CO-PROCESSING OF WASTE PLASTICS WITH COAL AND/OR PETROLEUM RESIDUUM

V.R. PRADHAN, A.G. COMOLLI, L.K. LEE, AND G. POPPER
HYDROCARBON TECHNOLOGIES, INC.
LAWRENCEVILLE, NEW JERSEY 08648 U.S.A.

DOE CONTRACT NUMBER: DE - AC22-92PC92148

ABSTRACT

The United States generates about 45 million tons of hydrocarbon waste and 73 million tons of waste paper per year. The approximate 20 million tons of plastic waste generated are discarded after use and end up in sanitary landfills. With existing recycle efforts, only 4% of the waste plastics are re-used. Waste plastics occupy about 21% by volume of U.S. landfills. These waste can be co-processed with either a coal feedstock or a combined coal/oil feedstock to produce clean transportation fuels and to recover the starting chemicals used for production of new plastics. HTI's two stage co-processing system has successfully generated premium liquid products using only dispersed catalysts and these feedstocks. The addition of waste plastics to the normal coal/oil co-processing or oil upgrading system results in a significant improvement in process performance and a reduction in product costs as compared to oil upgrading or coal/oil co-processing. An equivalent crude oil price of 20.48 dollars/barrel has been achieved, putting this technology nearly in the range of commercialization.

INTRODUCTION

The United States generates about 45 million tons of hydrocarbon waste and 73 million tons of waste paper per year. The approximate 20 million tons of plastic waste generated are discarded after use and end up in sanitary landfills. With existing recycle efforts, only 4% of the waste plastics are re-used. Waste plastics occupy about 21% by volume of U.S. landfills. Through the efforts of the U.S. Department of Energy at the Pittsburgh Energy Technology Center and Hydrocarbon Technologies, Inc. (HTI), a new and promising application for direct liquefaction has been found. This application involves the combined processing of random waste plastics and waste hydrocarbons with coal and/or petroleum residuum to produce clean transportation fuels and to recover the starting chemicals used for production of new plastics.

Co-processing refers to the combined processing of coal with other hydrocarbon feedstocks. Historically this has consisted of various petroleum-derived heavy oil feedstocks; however more recent work has included waste plastics and used rubber tires. The coal feedstocks used are those typically utilized in direct coal liquefaction: bituminous, subbituminous, and lignites. Petroleum-derived oil is typically a petroleum residuum, containing at least 75 W% material boiling above 524°C. The waste plastics and tires are those collected by municipal recycling programs. The feedstocks are combined and processed simultaneously with the dual objective

of liquefying the solid feed and upgrading the residuum from either the liquefied solids or petroleum oil to lower boiling (< 524°C) premium products. HTI's investigation of the co-processing technology has included work performed in laboratory scale (20 cc microautoclave and a two-stage continuous stirred tank system equipped with one liter reactors), bench scale (25 kg/day throughput) and PDU scale (3 tons/day throughput) operations. In a continuous operation the waste plastics/used tires feedstock and the coal feedstock would be prepared separately and combined with the oil feedstock to form a slurry immediately prior to hydroconversion. The products are then separated downstream and the light oils are sent to an in-line hydrotreater for further upgrading. HTI's approach to coal/oil co-processing has traditionally used a two-stage reaction system with either extrudate catalyst in both reactors or more recently a combination of a dispersed and a supported catalyst in the reactor stages. Current work has been performed with dispersed catalyst in both reactors eliminating the need for handling a supported catalyst. In-line hydrotreating of the light oil products have produced a naphtha fraction with sulfur and nitrogen levels less than 10 ppm, which is below current US requirements for transportation fuels.

EXPERIMENTAL

Three long-duration bench-scale runs in the Proof-of-Concept Bench Option Program, PB-01, PB-02, and PB-03, were completed during 1995-96. The first two runs, PB-01 and PB-02, results from which will be addressed in this paper, studied the coprocessing of waste plastics (from curb-side recycling in Northern NJ) with sub-bituminous coal (Wyoming Black Thunder mine) and petroleum resid (California Hondo-VTB); the Bench Run PB-03, that studied the effect of dispersed slurry catalysts and of recycle solvent-hydrotreatment on process performance during direct coal liquefaction, will not be addressed in this paper. Of the two bench-scale runs described here, PB-01 was carried out in an "all dispersed catalyst" reaction mode while PB-02 was carried out in a "hybrid" mode of operation, employing dispersed slurry catalyst in the first stage reactor and supported extrudate catalyst in the second stage reactor. The dispersed slurry catalyst employed was a combination of HTI's proprietary iron catalyst and Molyvan-A. Between 1000-5000 ppm of iron and 50-100 ppm of molybdenum were used for continuous co-liquefaction operations. The highlights of the reactor configuration included an interstage high pressure separator and an in-line fixed-bed hydrotreater. *Figure 1* shows a simplified schematic of HTI's Bench-Scale Unit.

