

STUDIES OF THERMAL AND CATALYTIC HYDROLIQUEFACTION OF MODEL COMPOUNDS, WASTE POLYMERS AND COAL BY HIGH PRESSURE TG/GC/MS

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INTRODUCTION

A recently developed on-line high pressure thermogravimetry (TG)/gas chromatography (GC)/mass spectrometry (MS) system [1] provides certain advantages over other on-line analysis techniques for high pressure reactors reported previously [2,3]. The high pressure TG/GC/MS system enables the simulation of solvent-free thermal and catalytic reactions for polymers and coal. During the reactions the total weight change is monitored and the volatile intermediate products are identified. It requires only very small amounts (10-100 mg) of sample and can be operated at high pressure under different atmospheres (N_2 , He, H_2 , etc.). Current efforts to recycle lower grade postconsumer polymers such as colored polyethylene and polystyrene or used rubber tires, are concentrated on co-processing with coal [4-6]. Purely thermal degradation processes involve both decomposition and condensation (recombination) reactions and the resulting product is highly olefinic and often aromatic. In order to improve the yield and selectivity of the process, a great deal of effort has been spent on finding the proper catalysts. Catalysts selected for the present studies include ZrO_2/SO_4^{2-} , $(NH_4)_2MoS_4$ and carbon black. Carbon black present in waste rubber tires has been reported to be very selective for the cleavage of specific alkylaryl bonds [7]. $(NH_4)_2MoS_4$ has been shown to improve the liquid yields in coal liquefaction [8]. The superacid catalyst Zr_2O_7/SO_4^{2-} possesses markedly higher hydrogenolytic activity compared to that of conventional SiO_2 -supported soluble Fe salts [9].

EXPERIMENTAL

Experiments with a styrene-butadiene rubber (SBR; nonvulcanized) sample in the presence of various catalysts (carbon black, $(NH_4)_2MoS_4$ and ZrO_2/SO_4^{2-}) and coprocessing runs of coal and polymers (polyethylene, polystyrene, waste rubber tire, commingled plastic mixture) were conducted in a high pressure TG/GC/MS system at a hydrogen pressure of 900 psi. The experimental procedure and schematic of the equipment were described in detail in a previous paper [1]. The styrene-butadiene rubber (SBR) (30% polystyrene, 20 mesh), polystyrene (MW 45000, -100 mesh), polyethylene, carbon black (Black Pearl 2000) and $(NH_4)_2MoS_4$ were obtained from Aldrich Chemical Company. The superacid catalyst ZrO_2/SO_4^{2-} was prepared as reported by Shabtai et al. [9]. In the case of commingled postconsumer plastic, the plastic bottles and containers were washed to remove contaminants and labels before sizing and shaving. Final size reduction was done by grinding in a K-TEC kitchen mill. A high volatile bituminous coal (DECS-6, Blind Canyon, Utah, obtained from the Penn State Coal Sample Bank) was used in a 1:1 mixture ratio with both model and waste polymers.

RESULTS AND DISCUSSION

The thermal and catalytic reactions of a styrene-butadiene rubber (SBR) polymer as a model compound of rubber tire were studied in a high pressure thermobalance at a hydrogen pressure of 900 psig. As shown by the weight loss profiles in Figure 1, the 10% superacid ZrO_2/SO_4^{2-} catalyst added has little influence upon the rate of decomposition of SBR polymer at a constant heating rate of 10 C/min. However, when the same sample is subjected to a different temperature program using a heating rate of 10 C/min up to 370 C and then kept under isothermal conditions for one hour before being heated up to 500 C at 10 C/min, the effect of the catalyst on the rate of decomposition of SBR polymer is clearly observed (Figure 2). The catalyst greatly increases the rate of degradation of the polymer at 370 C. The results suggest that at a constant heating rate the reactions are dominated by thermal processes so the catalyst effect is not observed. However, the difference between catalytic and thermal processes is brought out effectively at a relatively low isothermal temperature level (e.g., 370 C) chosen to minimize the contribution of thermal reactions.

