

LIQUEFACTION OF COMMINGLED WASTE PLASTICS CONTAINING PVC

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ABSTRACT

Direct liquefaction studies were conducted on a washed, commingled waste plastic(CWP), as received from the American Plastics Council and after addition of 5 wt.% of polyvinyl chloride (PVC). Both non-catalytic and catalytic experiments were performed; the catalytic experiments utilized 1 wt.% of HZSM-5. The experiments on the CWP-PVC mixture were conducted with and without the addition of 5 wt.% of calcium hydroxide. The effect of PVC on product yields was evaluated. Oil quality was examined by GC simulated distillation. The forms of occurrence of chlorine in the liquefaction products were determined by x-ray absorption fine structure(XAFS) spectroscopy utilizing the X-ray absorption near edge structure(XANES).

INTRODUCTION

Previous research⁽¹⁻¹¹⁾ has demonstrated that direct liquefaction of waste plastics is a very promising recycling option as well as a significant potential new oil resource. As discussed elsewhere, waste plastics can be liquefied at low hydrogen pressure^(5,8) and no solvent is needed,^(5,11) although waste automotive oil and petroleum resid^(6,10) can serve as excellent solvents, if desired. Solid acid catalysts, such as HZSM-5^(3-5,8) and sulfated zirconia⁽⁷⁾ are very active for plastic liquefaction and metal-promoted solid acid catalysts have been demonstrated to improve the oil product substantially.^(7,11) The coliquefaction or coprocessing of coal with plastics also looks promising.

An aspect of plastics liquefaction that has not been adequately studied is the liquefaction of plastics containing realistic amounts of polyvinyl chloride (PVC). Several groups, including our own, have worked with a washed commingled waste plastic(CWP) provided by the American Plastic Council (APC) that contains very little chlorine, due to the fact that PVC has a higher specific gravity than most other resins and separates out during washing. In the current study, we have investigated the liquefaction of the APC CWP with and without the addition of PVC, calcium hydroxide, and HZSM-5.

EXPERIMENTAL

Liquefaction: The liquefaction experiments were conducted in "tubing bomb" reactors with a volume of 50 ml, which were heated in a fluidized sand bath for 60 minutes while being shaken at a rate of 400 rpm. The reactors were charged with 10 g of plastic, with all combinations of additions of 5 wt.% of PVC and Ca(OH)₂ and 1 wt.% of HZSM-5. No solvent was used and hydrogen gas was added at low pressure (200 psig, cold). The HZSM-5 was a commercial catalyst⁽¹²⁾ with average particle sizes of 40-50 Å and a Si/Al = 4.⁽⁶⁾

At the end of each run, the reactor was cooled rapidly to room temperature in a second sand bath. Gas products were then collected and analyzed by gas chromatography. The other products were removed from the reactor with tetrahydrofuran (THF) and extracted in a Soxtech apparatus for 2 hours. Total THF conversion was determined from the amount of insoluble material that remained (residue). All insoluble materials were dried at 80°C overnight before weighing. Any added catalyst was subtracted from the residue sample weight. The THF solubles were subsequently separated into pentane soluble (oils) and pentane insoluble (preasphaltenes + asphaltenes(PA + AS)) fractions. The experimental errors for total conversion and oil yield are approximately ±3%.

The oil fraction was analyzed by GC - simulated distillation. The GC operating parameters were as follows: column - Petrocol B, 20" x 1/8" packed column; temperature - 0 - 360 °C with 10 °C/min ramp; detector - FID at 380 °C; flowrate - 35 ml/min He. The simulated distillation method is described in ASTM D-2887. The oil product was categorized into three fractions: gasoline (B.P. < 200 °C); kerosene (B.P. - 200-275 °C); and heavy oil (B.P. - 275 - 550 °C).

CL XAFS Spectroscopy: XAFS spectroscopy was carried out at beamline X-19A at the National Synchrotron Light Source at Brookhaven National Laboratory. Spectra were obtained at the chlorine K absorption edge (at ca. 2825 eV) from the oils, asphaltenes + pre-asphaltenes, and IOM residues separated from the products of the liquefaction runs. Some of the fractions were also examined at the calcium K absorption edge (at ca. 4038 eV). The samples were suspended in the X-ray beam in ultrathin polypropylene bags in a Lytle fluorescent detector.⁽¹³⁾ The x-ray beam path

was flushed with helium to minimize x-ray absorption by air. Spectra were collected from 75 eV below the chlorine edge to about 300 eV above the chlorine edge, at which point the K absorption edge arising from argon at 3107 eV was encountered. Over the near-edge or XANES region (from about 10 eV below the edge to 50 eV above the edge), the spectra were acquired with a step width of only 0.2 eV/point. The maximum in the derivative of the Cl XAFS spectrum of NaCl was taken as the zero point of energy for the Cl XAFS spectra and all spectra were calibrated with respect to this point. Most samples were sufficiently rich in chlorine to obtain an adequate spectrum with a counting time of 1 sec/point; however, multiple spectra were run and summed to give a single spectrum with improved signal/noise ratio if the chlorine content was relatively low.