RESULTS AND DISCUSSION

The reaction operating parameters, reactor temperature and space velocity, for each operating condition are presented in *Table 1*. The process performance discussed is that actually achieved at these operating conditions. The basis for the economic evaluation is defined by previous work and the assumptions described below and the process performance has been adjusted accordingly for this comparison. These conditions were carried out using a combination of dispersed slurry catalysts, based upon iron and molybdenum.

Typical feed conversions (based on the solubility of pressure filter solids in quinoline), obtained during equilibrium periods are presented in *Table 1*. As can be seen the feed conversions (W% maf feed) varies from 96.1 to 99.9 W% maf. The lowest conversion is for those conditions that contain coal as part of the feed. The conditions without coal are both over 99W% maf feed conversion. This indicates that little or no char (quinoline insoluble material) was formed in the reactors. The 524°C+ residuum conversion varies from 82.7 to 84.0 W% maf feed. Comparing the oil only condition to the oil/plastics condition shows an increase in the residuum conversion. Not surprisingly, the addition of plastic to the coal/oil condition also results in an increase in residuum conversion. The upgrading of the oil only results in a C4-524°C distillate yield of 76.0 W% maf feed. The addition of coal decreases the distillate yield by 6.3%. The addition of plastic to either of these conditions increases the distillate yield; though, more dramatically for the coal/oil condition than for the oil only condition.

Extremely significant to this comparison of process performance is the effect of plastic addition on hydrogen consumption. Not only does the addition of plastic to either oil only operation or coal/oil operation improve performance it also decreases hydrogen consumption. This is due to the plastic feed having a much higher relative concentration of hydrogen than either the coal or oil feedstock, 11.42 W% or 1.70 H/C atomic ratio for the plastic as compared to 10.13 W% or 1.45 H/C atomic ratio for the oil and 4.5 W% dry basis or 0.77 H/C atomic ratio for the coal. The light gas yield, C_1-C_3, also indicates the positive impact of adding plastics to either oil or coal/oil processing. Oil only operation results in a light gas yield of 5.0 W% MAF feed; coal/oil co-processing raises this by 2.4%. The addition of plastics to oil only operation decreases light gas yield by 0.7% and coal/oil co-processing by 2.1%. Plastics not only reduces the total hydrogen consumption but also uses it more efficiently in producing liquid and not gas products. *Figure 2* depicts the significant effect of waste plastics upon reducing the light gas-make and hydrogen consumption in heavy resid conversion or in coal/oil coprocessing. The overall quality of the light distillate products (*Table 2*) has also been excellent. The separator overhead product (SOH) coming out of the in-line hydrotreater are of premium quality with API gravities as high as 50 and H/C atomic ratios close to 2.0. The nitrogen and sulfur contents of the SOH product are very low (below 15 ppm sulfur and 1 ppm nitrogen), as shown in *Table 2*. It is also clear from *Table 2* that the addition of waste plastics either to heavy resid feed alone or to a mixture of coal and heavy petroleum resid, results in a substantial increase in the API gravities of the light distillate product; the lightest boiling naphtha (IBP-177°C) fraction also increases noticeably upon the addition of MSW plastics to the feed. The increase in the percent aromatic character of the SOH distillate during Conditions employing waste plastics in the feed can be attributed to the monomers of styrenic polymers present in the MSW plastic mixture.

The economic evaluation studies were based on construction of a fully-integrated grass-roots commercial coal/oil/plastics co-liquefaction complex to manufacture finished gasoline and diesel fuel liquid products. Byproducts from the complex include propane and butane, as well as elemental sulfur and anhydrous ammonia. The co-liquefaction plant in the complex is a multi reactor-train facility, and the total feed processing capacity has been selected assuming the construction of maximum-sized heavy-walled pressure vessels to carry out the co-liquefaction

reactions. Coal and waste plastics required in the co-liquefaction plant are prepared on site, and storage is provided for the oil received. Unconverted feed plus residual oil from the co-liquefaction plant are gasified to meet a part of the hydrogen requirements of the complex. Part of the fuel requirement is met by the waste process gases. Natural gas is imported to meet the remaining fuel requirements and to satisfy the remainder of the hydrogen requirements. All utility needs in the complex, including electric power, are produced on site. The equipment sizes and costs within the co-liquefaction plant have been factored from detailed engineering studies. The costs and operating requirements of the other process facilities and the off-sites have been estimated from the Bechtel Baseline Design Study, which was developed for the Department of Energy. Total plant costs have been adjusted to a current year time frame with construction at a US Gulf Coast location.

