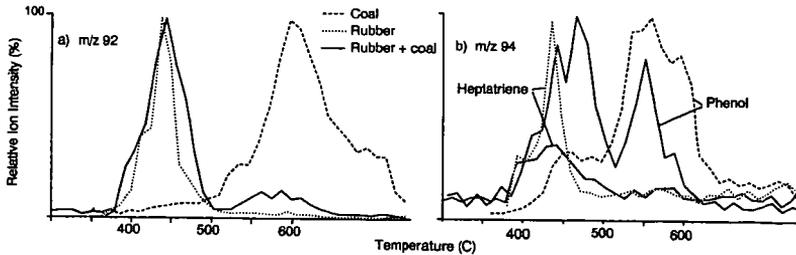


Figure 7. Evolution profile of a) m/z 92, toluene; b) m/z 94, phenol and heptatriene from the hydrolysis of coal, rubber and the mixture of coal and rubber.