

CHARACTERIZATION OF COAL/WASTE COPROCESSING SAMPLES FROM HRI RUN POC-2

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ABSTRACT

Coal and waste materials (plastics and rubber) were co-liquefied during Run POC-2 in HRI's 3 T/D direct liquefaction process development unit under the DOE-sponsored Proof-of-Concept program. Analytical characterizations were conducted of well-defined samples from representative periods of the run to provide information on the chemical transformation of these feedstocks and their distribution in product and recycle streams. The characteristics of the products and process streams were dependent on both feedstock changes and operating conditions. Several unusual process oil characteristics were observed when wastes were coprocessed with coal, especially during the coal/plastic operation. Implications of these results for future coal/waste liquefaction development and analytical characterization of the materials are discussed.

INTRODUCTION

Based on background work performed by the Consortium for Fossil Fuel Liquefaction Science¹ and the Pittsburgh Energy Technology Center, in July 1994 HRI completed nine days of coal/waste coprocessing during the DOE Proof-of-Concept direct liquefaction Run POC-2.^{2,4} Several key accomplishments of the run were: subbituminous coal was processed without deposition problems such as were encountered at the Wilsonville pilot plant; an in-line hydrotreater was operated to produce high-quality distillate low in heteroatoms; an overall material balance of 99.6% was achieved; and the plant successfully converted fifteen tons of plastic and waste tires into premium fuels with high conversion and a lower hydrogen requirement than during coal-only operation. A diagram of the plant² as configured for HRI Run POC-2 is shown in Figure 1. CONSOL analyzed 65 samples collected throughout the run; sample points are shown in Figure 1. Run conditions for coal and coal/waste operating periods are compared in Table 1. The main variables were feedstocks, reactor temperatures, space velocity, recycle type (ashy or solids-free), and solvent/feed ratio. The periods were relatively constant in severity, according to HRI's index.

ANALYTICAL APPROACH AND OBJECTIVES

Analysis of liquefaction process stream samples should always take place within a well-defined process framework. Sample origins and interrelationships should be understood in context to the process configuration and run conditions, and samples should cover representative periods of the entire run, not only the coprocessing periods. The analytical methods used here have been proven useful for liquefaction process stream characterization. Non-routine analyses were warranted in some cases for the coprocessing period samples. One objective was to determine the fates of the various waste feedstocks processed. Information is desired on the relative convertability of the feedstocks, the product streams to which the feedstocks are converted (bottoms vs. distillate), interactions of feedstocks, and their effects on product quality. In order to address these objectives, one must distinguish property characteristics reflecting feedstock differences from those caused by changes in other process conditions. In this case, process changes include: 1) ashy vs. ash-free recycle, 2) high make-up oil use in waste coprocessing periods, 3) high solvent/feed ratios in waste coprocessing periods, 4) ROSE-SR operations, and other factors, such as space velocity and catalyst age. Other performance issues of interest in HRI Run POC-2 include achievement of steady state unit performance (such as the ROSE deasher), retrograde reactions, and product stability issues.

EXPERIMENTAL AND SAMPLE DESCRIPTION

Information about the samples analyzed and methods used is given in Table 2. Sample points, SP-xx, given in the table correspond to those shown in Figure 1. In the following discussion, the abbreviations shown in Table 2 will be used, e.g., NSB for naphtha stabilizer bottoms, DAO for deashed oil. Experimental details about most of the analytical methods used have been provided elsewhere.^{6,7} GC/MS analyses were done with a DB-5 column, 30 m x 0.25 mm, 0.25 μ m film thickness. GC conditions were: 5 min at 10 °C; 2 °C/min to 100 °C, 4 °C/min to 320 °C, up to 20 min at 320 °C. The injection port was held at 300 °C. Carrier gas: He at 20 psig. One percent solution of make-up oil sample in tetrahydrofuran, or neat NSB samples were injected in the splitless mode. The mass spectrometer was scanned from 33 to 300 amu. Peak identifications were based on searches of the Wiley/NBS mass spectral library and retention times.

DISCUSSION

In this paper, we will highlight a few results that are of particular interest to coal/waste coprocessing. Most of the discussion will be concentrated on the

products (naphtha stabilizer bottoms (NSB) and ROSE-SR bottoms), the flashed second-stage oil (RLFVB), and ROSE-SR feed (VSB).

