

CO-LIQUEFACTION OF COAL AND POLYVINYL CHLORIDE (PVC)

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INTRODUCTION

The use of waste plastics as co-liquefaction agents for direct coal liquefaction (DCL) is being explored. Co-liquefaction of waste plastics with coal serves the aim of producing alternative fuels and effectively utilizing waste plastics¹. PVC is a plastic that is discarded heavily. However, there has been very limited study done on the liquefaction of PVC because it releases corrosive HCl into the gaseous phase, and various chlorinated organics into the liquid phase, at liquefaction temperatures (350-450°C).² A recent study showed that the vacuum pyrolysis of PVC at 500 °C resulted in an HCl-gas yield of 53%.³ Benzene is one of the main minor products.³

Ferric sulfide (Fe₂S₃) has been observed to behave as a good "once-through" catalyst for DCL.³ The addition of another metal, such as magnesium, to the Fe₂S₃ catalyst can enhance its activity. A mixed-metal ferric-sulfide-based Mg-Fe-S catalyst is used in this study for improving the yields as well as possibly capturing chlorine from the products of liquefaction into the residue.

In this paper, the effects of reaction parameters, i.e., temperature, time, hydrogen pressure, and the catalyst on PVC liquefaction, coal liquefaction, co-liquefaction of coal and PVC are presented. Distribution of chlorine among the liquefaction products for the non-catalytic/catalytic liquefaction runs is also presented. The effect of the catalyst on the chlorine distribution is assessed.

EXPERIMENTAL PROCEDURE

PVC is obtained from the Aldrich Chemical Company. The coal is DECS-6 from the Pennsylvania State Coal Bank (PSCB). The catalyst is made in an aerosol reactor and the atomic ratio of Mg to Fe-plus-Mg is 0.25, as prepared. A batch tubing-bomb reactor is used for the liquefaction experiment. The quantity of the feed, i.e., the mixture of coal, PVC, and the catalyst, is kept constant at three grams in all runs. Typical reaction conditions are 350-400°C temperature; at 15-60 min, and 0-2000 psig hydrogen pressure (hot). The reaction is carried out with vertical agitation in a heated, fluidized sand bath. After the reaction, the HCl gas is analyzed by dissolving the gas in water followed by titration. A gas chromatograph (GC) is employed in analyzing the HCl-free gas. The remaining solid product in the reactor is analyzed for the THF-soluble product (THF-S) and the THF-soluble and hexane-insoluble product (Hex-I). The amount of the THF-soluble and hexane-soluble product (Hex-S) is obtained by difference. The yields are calculated on a coal-alone basis by subtracting the contribution of PVC.

For the noncatalytic liquefaction of PVC-alone and coal-alone, an experimental design with 14 experimental conditions is used. The ratio of PVC-to-coal (P/C) is varied from 0.25 to 1.00 for the catalytic/noncatalytic co-liquefaction of coal and PVC. In the catalytic liquefaction runs that involve coal, the catalyst loading is kept at 8.4% on a weight-coal basis, *daf* (dry, ash-free). The catalytic runs for coal-alone and PVC-alone are conducted at the center point conditions of 400°C, 30 min, and 1000 psig hydrogen pressure (hot). For the catalytic run for PVC-alone, the catalyst loading is 8.4% on a dry basis.

RESULTS

Results of noncatalytic liquefaction of PVC-alone and coal-alone are modeled using second-order polynomials. The model equations are presented in Table I. The yields are influenced most significantly by the temperature. The parameters of time and hydrogen pressure have modest effects. It is noteworthy that for liquefaction of PVC-alone, the *HCl gas yield* is not influenced by the process parameters and always remains constant at 52%.

As shown in Figure 1, for the co-liquefaction of coal plus PVC, addition of PVC increases the *THF-S+Gas yield*, the *Hex-I yield*, and the *HCl-Free Gas yield*. Negative values of *HCl Gas yields* are observed, which suggest an interaction between coal and PVC. The *Hex-S yield* goes through a minimum. These results suggest that addition of PVC to coal has synergistic effects on some yields. The higher hydrogen content of PVC might be the reason for this effect.

For the catalytic liquefaction of coal-alone, increases in all the yields are observed. The catalyst has a minimal effect on the liquefaction of PVC-alone. The effect of the catalyst on the co-liquefaction is shown in Figure 2. The catalyst is showing a slight effect on the *THF-S+Gas yield*, and a negative effect on the *Hex-I yield* and the *Hex-S yield*. These results indicate that the presence of PVC in the feed reduces the activity of the catalyst. One reason might be that the chlorine species liberated in the liquefaction of PVC are destroying the activity of the catalyst.

Figure 3 shows that in the liquefaction of PVC-alone, most of the chlorine in the raw PVC goes to the gas phase in the form of HCl. Some goes to the Hex-I and THF-I portions. A little goes to the Hex-S portion. However, the pattern of the chlorine distribution changes dramatically if coal is introduced into the feed. The effect of feed ratio on the chlorine distribution in the products is shown in Figure 4. Addition of coal to the feed decreases the chlorine present in the gas phase while increasing the chlorine in the THF-I and Hex-I portions. These results indicate that addition of coal to PVC is beneficial in that the chlorine in the gas phase is decreased. However, an increase of the chlorine in the Hex-I is observed.