In addition, the catalytic reactions of SBR with other catalyst types, viz. carbon black and $(NH_4)_2MoS_4$ were studied. In order to compensate for the poor contact between the powdered catalyst and SBR, 10% of catalyst was added to the polymer samples. Comparison of the thermogravimetric curves (Figure 2) shows that the ZrO_2/SO_4^{2-} catalyst increases the weight loss by about 17% at 370 C whereas carbon black and $(NH_4)_2MoS_4$ have no measurable effect on the overall rate of SBR decomposition. As discussed in the literature [9], the ZrO_2/SO_4^{2-} catalyst

causes primarily hydrogenolytic bond cleavage resulting in more weight loss whereas the mild bifunctional catalyst, $(\text{NH}_4)_2\text{MoS}_4$, appears to be ineffective in bond-cleavage reactions. Indeed at the relatively low temperature of 300 C, this catalyst has been found to have little effect on liquids production [8]. The temperature applied in our isothermal experiments is somewhat higher, but the reaction severity is mild due to the very short residence time of the reactants (estimated to be about 15 sec).

Several main product evolution profiles of SBR with various catalysts are shown in Figure 3. The production of benzene is significantly promoted by the $\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst indicating that the solid superacid catalyst has very strong hydrogenolysis activity for α -alkyl-arene bond cleavage. The catalyst contains both the Bronsted acid and the Lewis acid sites [10]. The Bronsted acid sites protonate the aromatic ring and the subsequent α -cleavage results in the formation of benzene and aliphatic compounds. These findings are in agreement with the observation of Shabtai et al. [9] that the $\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst is very effective in the hydrogenolytic α -cleavage of 1,2-dinaphthylethane. The presence of Bronsted acid sites also promotes trans-alkylation reactions between alkylbenzenes and styrene as evidenced by the increased evolution of isomeric methylstyrenes (Figure 3b), ethylstyrene and benzene. The increased yield of styrene (Figure 3c) and α -methylstyrene can be explained by the parallel Lewis acid functionality character of the catalyst. When the Lewis acid sites abstract hydride ions from the benzylic carbons, benzylic carbonium ions are formed. Subsequently, styrene and α -methylstyrene are formed by β -scission of the benzylic carbonium ion. Mild hydrogenation activity of the $\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst was indicated by the increased yield of saturated products such as ethyl benzene (Figure 3d) and isopropylbenzene.

Although, the $(\text{NH}_4)_2\text{MoS}_4$ catalyst does not affect the overall rate of decomposition significantly, some changes in the product composition are observed. The $(\text{NH}_4)_2\text{MoS}_4$ catalyst behaves as a bifunctional catalyst, showing both ring hydrogenation (more ethylbenzene (Figure 3d) and isopropyl benzene) and hydrogenolysis (more styrene (Figure 3c) and α -methylstyrene (Figure 3b)) activity. Carbon black does not produce a measurable effect at 370 C, but at temperatures above 400 C it has some ring hydrogenation activity as indicated by the higher yield of saturated products (ethylbenzene (Figure 3d) and isopropylbenzene).

Experiments on the thermal (non-catalytic) decomposition of Blind Canyon DECS-6 coal, waste rubber tire, commingled plastic, polyethylene and polystyrene samples were performed at a hydrogen pressure of 900 psi with a linear heating rate of 10 C/min. The weight loss profiles are shown in Figure 4. The TG curves indicate the different course of decomposition the various samples. Coal continues to lose weight due to pyrolysis and char gasification at temperatures up to 600 C. The high (33%) rubber residue must be mainly due to the presence of carbon black. The post-consumer plastic and polyethylene samples follow a similar weight loss course except for a slightly higher decomposition temperature and residue yield of the waste plastic. This is in agreement with the fact that polyethylene represents the main constituent of the commingled plastic. Polystyrene, on the other hand, decomposes at relatively low temperatures.

Co-processing runs of coal with waste rubber tire, commingled waste plastic, polyethylene and polystyrene (ratio 1:1) were carried out at a constant heating rate of 10 C/min under 900 psi hydrogen pressure. Figure 5 shows the TG curves of coal and polystyrene as an example of non-catalytic co-processing. The dotted line is the predicted weight loss curve of the mixture, which is the linear sum of their individual components. The mixtures of coal with the various polymers studied all show approximately additive rate and yield behavior when applying a 10 C/min heating rate. Because of the continuous temperature rise unimolecular decomposition reactions prevail and the total weight loss is primarily controlled by the thermal behavior of the individual components. However, when using a suitable isothermal procedure, as described previously for studying the catalytic effect, both the TG and GC/MS profiles indicate a strong interaction between the coal and the polystyrene (Figure 6). The weight loss of the mixture is increased compared to the predicted value at 370 C (Figure 6a). The results are confirmed by the total product evolution profiles. The coal has lost about 18% weight at the end of the 370 C period but volatile products are not detectable by MS due to their low intensity. Therefore, the total ion chromatogram is not shown in Figure 6. The yield of the volatile polystyrene products detectable at 370 C can be seen in the total ion chromatogram (TIC) in Figure 6b. Since the polystyrene is not yet completely degraded after 60 mins at 370 C, the remaining polystyrene reacts further when the temperature is increased, resulting in additional product evolution at temperatures above 400 C. The total ion chromatogram of the mixture (Figure 6c) shows that the products are formed mostly during the isothermal period. The strong interaction between coal and polystyrene may be due to some extent to the mineral matter in the coal acting as a catalyst and accelerating the decomposition of the polystyrene. Seehra et al. [11] studied mixtures of coal with polymers such as polystyrene, polyethylene and rubber tire by ESR techniques and reported that free radical concentrations are increased when mixing coal with polystyrene and polyethylene. This may well be due to the occurrence of interactions between