Plastics and Rubber Product Oils

Gas chromatography/mass spectrometry (GC/MS) total ion chromatograms are shown in Figure 2 for NSB product oils and the make-up oil. The make-up oil is used to supplement recycle when there is insufficient process-derived solvent. The NSBs contain paraffins with carbon numbers ranging up to about 24 (tetracosane, boiling point 736 °F); this generally is consistent with the expected boiling point of these products. The product from the coal/plastics and coal/rubber periods had more material boiling in the range 600-750 °F, in agreement with HRI's distillation data.⁴ The make-up oil has a higher boiling point distribution than the NSBs, although the boiling points of the two overlap. The make-up oil may contribute to some of the higher boiling components seen in the NSBs from the coal/plastics and coal/rubber periods. Distillation, hydrogenation, and hydrocracking are all routes by which this higher-boiling make-up material may find its way into the NSB boiling range. Make-up oil comprised 27 wt % of the period 43 recycle stream composition and 43 wt % of the period 45 recycle stream composition, compared with none during the coal period 36. The contribution of make-up oil was exacerbated by the higher solvent/feed ratio of ≈ 2.4 in the waste/coal periods vs. 1.2 in the coal period. Thus, the higher-boiling material seen in the coprocessing period NSBs seems attributable to plant operating conditions, and not specifically to the feedstocks used. Since the plant was not in solvent balance during the coal/waste periods, sample and yield data may not represent plant operation at steady-state conditions.

Unusual Materials from Plastics Period

Significant amounts of ethylbenzene (EB) and methyl ethylbenzene (MEB) components were found in the NSB only from the plastics period, as determined by GC/MS (Figure 1, see marked peaks at retention times 16.77 and 21.85 minutes). Proton NMR confirms this, since distinctive peaks from ethylbenzene or diethylbenzene are present only in the spectrum (not shown) of the plastics period NSB product. These components are believed to be products from the liquefaction of the polystyrene. Thus, the presence of these components is attributable to the feedstock.

The DAO from the plastics period was extracted with THF and found to contain insolubles. This insoluble material is gray in color, waxy in appearance, and melts below 100 °C. Diffuse reflectance FTIR showed the material to contain methylene and methyl aliphatic groups, with essentially no aromatics or heteroatoms. Except for a more intense methyl C-H stretch peak in the DAO insolubles spectrum, it is very similar to that of a polyethylene film sample. The sharp doublets around 1470 and 720 cm^{-1} are excellent matches with polyethylene. The peak at $\approx 720 \text{ cm}^{-1}$ is indicative of long-chain paraffins. The elemental composition of the DAO insolubles is similar to that of the polyethylene feed, and they are almost identical in H/C ratio (not shown). Since this is apparently non-distillable wax, much heavier than previously observed,⁸ we suspect that this material results from polyethylene liquefaction. In fact, the evidence strongly suggests that this material is unreacted or partially reacted polyethylene.

Variations in IOM across the vacuum still and ROSE unit were observed in CONSOL data. The coal conversion determined by CONSOL (Table 3) was 57.5% based the RLFVB sample, 96.8% based on the VSB sample, and 77.3% based on the ROSE bottoms sample (sequential points through the process). In addition to the increased IOM in the ROSE bottoms, a significant amount of the waxy IOM is recycled in the DAO. A relatively high preasphaltene concentration in the period 43 DAO coincides with the presence of IOM in this stream (Table 3). These results may reflect unusual solubility characteristics of liquefied plastics, especially polyethylene. The results suggest that for studying plastics liquefaction, one may need to develop a practical method to distinguish "dissolved" plastic (unchanged in molecular weight) from "converted" plastic (decreased in molecular weight).

The NSB from the plastic/coal period contained about 14 ppm (mg/kg) of sediment not present in other samples from this run, or in product oil samples from prior Wilsonville pilot plant runs or from HRI bench-scale runs. A portion of the sediment is slightly soluble in THF or pyridine. A sample of sediment was obtained for characterization by filtration of the NSB through a silver membrane filter, followed by a hexane wash and vacuum drying. The filter deposit was characterized in-situ by diffuse reflectance FTIR and SEM/EDX. FTIR indicated a primarily aliphatic material with a hydrogen-containing functional group (such as O-H); some aromatic and some carbonyl seem also to be present. SEM/EDX showed the deposit to consist primarily of sulfur, with smaller amounts of carbon and oxygen also evident. The collective evidence suggests that the bulk of the sample is elemental sulfur, which has little infrared activity and limited solubility in common solvents.