Figure 5 shows the effect of the catalyst on the chlorine distribution in catalytic co-liquefaction runs. The addition of the catalyst carries mixed effects. The amount of chlorine in the gas phase and the Hex-S portion decreases at the expense of an increased amount in the THF-I and Hex-I portions. Finally, utilization of the catalyst is serving the purpose of sequestering chlorine, on a qualitative basis, as it is observed that the amount of chlorine in the residue (THF-I portion) increases upon employing the catalyst.

CONCLUSIONS

The product from the liquefaction of PVC-alone is mostly the HCl gas. All the yields of PVC-alone liquefaction and coal-alone liquefaction are influenced mostly by temperature. Time and hydrogen pressure have modest effects. Addition of PVC to coal has a synergistic effect for some of the liquefaction product yields. Negative values of *HCl gas yield* indicate an interaction between coal and PVC during co-liquefaction. The mixed-metal catalyst is not influencing the co-liquefaction yields much. The addition of coal to PVC is beneficial in reducing the chlorine present in the gas phase. The residue (THF-I portion) is observed to capture chlorine during co-liquefaction experiments. However, more chlorine is going into the Hex-I portion during co-liquefaction than for the liquefaction of PVC-alone. Addition of the catalyst to the feed brings mixed effects to the chlorine distribution in the products. In the presence of the catalyst, more chlorine is observed in the THF-I portion.

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TABLE I

Model Equations for the Liquefaction Yields of PVC-Alone and Coal-Alone, as Functions of Normalized Values of Temperature, Time and Hydrogen Pressure*

PVC-Alone

$$\text{THF-S+Gas Yield \%} = 78.19 + 10.12 \cdot T + 7.80 \cdot t + 1.69 \cdot P + 1.12 \cdot T \cdot P - 5.21 \cdot T^2 - 6.62 \cdot t^2 - 3.85 \cdot P^2$$

$$\text{Hex-I Yield \%} = 18.60 + 1.87 \cdot T + 5.18 \cdot t - 5.81 \cdot T^2 - 9.32 \cdot t^2 - 5.19 \cdot P^2$$

$$\text{HCl-free Gas Yield} = 3.12 + 2.09 \cdot T + 0.99 \cdot t + 0.51 \cdot P + 0.62 \cdot T \cdot P + 0.70 \cdot T^2 + 0.51 \cdot P^2$$

$$\text{Hex-S Yield} = 4.91 + 6.1 \cdot T + 2.32 \cdot t + 0.79 \cdot P + 2.07 \cdot T \cdot P - 2.30 \cdot t^2 + 1.20 \cdot P^2$$

Coal-Alone

$$\text{THF-S+Gas Yield \%} = 29.80 + 7.74 \cdot T + 3.91 \cdot t + 4.30 \cdot P + 2.13 \cdot T \cdot P - 6.12 \cdot T^2 - 3.12 \cdot t^2 + 1.07 \cdot P^2$$

$$\text{Hex-I Yield \%} = 13.37 - 3.06 \cdot T - 1.53 \cdot t + 1.86 \cdot P - 1.63 \cdot T \cdot P - 1.97 \cdot P \cdot t - 6.65 \cdot T^2 + 0.90 \cdot P^2$$

$$\text{HCl-free Gas Yield} = 3.37 + 5.06 \cdot T + 1.35 \cdot t + 0.55 \cdot P + 1.16 \cdot T \cdot P + 0.89 \cdot T \cdot P + 2.6327 \cdot T^2$$

$$\text{Hex-S Yield} = 12.95 + 5.96 \cdot T + 6.55 \cdot t + 1.65 \cdot P + 1.82 \cdot T \cdot P - 4.47 \cdot t^2$$

* T = (Temperature - 400)/50; t = (time - 30)/30; P = (Hydrogen Pressure - 1000)/1000

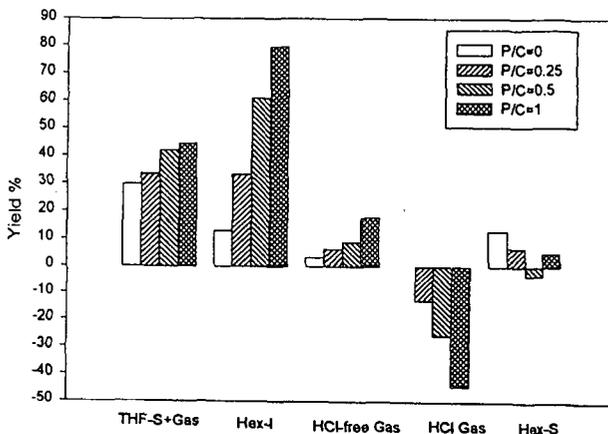


Figure 1. Effect of Feed Ratio on Co-Liquefaction of PVC and Coal at 400°C, 30 min and 1000 psig H₂(hot)