XAFS spectral analysis consisted of (i) calibration of the XAFS spectrum relative to the NaCl standard spectrum, (ii) subtraction of the pre-edge slope from the XAFS spectrum, and (iii) division of the spectrum into two distinct regions for the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS). In this report, only the XANES data will be described.

RESULTS AND DISCUSSION

Liquefaction results: The liquefaction results are briefly summarized in Figures 1 and 2. Chemical compositions of the feedstock (CWP + PVC), the IOM samples and the oil products are given in Table 1. Two points should be noted regarding Figure 1. First, the yields are given as oil + gas, as the gas yields of all experiments was not determined. However, for most of the samples the gas yield was determined and found to be $\leq 5\%$. Second, the yields indicated for the CWP alone and the CWP + 1% HZSM-5 are for experiments that utilized a cold hydrogen pressure of 800 psig rather than 200 psig. It is seen that neither the oil + gas yields nor the total conversion were much affected by the presence of either PVC or HZSM-5 at 445 °C. Furthermore, the oil quality as reflected by the relative fractions of gasoline, kerosene and heavy oil does not vary dramatically. In general, there is some increase in both the quantity and quality of the oil produced with the addition of HZSM-5; at this relatively high temperature, however, the results of the thermal runs are almost as good as those of the catalytic runs. Perhaps the most significant result is the fact that the presence of 5% PVC does not appear to have any significant damaging effect on either oil yields or quality.

The distribution of the most critical elements (C, H, Ca, and Cl) in the IOM and oil samples is given in Table 1. It is seen that the addition of calcium hydroxide increased the amount of Cl retained in the IOM significantly, and somewhat more for the case where 1% HZSM-5 was added than for the thermal run. Similarly, the oil samples exhibited a decrease in Cl content when Ca was present. However, the decrease was larger for the thermal run than for the catalytic run. It should be emphasized that *none* of the oils would be acceptable in most refineries because of their relatively high Cl contents.

Cl XANES spectra: As shown in Figure 3, quite different chlorine XANES spectra were obtained from the oil and IOM fractions. Strong chlorine XANES spectra were also obtained from the AS+PA fractions, but they were closely similar to the IOM spectra obtained from the baseline situation (no catalyst, no Ca additive). The Ca additive appears to have little effect on the appearance of the Cl XANES spectra of the oil and AS+PA fractions; these spectra show relatively little variation. However, the Ca additive clearly did affect the appearance of the Cl XANES spectra of the IOM fractions. As shown in Figure 3, the sharp peak at -4.8 eV is much reduced in intensity when the Ca additive is present. The presence or absence of the HZSM-5 catalyst had relatively little effect on the appearance of the spectra.

The chlorine spectrum of the oil clearly arises from organochlorine species. The peak position of the first prominent sharp peak at -1.45 eV is consistent with data in the literature for organic chlorides⁽¹²⁾, with the possible exception of aryl chlorides, which tend to have a more positive peak position in the range -1.0 to -0.5 eV. Furthermore, a similar sequence of three increasingly broader and weaker peaks at about -1.5 eV, 4 eV, and 12 eV is observed in a number of organochlorine compounds. In contrast, the chlorine spectrum of the IOM with the Ca additive is largely consistent with inorganic occurrences of chloride anions, and we have observed similar spectra from hydrated calcium chlorides. The prominent sharp peak observed at -4.8 eV observed in the spectra of all of the AS+PA fractions and of the two IOM fractions without Ca additive, however, is difficult to explain at this time and indicates a complication that cannot be explained by a simple separation of the PVC-derived chlorine into organic and inorganic chlorides. The width of the peak is narrow and

very similar to that observed for the organochlorine occurrence in the oil, but the remainder of the spectrum appears to be more like that of an inorganic chloride. Possibly, a chlorine occurrence based on the hypochlorite molecular anion (OCl^-) may offer an explanation for this peak.

It is also worth comparing the results obtained here with data obtained earlier⁽¹⁵⁾ on coliquefaction of PVC-doped waste plastics with a North Dakota lignite. In those experiments, no organochlorine compounds were found in the oil; rather the chlorine XANES spectrum obtained from the oil was consistent with a hydrochloride adduct attached to presumably a quaternary nitrogen functionality in the oil derived from the coal. In the present coal-absent system, there is virtually no nitrogen to form such HCl adducts. Also, the Cl XANES indicated the formation of significant NaCl in the lignite/waste plastics/PVC experiments, suggesting that sodium may be a better sink for chlorine than calcium.

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Table 1. Chemical composition of oils and IOM samples (wt. %).