The Bechtel Baseline Design Study also provided the economic criteria and financing model used in this evaluation. This model assumes a 25 percent equity financing with a 25 year debt life and an 8 percent interest rate on the debt. The liquid product selling price was calculated so as to provide a discounted cash flow rate of return of 15 percent on the equity. Cash flows were calculated assuming an on-stream factor of 90 percent (328.5 days per year) after the second year of operation. A four-year construction period was assumed, followed by an operating project life of 25 years. Capital costs including working capital were depreciated over a ten-year period, using straight-line depreciation. A federal tax rate of 34 percent was assumed for the life of the project. Feed costs and product selling prices were inflated at an annual rate of 3 percent. Labor and maintenance staffing requirements and wage rates were developed based on the Baseline Design. Catalyst and chemicals costs were calculated for each plant within the complex, as factored from the Baseline Design. The results of the economic analyses are reported in *Table 3*. The most significant criterion reported is the equivalent crude oil price. This concept was developed by Bechtel in their Baseline Design Study, and modified slightly for use in this study. From analysis of published data, a correlation was found between crude oil and product prices, depending on the specific product and the price of the product. Relationships were developed for the ratio of the prices of crude oil to the price of the wholesale finished products (gasoline and distillate fuel oil). For a given product slate and product cost, multiplying the product cost by the ratio produces the equivalent crude oil price. This is the price that crude oil on the world market would minimally need to sell at for the proposed facility to have a 15% rate of return on the invested equity. The addition of plastic to either the coal/oil or the oil only feedstock decreases the equivalent crude oil price by 6.07 - 6.71 dollars/barrel. The oil/plastics operation achieves an extremely low value of 20.48 dollars/barrel, putting it nearly in the range of economically commercializing.

CONCLUSIONS

Co-processing of waste plastics with either oil only feedstock or coal/oil feedstock results in a significant improvement in process performance. Total feed conversion is enhanced as are 524°C+ residuum conversion and C_4-524°C distillate yield. The addition of waste plastics to the feed increases hydrogen efficiency as both hydrogen consumption and C_1-C_3 light gas yield

decrease. Co-processing of plastics with oil reduced the equivalent crude oil price required to have a 15% rate of return on equity to 20.48 dollars/barrel. This puts the technology in the reach of immediate commercialization with either a small increase in world crude oil prices or minor improvements in the technology to further reduce this value.

TABLE 1: Performance Comparison - Yields

	Oil	Coal/Oil	Coal/Oil /Plastics	Oil /Plastics
Feed Composition, W%				
Coal	0	50	33.3	0
Plastic	0	0	33.3	50
Oil	100	50	33.3	50
Space Velocity, Kg/hr/m^3rxn stage	1060	870	980	1250
Reactor temperature, °C				
First Stage	441	442	449	451
Second Stage	451	450	459	460
Process Performance, W% maf feed				
Feed Conversion	99.9	96.1	96.7	99.7
C_4-524°C Distillate Yield	76.0	69.7	73.9	76.2
524°C+ Conversion	83.3	82.7	83.7	84.0
Hydrogen Consumption	1.72	4.21	3.17	1.35
C_1-C_3 Gas Yield	5.00	7.37	5.31	4.31

TABLE 2: Performance Comparison - Quality

	Oil	Coal/Oil	Coal/Oil /Plastics	Oil /Plastics
Feed Composition, W%				
Coal	0	50	33.3	0
Plastic	0	0	33.3	50
Oil	100	50	33.3	50
SOH Distillate, ASTM D86, W%				
IBP-177°C	39.6	42.1	52.4	53.4
177-343°C	52.1	50.9	40.7	41.7
343°C+	8.3	7.0	6.9	4.9
SOH Quality				
Gravity, °API	49.0	46.1	46.3	51.0
H/C Ratio	1.99	1.96	1.90	1.97
Nitrogen, ppm	32.2	15.5	17.9	5.4
Sulfur, ppm	96.9	52.7	46.2	17.5
%Aromaticity	7.25	17.82	23.49	14.89

TABLE 3: Economic Comparison (12,000 tons/day total feed)

	Oil	Coal/Oil	Coal/Oil /Plastics	Oil /Plastics
Feed Rate				
Coal, tons/day	0	6,000	4,000	0
Oil, barrels/day	66,730	33,365	22,243	33,365
Plastics, tons/day	0	0	4,000	6,000
Liquid Products, barrels/day				
Gasoline	15,148	14,339	15,192	15,328
Diesel Fuel	36,787	34,822	36,896	37,225
Total	51,935	49,161	52,088	52,553

Total Plant Investment, $MM	1,945	2,379	2,078	1,733
Net Operating Cost, $MM/yr	566.8	561.4	486.1	449.7
Net Product Cost, $/barrel	33.22	34.76	28.41	26.05
Equivalent Crude Oil Price,	**27.19**	**28.70**	**22.63**	**20.48**