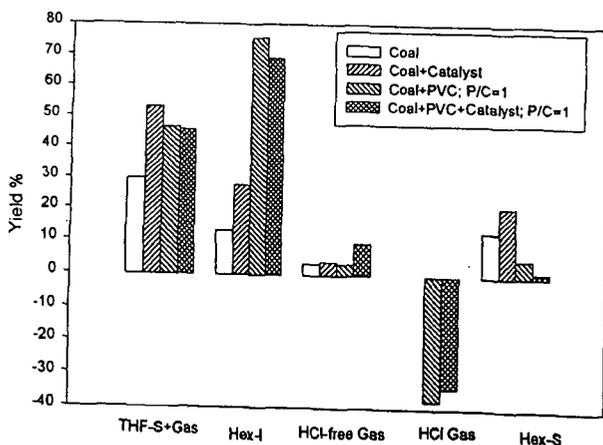


Figure 2. Effect of the Catalyst on Co-Liquefaction of PVC and Coal at 400°C, 30 min and 1000 psig H₂(hot)

Parts of Chlorine in the Product Per
100 Parts of Chlorine in the Feed

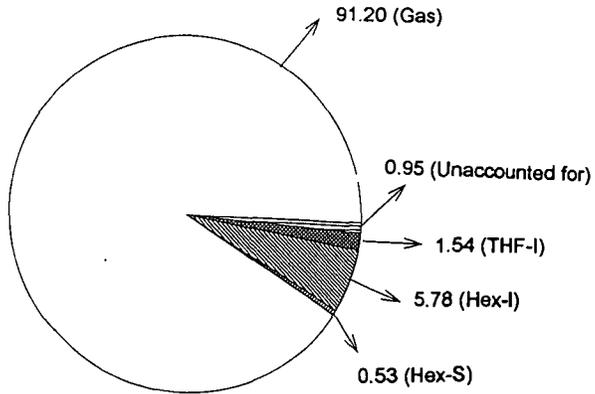


Figure 3. Distribution of Chlorine among the Products for Liquefaction of PVC-alone.
Reaction Conditions -- 400°C, 30 min and 1000 psig H₂ (hot)

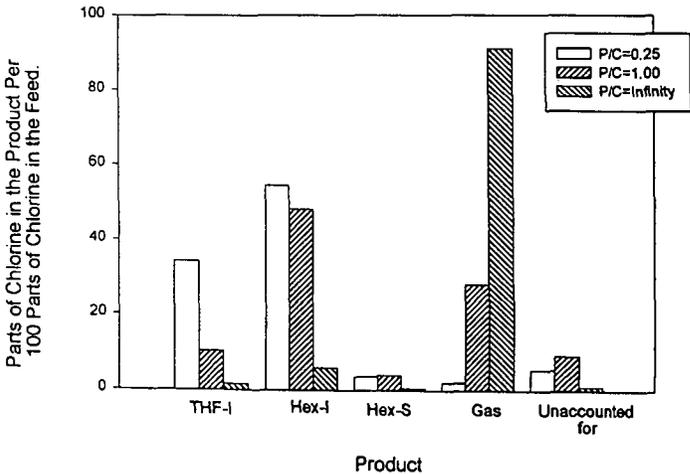


Figure 4. Effect of the Feed Ratio on the Chlorine Distribution in Noncatalytic Co-Liquefaction
Reaction Conditions -- 400°C, 30 min and 1000 psig H₂(hot)

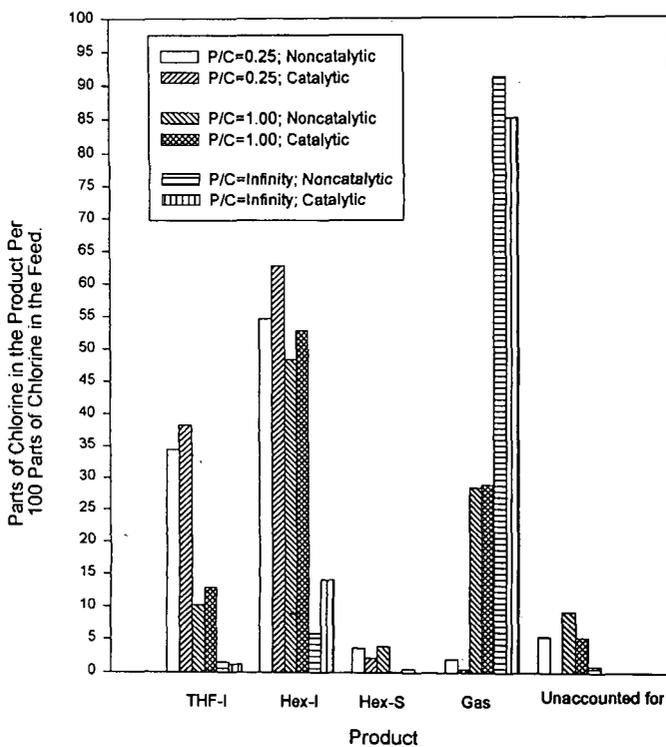


Figure 4. Effect of the Feed Ratio on the Chlorine Distribution in Catalytic Co-Liquefaction Reaction Conditions -- 400°C, 30 min and 1000 psig H₂(hot)