IOM Samples	C	Ca	Cl
CWP-PVC	63	1.2	3.4
CWP-PVC-Ca	51	31	5.5
CWP-PVC, HZSM-5	45	0.7	3.9
CWP-PVC-Ca, HZSM-5	39	32	7.0
Oil Samples	C	H	Cl
CWP-PVC Feedstock	83	14	2.8
CWP-PVC	82	13	0.07
CWP-PVC-Ca	82	13	0.4
CWP-PVC, HZSM-5	84	12	0.1
CWP-PVC-Ca, HZSM-5	87	12	0.08

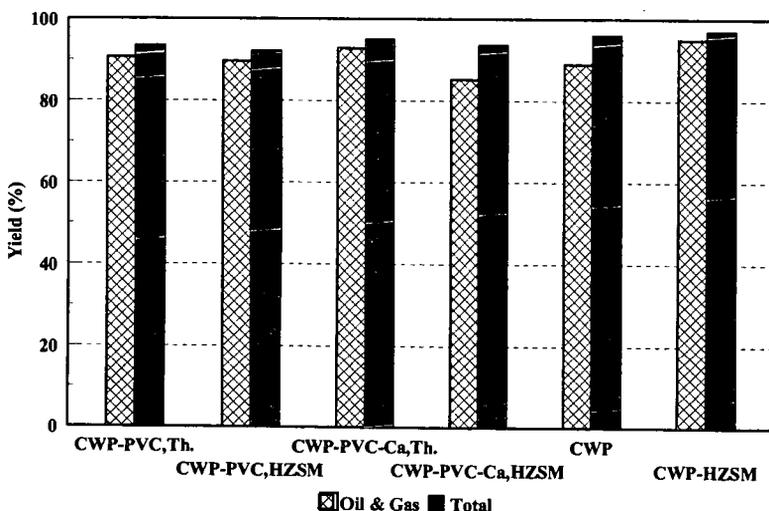


Figure 1. Liquefaction yields for the commingled waste plastic with and without additions of PVC(5%), calcium hydroxide(5%), and HZSM-5(1%).

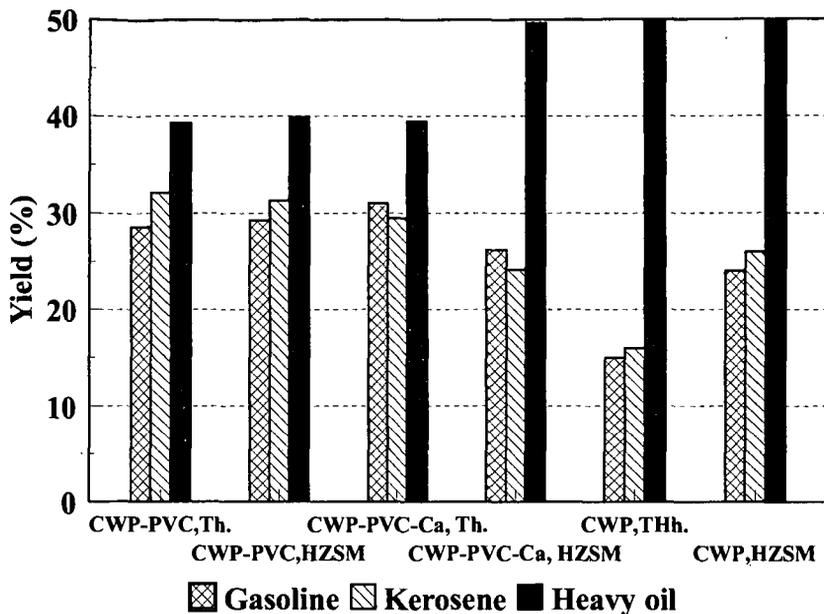


Figure 2. Simulated distillation analysis of the oil product from liquefaction of CWP with and without addition of PVC, calcium hydroxide, and HZSM-5.

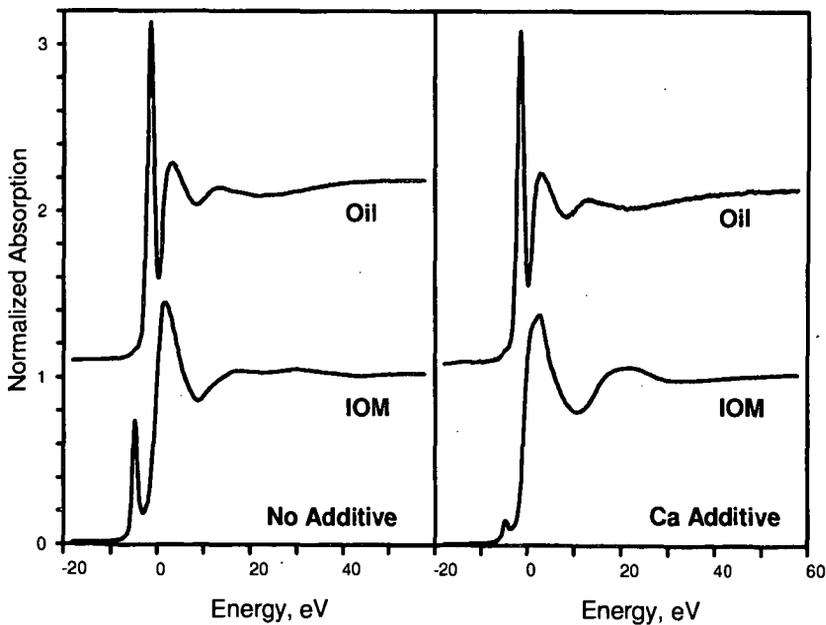


Figure 3. Chlorine K-edge XANES spectra of IOM and oil samples with and without calcium hydroxide additive.