CONCLUSIONS

Analyses were conducted on process oil samples from representative periods of HRI Run POC-2 in which coal, coal/plastic and coal/rubber were the feedstocks. Differences are apparent, some related to feedstock changes, others to operating condition changes. The high rate of make-up oil use in coal/plastics and coal/rubber periods may result in some of the higher boiling paraffinic components seen in NSBs from these periods. Significant amounts of ethylbenzene and methyl ethylbenzene components are present in the NSB product from coal/plastics operation; these appear to be products from the liquefaction of the polystyrene. There are unusual IOM characteristics in the coal/plastics period 43, perhaps as a result of unusual solubility characteristics of liquefied plastics, especially polyethylene. Heavy wax found as IOM in the DAO seems to be unreacted or partially reacted polyethylene. There is an apparent increase in conversion, followed by a decrease in conversion through a portion of the process. The conversion to THF solubles increased from 57% based on the second-stage product sample (RLFVB) to 97% based on the ROSE feed sample (VSB), and then decreased to 77% based on the ROSE bottoms sample. These results suggest a need to develop a method to distinguish "dissolved" plastic (unchanged in molecular weight) from "converted" plastic (decreased in molecular weight). The NSB sample from coal/plastics operation also contained a sediment not found in other samples.

Many products from liquefaction of plastics and rubber may not be chemically distinct from coal liquefaction products. It appears to be necessary to rely on "marker" compounds or materials (such as ethylbenzene from polystyrene) to demonstrate a non-coal origin of some product components. Proper interpretation of results is facilitated by analysis of liquefaction process stream samples within a well-defined process framework. Characteristics of products from HRI's Run POC-2 operation with coal/waste do not solely reflect feedstock differences from coal-only operation. Other conditions changed, as well, and the plant was not operating at steady-state when those materials were generated.

Run POC-2 operating experience should make it easier to avoid high make-up oil use in future runs with these feedstocks, since high make-up oil use lowers the quality of the analytical and yield information. There was no evidence that polystyrene did not convert completely, but there seem to be problems associated with polyethylene liquefaction (waxy DAO insolubles). The high oxygen content (32 %) of polyethylene terephthalate makes it less desirable as a feedstock, though it manifested no problems. It appears that polystyrene would be the preferred feedstock, based on this test. Liquefaction of the plastic feedstocks separately from each other would help resolve some issues. Coal/plastics product oil stability should be explored further.

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TABLE 1. CONDITIONS FOR COMPARISON PERIODS OF COAL AND COAL/WASTE LIQUEFACTION

Process Condition	Period			
	21	36	43	45
Feed	100% Coal	100% Coal	30% Plastics, 70% Coal	25% Rubber, 75% Coal
Reactor Temp., °F				
K-1 (Ebullated-Bed)	775	810	810	810
K-2 (Ebullated-Bed)	830	835	830	830
K-3 (Fixed-Bed)	705	720	720	720
Severity, HRI Index	5.16	5.25	5.16	5.16
SV, lb MF coal/h/ft ³ reactor, per stage	30	40	30	30
Recycle/feed ratio	1.2	1.2	2.0	2.0
Recycle type	Ashy	Ashy	Solids-Free	Solids-Free
Other Information: run operated from June 1 through July 28, 1994; Black Thunder Mine subbituminous coal; ROSE-SR used for solids separation; 700°F extinction recycle operation; catalyst addition rate in lb/T MF coal was 1.0-2.0 in K-1 and 2.0-2.5 in K-2; plastics were new in ratio 50/35/15 high-density polyethylene/polystyrene/polyethylene terephthalate; rubber was from scrap tires; Ni/Mo supported catalysts were Akzo AO-60 in K-1 and K-2 and Criterion 411 in K-3 (the on-line hydrotreater).				

TABLE 2. CONSOL ANALYSES OF SAMPLES FROM HRI WASTE/COAL COPROCESSING RUN POC-2

Sample Description (Name); Vessel; Sample Point	Periods	Technique & Information Sought (Refer to Key)
Atmospheric Still Bottoms (ASB); N-2 BTMS; SP-4	5, 15, 21, 36, 43, 45	A,B
Vacuum Still Bottoms (VSB); N-3 BTMS; SP-6	21, 36, 43, 45	E; THF Extract - A,B,F
Naphtha Stabilizer Bottoms (NSB); N-5 BTMS; SP-3	15, 21, 36, 43, 45	A,B,C,D
Recycle Oil; 0-43 Oil; SP-11	5, 15, 34, 36, 43, 45	A,G,H; Dist. - A,B,G; Resid - E; Resid THF Extract - A,B,F
Reactor Liquid Flash Vessel Bottoms (RLFVB); 0-46 Material; SP-9	5, 15, 21, 34, 36, 43, 45	A,G,H; Dist. - A,B,G; Resid - E; Resid THF Extract - A,B,F
ROSE Btms; 0-63; SP-27A/B	15, 21, 34, 36, 43, 45	E; THF Extract -A,B,F
Deashed Oil (DAO); 0-65 DAO; SP-25	15, 21, 34, 36, 43, 45	A,B,F; E(Some Periods); D
Make-Up Oil (M/U); Tank 4 Oil; SP-28	1	A,B,C,G

KEY TO TECHNIQUES AND INFORMATION SOUGHT:

A = ¹H-NMR for hydrogen distribution (7 classes), aromaticity (degree of hydrogenation), paraffinicity, hydrogen donors; B = FTIR in THF solution for phenolic -OH content; C = GC-MS for composition, carbon numbers of paraffins; D = special analyses as described in Discussion section (Period 43); E = THF extraction and ash for resid, ash and IOM content, for coal and resid conversion; F = solvent fractionation (oils, asphaltenes, preasphaltenes) for resid composition; G = microautoclave test with standard coal for donor solvent quality; H = 850°F distillation for distillate content.