the feed components (or their intermediate products). The possible occurrence of these reactions can be another explanation for the increased weight loss of the mixture.

CONCLUSIONS

Isothermal runs at relatively low temperature (370 C) are found to be effective in bringing out differences between catalytic and thermal processes, whereas at linear heating rates of 10 C - 20 C/min thermal reactions overwhelm the catalytic effect.

The ZrO_2/SO_4^{2-} superacid catalyst possesses high hydrogenolytic activity and causes a strongly increased rate of decomposition of SBR polymer at 370 C. The $(NH_4)_2MoS_4$ catalyst exhibits some ring hydrogenation activity at 370 C. Carbon black, on the other hand, has no measurable effect at 370 C, but shows some hydrogenation activity above 400 C.

Under thermally controlled (non-catalytic) conditions, mixtures of coal and polymers behave at first approximation in an additive manner. However, at lower temperatures, a synergistic effect is observed for polystyrene/coal mixtures.

High pressure TG/GC/MS is demonstrated to be a viable and useful technique for studying at a molecular level the effects of catalysts and blending under simulated process conditions, thus providing insight into the underlying reaction mechanisms.

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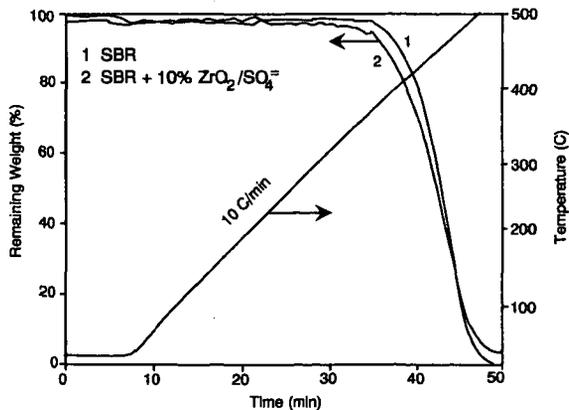


Figure 1. TG curves of SBR polymer at 900 psig (H₂).

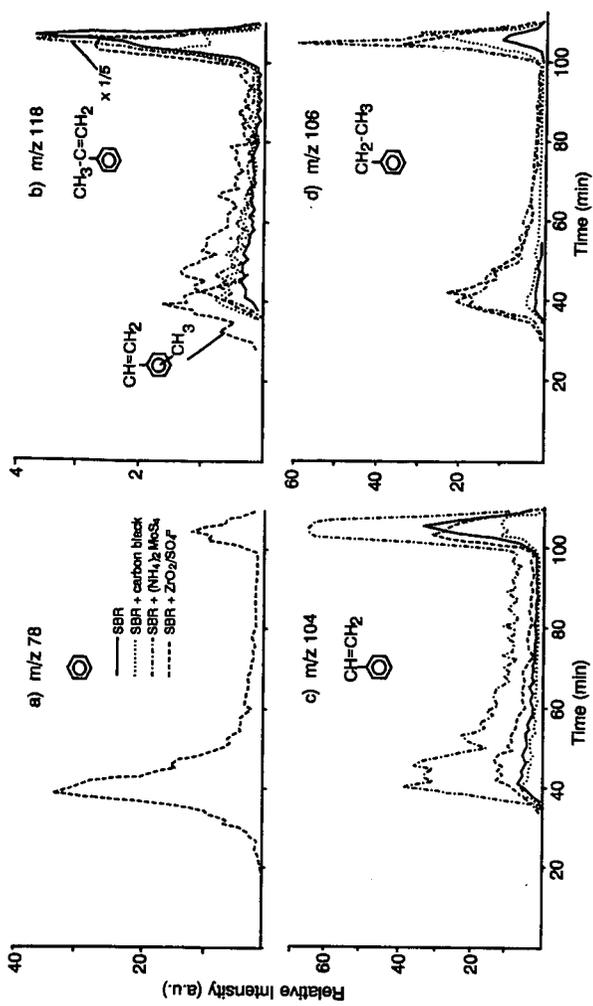


Figure 3. Effect of catalysts on evolution profiles of SBR polymer decomposition products. a) m/z 78, benzene; b) m/z 118, methylstyrene; c) m/z 104, styrene; and d) m/z 106 ethylbenzene.