TABLE 3. DATA INDICATING UNUSUAL IOM CHARACTERISTICS IN COAL/PLASTICS PERIOD

Period	Sample	Coal Conversion, wt % (a)	Phenolic -OH In Soluble Resid, meq/g	Component of Soluble Resid, wt %	
				Asph.	Preas.
15 Coal	Recycle Oil	87.3	0.18	7.3	6.5
	RLFVB	89.3	0.24	12.4	7.7
	VSB	—	0.20	13.1	3.2
	ROSE Btms	86.1	0.29	28.8	14.7
	DAO	—	0.14	5.5	0.7
21 Coal	RLFVB	92.5	0.27	18.4	6.1
	VSB	91.9	0.22	18.6	2.8
	ROSE Btms	91.8	0.28	18.8	8.3
	DAO	—	0.14	7.0	1.4
36 Coal	Recycle Oil	91.3 (91.0*)	0.35 (0.30*)	13.4 (12.2*)	7.7 (5.4*)
	RLFVB	—	0.45	21.8 (20.0*)	3.7 (3.9*)
	VSB	91.2	0.36	20.7	2.7
	ROSE Btms	91.9 (90.1*)	0.55 (0.44*)	25.9 (23.5*)	8.5 (12.7*)
	DAO	—	0.24 (0.29*)	5.8 (8.6*)	0.1 (0.3*)
43 Coal/Plastics	Recycle Oil	—	0.12	21.0	2.6
	RLFVB	57.5	0.28	19.8	9.8
	VSB	96.8	0.16	13.2	1.0
	ROSE Btms	77.3	0.23	22.0	6.7
	DAO	—	0.13	5.0	11.1

* From Per. 34, at same conditions, but without Mo additive used in Per. 36.
 (a) MAF % Conversion = $[(100 - \text{ash\% in dry feed}) - (\text{sample \% IOM}) * (\text{ash\% in dry feed}) / (\text{sample \% ash})] * 100 / (100 - \text{ash\% in dry feed})$; plastics ash content was assumed to be 0%.

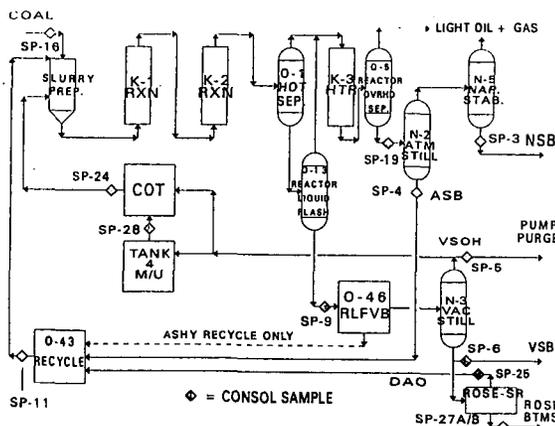


Figure 1. Diagram of the HRI Proof-of-Concept Plant Showing Sample Points, as Configured for Run POC-2.

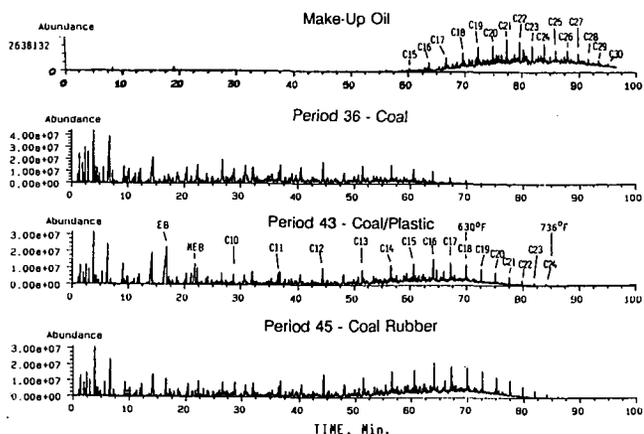


Figure 2. GC-MS Total Ion Chromatograms of Make-Up Oil and Product Oils From HRI Run POC-2.