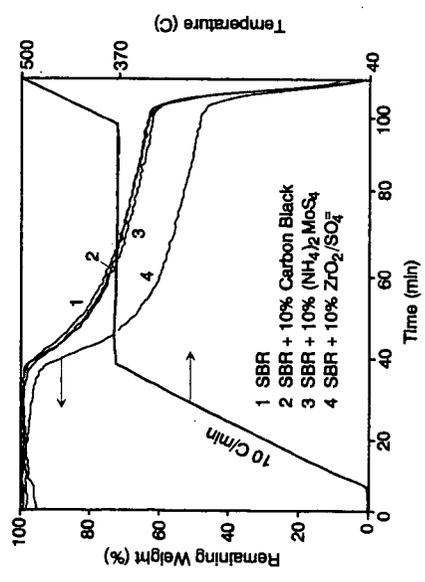


Figure 2. TG curves of SBR polymer with various catalysts at 900 psig (H_2).

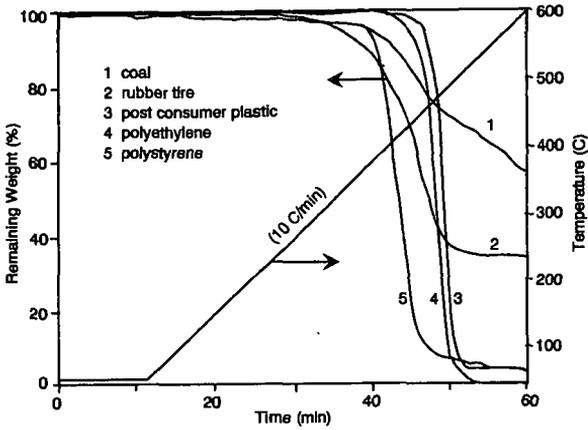


Figure 4. TG curves of various polymers at 900 psig (H_2).

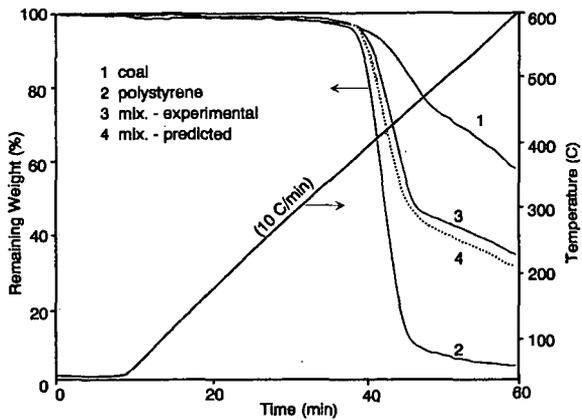


Figure 5. TG curves of coal and polystyrene at 900 psig (H_2).

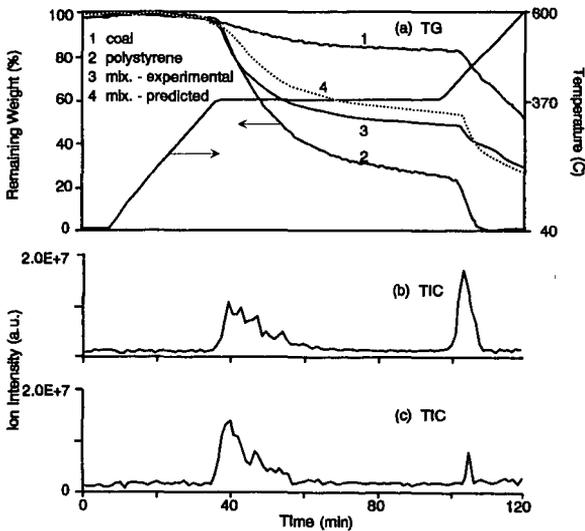


Figure 6. Effect of blending on coprocessing of coal and polystyrene at 900 psig (H_2). a) TG curves; b) total ion intensity profile of polystyrene; c) total ion intensity profile of coal and polystyrene.